SYNTHESIS, ELEMENTAL ANALYSES AND IR SPECTRAL STUDIES OF A NOVEL COMPLEX OF 2-BUTANONESEMICARBAZONE

Reports submitted to University of Kerala in partial fulfilment of the Requirement for the award of the degree of Bachelor of Science in Chemistry

BY

23521100045	GOWRI S R
23521100046	HEERA S J
23521100047	HEMA HEGIN
23521100048	JINCY J
23521100049	MIDHULA M M
23521100050	NEETHU P V

ALL SAINTS' COLLEGE

THIRUVANANTHAPURAM

2024

DECLARATION

We hereby declare that this project titled "**SYNTHESIS, ELEMENTAL ANALYSES AND IR SPECTRAL STUDIES OF A NOVEL COMPLEX OF 2-BUTANONESEMICARBAZONE**" is the bonafide record of the project carried out by us under the supervision and guidance *of Dr. SIJI V. L, Department of Chemistry, All Saints' College, Thiruvananthapuram* and that no part of the report has been submitted by us for any other degree, diploma or similar titles of any other University.

GOWRI S R Gowri
HEERA S J
HEMA HEGIN
JINCY J
MIDHULA M M
NEETHU P V

GUIDE

DR. SIJI V L
Assistant professor
Department of Chemistry
All Saints' College
Thiruvananthapuram

EXTERNAL EXAMINERS

1.

2.

CERTIFICATE

This is to certify that this project titled "**SYNTHESIS, ELEMENTAL ANALYSES and IR SPECTRAL STUDIES OF A NOVEL COMPLEX OF 2-BUTANONESEMICARBAZONE**" submitted *by* **GOWRI S R, HEERA S J, HEMA HEGIN, JINCY J ,MIDHULA M M and NEETHU P V** is a bonafide record of the project carried out by them under my supervision and guidance and that no part of the report has been presented for any other degree, diploma or any other similar title of any other University.

Thiruvananthapuram

23-03-2024

(Supervising Teacher)

Dr. Siji V. L

Assistant Professor

Department of Chemistry

All Saints' College

Thiruvananthapuram

DR. SIJI V.L
ASSISTANT PROFESSOR
DEPARTMENT OF CHEMISTRY
ALL SAINTS' COLLEGE
CHACKAI, THIRUVANANTHAPURAM

THIRUVANANTHAPURAM

Sunita

Dr. SUNITA KURUR
Assistant Professor & HoD
Department of Chemistry
All Saints' College,TVPM.

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GOWRI S R
HEERA S J
HEMA HEGIN
JINCY J
MIDHULA M M
NEETHU P V

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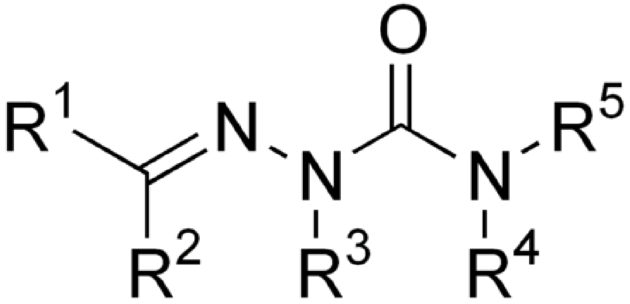
CHAPTER I

INTRODUCTION

Coordination chemistry is a branch of inorganic chemistry that deals with the study of coordination compounds, which are composed of a central metal atom or ion bonded to one or more surrounding ligands. Semicarbazones, an important class of organic compounds, have gained significant attention in coordination chemistry due to their versatile coordination modes and potential applications in various fields. This essay aims to provide an overview of semicarbazone coordination chemistry, including their synthesis, properties, and applications (Williamson and Kenneth L, 1999)

SEMICARBAZONES

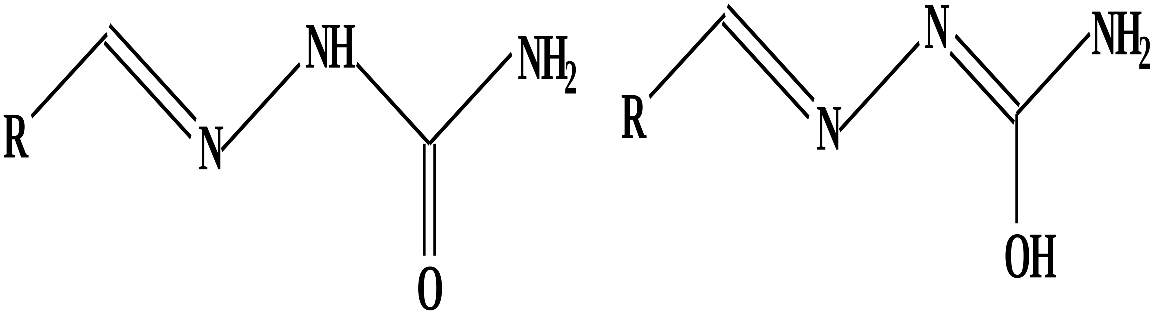
Semicarbazone is a derivative of imines formed by a condensation reaction between a ketone or aldehyde and semicarbazide. They are classified as imine derivatives because they are formed from the reaction of an aldehyde or ketone with the terminal -NH_2 group of semicarbazide, which behaves very similarly to primary amines.



General chemical structure of a semicarbazone

Semicarbazones are compounds with versatile structural features and can coordinate to the metal either as a neutral ligand or as a deprotonated anion. Semicarbazones exist in tautomeric keto (A) and enol (B) forms (Das *et al*., 1999).

(Scheme 1).



A **B**

Scheme 1

SYNTHESIS OF SEMICARBAZONES

Semicarbazones are typically synthesized by the condensation reaction between aldehydes or ketones and semicarbazide, a derivative of hydrazine. The reaction results in the formation of a C=N double bond, with the nitrogen atom of the semicarbazide group acting as a nucleophile, attacking the carbonyl carbon of the aldehyde or ketone(S. K. Pandey and S. B. Pandey, 2018).

According to IUPAC recommendations for the nomenclature of (Panico *et al.*, 1993) organic compounds derivatives of semicarbazide of the type $R–CH=N–NH–CX–NH_2$ and $R^1R^2C=N–NH–CX–NH_2$ which are usually obtained by the condensation of the semicarbazide with suitable aldehyde or ketone, may be named by adding the class name ‘semicarbazone’ (X=O) after the name of the condensed RCHO or ketone, $R^1R^2C=O$. It is usual to include in this class of derivatives with substituents on the amide nitrogen, $R^1R^2C=N–NH–CX–NR^3R^4$ or on the X atom $R^1R^2C=N–N=CR^3–NH_2$ or on the ‘hydrazinic’ nitrogen, $R^1R^2C=N–NR^3–CX–NH_2$. These classes of compounds usually react with metallic cations giving complexes in which the semicarbazones behave as chelating ligands.

COORDINATION MODES OF SEMICARBAZONES

Semicarbazones exhibit versatile coordination modes with metal ions due to the presence of multiple donor atoms, such as nitrogen and oxygen. Common coordination modes include:

a. Neutral bidentate (N,O) coordination: In this mode, the semicarbazone acts as a neutral ligand, with the nitrogen atom of the imine group (C=N) and the oxygen atom of the carbonyl group (C=O) coordinating to the metal ion.
b. Anionic tridentate (N,N,O) coordination: In this mode, the semicarbazone acts as an anionic ligand, with the two nitrogen atoms (one from the imine group and the other from the amine group) and the oxygen atom coordinating to the metal ion.
c. Anionic tetradentate (N,N,N,O) coordination: In this mode, the semicarbazone acts as an anionic ligand, with the three nitrogen atoms (two from the imine group and one from the amine group) and the oxygen atom coordinating to the metal ion.

The coordination possibilities derived from the many potential donor atoms in the semicarbazones are increased if the substituents include additional donor atoms and they can also be modified by placing substituents on the backbone donor atoms. The π-delocalization and the configurational flexibility of their molecular chain can give rise to a great variety of coordination modes. In some metal complexes, semicarbazone can act as a tridentate ligand with a donor atom apart from ketone/enol oxygen atom and azomethine nitrogen.

FACTORS INFLUENCING THE COORDINATION MODES OF SEMICARBAZONES

Several factors can influence the coordination modes of semicarbazones in metal complexes, including:

i.Metal ion properties: The type of metal ion, its oxidation state, and its preferred coordination geometry can dictate the coordination mode of the semicarbazone ligand.

For instance, transition metals with higher oxidation states tend to favour anionic ligands, leading to tridentate or tetradentate coordination modes.

ii.Ligand structure: The nature of the substituents on the semicarbazone ligand can affect its coordination mode. Bulky substituents can sterically hinder the coordination of certain donor atoms, leading to different coordination modes.

iii.Reaction conditions: Factors such as solvent, pH, and temperature can influence the coordination mode by affecting the protonation state of the semicarbazone ligand and its nucleophilicity (S. K. Pandey and S. B. Pandey, 2018)

The coordination possibilities derived from the many potential donor atoms in the semicarbazones are increased if the substituents include additional donor atoms and they can also be modified by placing substituents on the backbone donor atoms. The π-delocalization and the configurational flexibility of their molecular chain can give rise to a great variety of coordination modes (Casas *et al.*, 2000). In some metal complexes, semicarbazone can act as a tridentate ligand (Basuli *et al.*, 2000) with a donor atom apart from ketone/enol oxygen atom and azomethine nitrogen.

PROPERTIES AND APPLICATIONS OF SEMICARBAZONE-BASED COORDINATION COMPOUNDS

Semicarbazone-based coordination compounds possess unique properties that make them suitable for various applications, including:

a. Antimicrobial activity: Some semicarbazone complexes exhibit antimicrobial activity against bacteria, fungi, and other pathogens, making them potential candidates for drug development.

b. Catalysis: Semicarbazone complexes can act as catalysts in organic reactions, such as the oxidation of alcohols, epoxidation of alkenes, and polymerization reactions.

c. Sensing and detection: Semicarbazone complexes can be used as chemosensors for the selective detection of metal ions, anions, and other analytes in environmental and biological samples.

d. Materials science: Semicarbazone complexes can be used as building blocks for the construction of coordination polymers and metal-organic frameworks (MOFs), which have potential applications in gas storage, separation, and catalysis (J. Wang, X. Zheng, and F. Yang,2019)

SEMICARBAZONE-BASED COORDINATION COMPOUNDS IN MEDICINAL CHEMISTRY

Semicarbazone-based coordination compounds have shown potential in medicinal chemistry due to their antimicrobial, antitumor, and antioxidant activities. Some notable examples include:

1. Anticancer agents: Certain semicarbazone complexes have demonstrated cytotoxic activity against various cancer cell lines, with some showing selective activity towards specific cancer types. These complexes often induce apoptosis or disrupt DNA synthesis in cancer cells.
2. Antibacterial and antifungal agents: Semicarbazone complexes have been reported to exhibit antimicrobial activity against various bacteria and fungi, including drug-resistant strains. The exact mechanism of action is often dependent on the specific metal ion and the type of semicarbazone ligand used.
3. Antioxidants: Some semicarbazone complexes possess antioxidant properties, which can help protect cells from oxidative damage caused by reactive oxygen species (ROS). These complexes may find potential applications in the treatment of

diseases associated with oxidative stress. (S. Saravanan *et. al*.2020)

The activities of these compounds could be due to their power of chelation with traces of metal ions present in biological system. The great advantage of semicarbazone derivatives over their thiosemicarbazone analogues seems to be their lower toxicity. Di-2-pyridyl ketone N^4-phenyl-3-semicarbazones tautomerizes into keto and enol forms and as a result a small negative charge resides on the nitrogen atom of the pyridine ring which enhances its biological activity (Cerecetto and Gonzalez, 2002). Salicylaldehyde semicarbazone is inactive against the rapidly dividing human breast cancer cell line MCF-7, while the copper conjugates of semicarbazones are found to be potent antiproliferative agents due to their facile (Cu^{2+}/Cu^{+}) redox couple and can generate considerable intracellular oxidative stress (Patole *et al.*, 2004). N^1-(2,6-dimethylphenyl)-N^4-(2-hydroxybenzaldehyde) semicarbazone emerged as a prototype with wide spectrum anticonvulsant properties active in five models of seizure with no neurotoxicity and hepatotoxicity. Semicarbazones are versatile ligands with therapeutic effects. Studies showed that benzaldehyde semicarbazone induced an antinociceptive effect in different experimental models and also inhibited the edema induced by carrageenan and the angiogenesis induced by subcutaneous sponge disc (Rocha *et al.*, 2006). The *in vitro* anticancer studies on MCF-7 human breast cancer cells reveal that the nickel(II) complex of ortho-naphthaquinone semicarbazone is more active in the inhibition of cell proliferation than the thiosemicarbazone analogue.

SEMICARBAZONE-BASED COORDINATION COMPOUNDS IN MATERIALS SCIENCE

Semicarbazone-based coordination compounds have been widely explored in materials science due to their potential applications in areas such as:

i. Metal-organic frameworks (MOFs): Semicarbazone ligands can be used as organic linkers to construct MOFs with various topologies and pore structures. These MOFs can be used for gas storage, separation, sensing, and catalysis applications.

ii. Coordination polymers: Semicarbazone ligands can act as bridging ligands to form coordination polymers with diverse structures and properties. These materials have potential applications in areas such as luminescence, magnetism, and electrical conductivity.

iii. Nanomaterials: Semicarbazone complexes can be used as precursors for the synthesis of metal nanoparticles, metal oxide nanoparticles, and other nanomaterials. These materials have potential applications in catalysis, sensing, and biomedical imaging.

SEMICARBAZONE-BASED COORDINATION COMPOUNDS IN CATALYSIS

Semicarbazone-based coordination compounds have shown promise as catalysts for various organic transformations, including:

1. Oxidation reactions: Some semicarbazone complexes can efficiently catalyze the oxidation of alcohols to aldehydes or ketones using environmentally benign oxidants such as molecular oxygen or hydrogen peroxide.

2. Epoxidation reactions: Certain semicarbazone complexes can catalyze the epoxidation of alkenes with high selectivity and conversion, using either hydrogen peroxide or alkyl hydroperoxides as oxidants.

3. Polymerization reactions: Semicarbazone complexes have been used as catalysts for the ring-opening polymerization of cyclic esters and the controlled radical polymerization of vinyl monomers, resulting in the synthesis of polymers with well-defined structures and properties (S. Saravanan *et. al.*2020).

SEMICARBAZONE-BASED COORDINATION COMPOUNDS IN SENSING AND DETECTION

Semicarbazone-based coordination compounds have been used as chemosensors for the selective detection of various analytes, such as:

1. Metal ions: Certain semicarbazone complexes can act as selective sensors for metal ions in environmental and biological samples, with changes in their optical or electrochemical properties upon metal ion binding.

2. Anions: Some semicarbazone complexes can selectively recognize and bind to anions, resulting in changes in their spectroscopic properties that can be used for anion sensing.

3. Small molecules: Semicarbazone complexes have been employed as sensors for the detection of small molecules, such as nitric oxide, hydrogen sulphide, and other biologically relevant molecules (S. Saravanan *et. al.*2020)

SEMICARBAZONE-BASED COORDINATION COMPOUNDS IN ENVIRONMENTAL REMEDIATION

Semicarbazone-based coordination compounds have shown potential in environmental remediation applications, including:

i. Heavy metal ion removal: Semicarbazone ligands and their complexes can selectively bind and remove heavy metal ions, such as lead, mercury, and copper, from contaminated water and soil. This process, known as chelation, can help to reduce the toxicity and bioavailability of these metals in the environment.

ii. Organic pollutant degradation: Some semicarbazone complexes have been reported to catalyze the degradation of organic pollutants, such as dyes, phenols, and pharmaceuticals, through advanced oxidation processes. These processes involve the generation of highly reactive radicals, such as hydroxyl radicals, which can effectively degrade the target pollutants.

Salicylaldehyde semicarbazone, 2-hydroxy-naphthaldehyde thiosemicarbazone and 2, 4-dihydroxybenzaldehyde semicarbazone have been used for the spectrofluorimetric determination of a number of metal ions (Singh *et al.*, 1978). Semicarbazones are highly crystalline and very useful for purification and characterization of carbonyl compounds. These compounds are useful as efficient protecting groups for aldehydes and ketones. Semicarbazones have been widely used as spectrophotometric agents for the analysis of metal ions. Chalcogen semicarbazones are used as unique organic reagents for many approaches and methods of metal analysis, separation and concentration. Some of the semicarbazones produce highly colored complexes with metal ions. These compounds have been proposed as analytical reagents that can be used in selective and sensitive determinations of metal ions (Atalay and Akgemci, 1998).

CHAPTER II

OBJECTIVE AND SCOPE OF THE PRESENT INVESTIGATION

The diverse coordination chemistry of semicarbazone-based compounds, coupled with their potential applications in various fields, makes them an attractive area of research. Interest in the field of semicarbazones is due to their unusual coordination modes when bound to metals, high pharmacological potentiality and good chelating property.

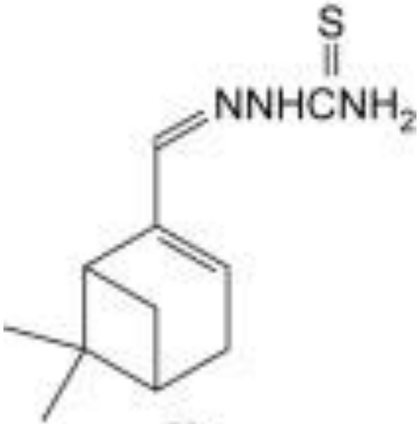
The primary objective of this study has been to synthesize and characterize a novel Cu(II) complex of 2-butanonesemicarbazone. The ligand and the complex were characterized by elemental analyses, molar conductivity and infrared spectral studies. A description of the reagents used and the synthesis of the ligand and the complex are also presented.

CHAPTER III

REVIEW

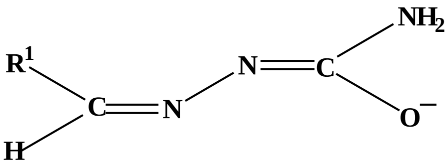
The antitubercular activities of metal complexes of semicarbazones and thiosemicarbazones have been reported by Domagk for the first time (Domagk *et al.*, 1946).

Seventeen semicarbazone and thiosemicarbazone derivatives were prepared and tested in vitro against a chloroquine resistant strain of Plasmodium falciparum (W2) to evaluate their antiplasmodial potential. Three thiosemicarbazones were found to be active against the parasite and non-toxic to human peripheral blood mononuclear cells (PBMC). Among these, compound **5b** presented the lowest IC_{50} value against *P. falciparum* (7.2 μM) and was the least toxic in the PBMC proliferation assay (IC_{50} = 73.5 μM). It was selected for in vivo tests on mice infected with Plasmodium berghei (strain NK-65). The thiosemicarbazone **5b** was able to reduce the parasitaemia by 61% at 20 mg/kg on day 7 after infection without any sign of toxicity to the animals. In comparison, the standard drug chloroquine at 15 mg/kg showed a reduction around 95%. These in vitro and in vivo results make **5b** an interesting lead for further development (Chiyanzu *et al.*; 2003).



5b

A review of *ca.* 70 semicarbazone structures included in the Cambridge Structural Database (CSD) (Allen *et al.*, 1983) shows that in free unsubstituted semicarbazones in solid state the C–N–NH–CO–NH_2 backbone is usually almost planar with the oxygen atom trans to the azomethine N atom (Configuration E; Scheme 2)



Configuration E

Scheme 2

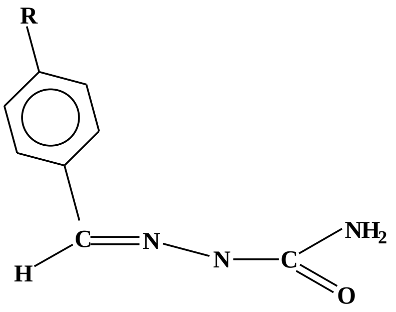
Few semicarbazones are exception to this rule. Although there are several electronic and steric factors that may contribute to the adoption of this arrangement, the most important is probably that the trans arrangement places the amine and azomethine nitrogen atom in relative positions suitable for intramolecular hydrogen bonding (Chattopadhyay *et al.*, 1989).

A series of thioureido derivatives of acetophenone semicarbazone were synthesized and evaluated for anticonvulsant activity. Some compounds provided significant protection against maximal electroshock (MES)and subcutaneous pentylenetetrazol (scPTZ) induced seizures. The compound (2e) was the most active compound in the series with a dose of 30 mg $kg^{-1}$and ED_{50}23.5mg $kg^{-1}$and equipotent to phenytoin ED_{50}23.2 mg kg^{-1}. The toxicity of the compounds was assessed by determination of their approximate $TD_{50}$and LD_{50}values in order to have a better assessment of their pharmacological profile and protective index (S.N. Pandeya *et al.*,1998) Aryl semicarbazones fulfilled the essential demands of the pharmacophore when compared with the phenytoin, carbanazepine, denzinamide and remacemide. Variously substituted aryl semicarbazones with the order of anticonvulsant activity are found to be 4-F>2-Br=3-Br=4-Cl>4-CH_3>4-Br>3-Cl>3-CH_3 with respect to the primary aryl group (Yogeeswari *et al.*, 2006).

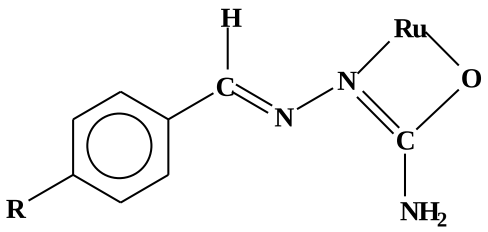
Benzaldehyde semicarbazones (Scheme 3) in their reaction with ruthenium display three different coordination modes (Scheme 4, 5 and 6)

1. an unusual four membered chelate formation as an N, O-donor
2. N, O-coordination forming a stable five membered chelate
3. C, N, O-tricoordination

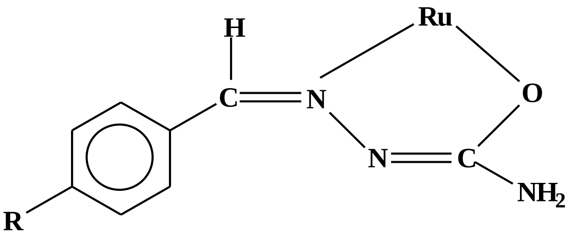
depending on the nature of the ruthenium starting materials and the experimental conditions (Basuli *et al.*, 2001).



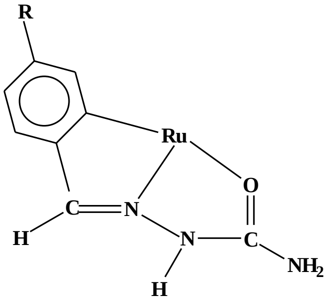
Scheme 3



Scheme 4



Scheme 5



Scheme 6

Semicarbazone of benzophenone (Vijayan *et al.*, 2002) and 2-amino-5-chlorobenzophenone (Sethuraman *et al.*, 2006) have been grown as a single crystal by slow evaporation solution growth technique. The grown crystals have been characterized and the second harmonic generation property of semicarbazone of 2-amino-5-chlorobenzophenone was analysed.

Compounds able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing and dynamic image processing (Kolinsky, 1992; Eaton, 1991).

2-Formyl pyridine semicarbazone complexes of cobalt(II), nickel(II), copper(II) and zinc(II) compositions $[ML_2X_2].nH_2O$ (M = Co, Ni, Cu, Zn; X = Cl, NO_3, ClO_4; L = NC_5H_4–CH–N–NH–C(O)–NH_2; n = 0,1) and $[CuLX_2].nH_2O$ (X = Cl, Br, NO_3, n = 0-0.5) have been reported. Complex $[CuL(NO_3)_2]$ has polynuclear $[CuLX_2].0.5H_2O$ (X = Cl, Br), binuclear and other compounds, mononuclear structures. Semicarbazone in the complexes behave as tridentate N, N, O ligand through pyridine and azomethine nitrogen atoms and through carbamide oxygen to form two five membered metallocycles (Gulya *et al.*, 2009).

4-(4-Flurophenoxy) benzaldehyde semicarbazone (C0102862, V102862) was discovered as a lead molecule and is being developed as a potent antiepileptic drug, with maximal electroshock (MES) ED50 of ip 12.9 mg kgr1. In MES (oral screen), this compound has a protective index (PI= TD50/ED50> 315) higher than carbamazepine (PI 101), phenytoin (PI> 21.6) and valproate (PI 2.17). The compound is a potent sodium channel blocker. Other semicarbazones have demonstrated activity in various chemoshock screens, like subcutaneous pentylenetetrazole, subcutaneous strychnine, subcutaneous picrotoxin and subcutaneous bicculine. Semicarbazones are also GABA-transaminase inhibitors. Extensive structure—activity relationship has demonstrated that F, Cl, Br and NO_2 substituents in the arylhydrophobic pocket and a hydrogen bonding domain (HBD) are generally found in active anticonvulsant agents.
(Surendra Nath Pandeya, 2012)

Organic compounds with asymmetric charge distribution π-electron system show nonlinear optical responses, which are due to the presence of electron rich donor and deficient acceptor substituents in the system (Prasad and Williams, 1991).

Interest in coordination chemistry of transition metal complexes of semicarbazones have been a subject of enthusiastic research because of their bioinorganic relevance (Dimmock *et al.*, 1996).

The copper complexes of semicarbazone, oxime, phenylhydrazone and thiosemicarbazone derivatives are found to be potent cytotoxic agents in both murine and human tissue cultured cell lines as well as in solid tumors (West *et al.*, 1996).

Consistent advances in the design of novel anticonvulsant agents have been obtained (Dimmock *et al.*, 2000) which included various aryl semicarbazones and (aryloxy)aryl semicarbazones.

The significant anticonvulsant potential in animal epilepsy models for the N^4-(substituted phenyl) semicarbazones have been demonstrated (Pandeya *et al.*, 2002).

The inhibition efficiency of corrosion on mild steel using acids by three different novel Semicarbazones as inhibitors have been studied using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The inhibition efficiency, corrosion rate, the nature of anchoring sites and the adsorption characteristics have been determined from the results. It was found that the newly synthesized compounds behaved as mixed type inhibitors with high inhibition efficiency. The inhibition efficiency increases with increasing the inhibitors concentration but decreases with increasing the temperature. Addition of halide ion enhances the inhibition efficiency. The adsorption of the inhibitors on the mild steel surface obey Langmuir adsorption isotherm. Scanning Electron Spectroscopy is used to examine the surface morphology of mild steel samples both in the presence and absence of inhibitors at optimum conditions. Scanning Electron Microscope reveals the formation of a smooth, dense protective layer in the presence of inhibitor. (Rathika Govindasamy and Swetha Ayappan,2015).

A series of 1-(2-Oxo-2-phenyl-ethyl)-2-phenyl-1H-indole-3yl)methylene) semicarbazone derivatives (4a–g and 6a–c) were synthesized by the condensation of derivatives of 1-(2-Oxo-2-phenyl-ethyl)-2-phenyl-1H-indole-3-carbaldehyde and semicarbazide in ethanol under microwave irradiation procedure. Both conventional and microwave-irradiated syntheses have been carried out to compare their yields and reaction time. The structures of the synthesized compounds were confirmed by spectral data. The antimicrobial activities of the synthesized compounds were screened using broth dilution method. Among all the screened compounds some of the compounds exerted good antifungal activity against C. albicans and C. rugosa. All the compounds exhibited moderate activity against bacteria such as B. subtilis, S. aureus, S. epidermidis, E. coli, P. aeoginosa, and K. pneumoniae. (S Vijaya Laxmi and B Rajitha; 2012)

CHAPTER IV

MATERIALS AND METHODS

1. Solvents

Methanol, diethyl ether and acetic acid were of AR grade and used without further purification.

2. Metal Salt

AR grade metal salt was used for the preparation of complex.

3. Other reagents

For the preparation of the ligand, 2-butanone and semicarbazide were used as received.

Analysis

Estimation of carbon, hydrogen and nitrogen

Carbon, hydrogen and nitrogen in the ligand and complex were carried out using a Vario EL-III CHNS analyzer at Sophisticated Analytical Instrument Facility, Cochin University of Science and Technology, Kochi, India.

Physicochemical Methods

Conductivity measurements

The molar conductance of the complex in methanol solution (10^{-3} M) was measured at 298 K with a Systronics model 303 direct-reading conductivity bridge.

Infrared spectral studies

The IR spectra of the ligand and its complex were recorded in KBr pellets in the range 4000-400 cm^{-1}. The spectrum was recorded on a Thermo Nicolet, Avator 370 spectrometer at SAIF, Kochi, India.

SYNTHESIS OF SEMICARBAZONE LIGAND

Synthesis of the 9-anthraldehydesemicarbazone (NASC)

NASC was prepared in methanol solution by the condensation of 9-anthraldehyde and semicarbazide in acid medium. A methanolic solution (30 ml) of semicarbazide (1 mmol) was added to a solution of 9-anthraldehyde (1 mmol) in methanol and the reaction mixture was refluxed for 3 h on a water bath. To this few drops of dil. acetic acid were also added to change the pH. On slow evaporation colorless crystals of the semicarbazone were separated out. It was recrystallized from methanol (yield: 80%) and the melting point is found to be 161 °C. These crystals were filtered, washed with ether and dried over P_4O_{10} *in vacuo.* The compound was characterized by elemental analyses, IR and electronic spectral studies.

4. **Solvents**

   Methanol, diethyl ether and acetic acid were of AR grade and used without further purification.

5. **Other reagents**

   For the preparation of the ligand, 2-Butanone and semicarbazide were used as received.

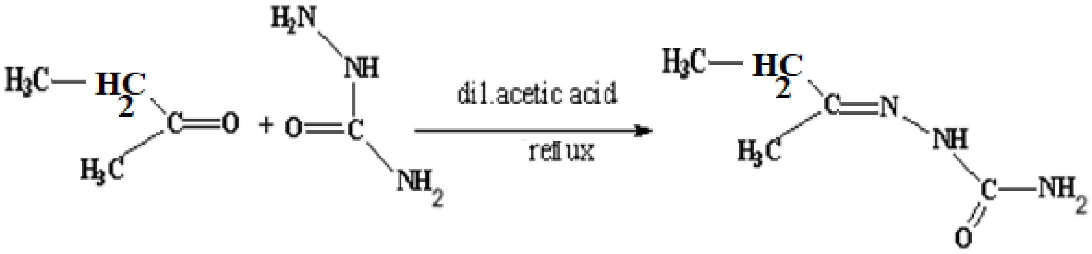
Physicochemical Methods

Infrared spectral studies

The IR spectrum of the ligand was recorded in KBr pellets in the range 4000-400 cm^{-1}. The spectrum was recorded on a Thermo Nicolet, Avator 370 spectrometer at SAIF, Kochi, India.

Synthesis of 2-butanonesemicarbazone (TBSC)

The compound (TBSC) was prepared in methanol solution by the condensation of 2-butanone and semicarbazide in acid medium. An equimolar mixture of semicarbazide (1 mmol) and 2-butanone (1 mmol) was heated under reflux for 3 h in methanol in presence of three to four drops of dilute acetic acid. On slow evaporation, colorless crystals of the compound separated out. It was filtered, washed with ether. The compounds were recrystallized from methanol and the melting point was found to be 190^0C.



Synthesis of copper(II) complex

The complex [Cu(TBSC)$_2$(SO$_4$)] was synthesized by refluxing methanolic solution of TBSC (2 mmol) with an aqueous solution of $CuSO_4 \cdot 5H_2O$ (1 mmol) for 4 h. The resulting solution was allowed to stand at room temperature and upon slow evaporation crystals separated out, which were collected, washed with methanol and dried over P_4O_{10} *in vacuo*. The compounds were recrystallized from methanol and the melting point was found to be 215 ^{0}C.

CHAPTER V

RESULTS AND DISCUSSION

The ligand is soluble in methanol, DMF and chloroform. However, the IR spectrum of TBSC indicates that in solid state they remain in keto form.

Elemental analysis

The elemental analyses data are in good agreement with the stoichiometry of 2-butanonesemicarbazone and its Cu(II) complex. The semicarbazone, can exist in keto or enol form. However, the IR spectrum of TBSC indicates that in solid state they remain in keto form. The analytical data of ligand and its Cu(II) complex are presented in Table 1.

Conductivity measurements

Conductance gives the information about the nature of anions, whether they are coordinated to the metal or not. These informations enhance us to interpret the possible structures. Conductances are usually measured in non-aqueous media. Water is not used as solvent due to hydrolytic problems. The non-aqueous solvents used are nitrobenzene, acetonitrile, methanol, DMSO, DMF and dioxan. The molar conductivity value (Table 1) of the compound in methanol shows that the compound is non-electrolyte.

Table 1

Analytical and physical data of TBSC and its Cu(II) complex

Compound	Color	Λ^a_m	Composition % found (calc.)		
			C	H	N

TBSC	Colorless	-	46.47 (46.49)	8.58 (8.59)	32.53 (32.54)
[Cu(TBSC)$_2$SO$_4$]	Blue	19.5	28.71 (28.73)	5.32 (5.31)	20.10 (20.11)

Molar conductivity, 10^{-3} M methanol at 298 K

Infrared Spectrum

For the determination of molecular structure, IR spectroscopy is regarded as one of the efficient and powerful tool. Infrared radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave region. The limited portion between 4000-400 cm^{-1} is of great practical use, but there has been some interest in the near IR (14290-4000 cm^{-1}) and the far IR regions, 700-200 cm^{-1}. Although the IR spectrum is characteristic of the entire molecule, it is true that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic bands that permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characterestic group frequencies. We shall rely heavily on these characteristic group frequencies. Infrared radiation of frequencies less than about 100 cm^{-1} is absorbed and converted by a molecule into energy of molecular rotation. This absorption is quantised; thus a molecular spectrum consists of discrete lines (Roeges, N. P. G, 1994).

IR radiation in the range from about 10000-100 cm^{-1} is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is also quantised, but vibrational spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. It is with this vibrational-rotational band, particularly those occurring between 4000-400 cm^{-1} that we shall be concerned. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bands and the geometry of the atoms. There are two types of molecular vibrations: stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of group of atoms with respect the remainder of the molecule without movement of atoms in the group with respect to one another. For example, twisting, rocking and torsional vibrations involve in bond angles with reference to a set of coordinate arbitrarily set up within the molecule. Only those vibrations that result in a rhythmical change in dipole moment of the molecule are observed in IR. The alternating electric field, produced by changing charge distribution accompanying a vibration couples the molecular vibration with the oscillating electric field of the electromagnetic radiation. Thus IR spectroscopy is regarded as a powerful tool for the identification of molecular structure. The basic theory involved is that the stretching mode of the ligands changes upon complexation due to weakening or strengthening of the bond in the bond formation resulting in subsequent change in the position of the bands appearing in IR spectrum. The changes in the structural features of the ligand are observed as changes in bands observed, mainly in the fingerprint region that is in the 1500-750 cm^{-1}. Shift in some of the characteristic vibrational frequency of the ligand upon complexation provides evidence for the mode of binding of the ligand to the metal ion. Hence in complexes of ligands containing C=O, C=N etc shift in stretching frequency of the corresponding group has been taken as evidence for oxygen or nitrogen coordination. The shift may be positive or negative. The appearance of the ν(C=O) band and ν(NH) indicates that in the solid state the ligand exists in keto form.

IR spectrum of the ligand

The tentative assignments of important IR bands of TBSC are presented in Table 1 and the spectrum of ligand is shown in Fig. 1. The ν(C=O) band is present at 1684 cm^{-1}. The band at 1619 cm^{-1} for 2-butanonesemicarbazone is assigned to ν(C=N). These values are in agreement with earlier reports of *N*(4)-substituted semicarbazones (Reena *et al.*, 2008, Siji *et al.*, 2010). The IR spectral band of 2-butanonesemicarbazone observed at 1035 cm^{-1} correspond to ν(N–N). The strong band at 3324 cm^{-1} is assigned to ν(^{4}NH) vibrations of 2-butanonesemicarbazone. Another band observed at 3172 cm^{-1} for 2-

butanonesemicarbazone due to ν(^{2}NH) vibrations indicates that the ligand exist in the keto form in the solid state.

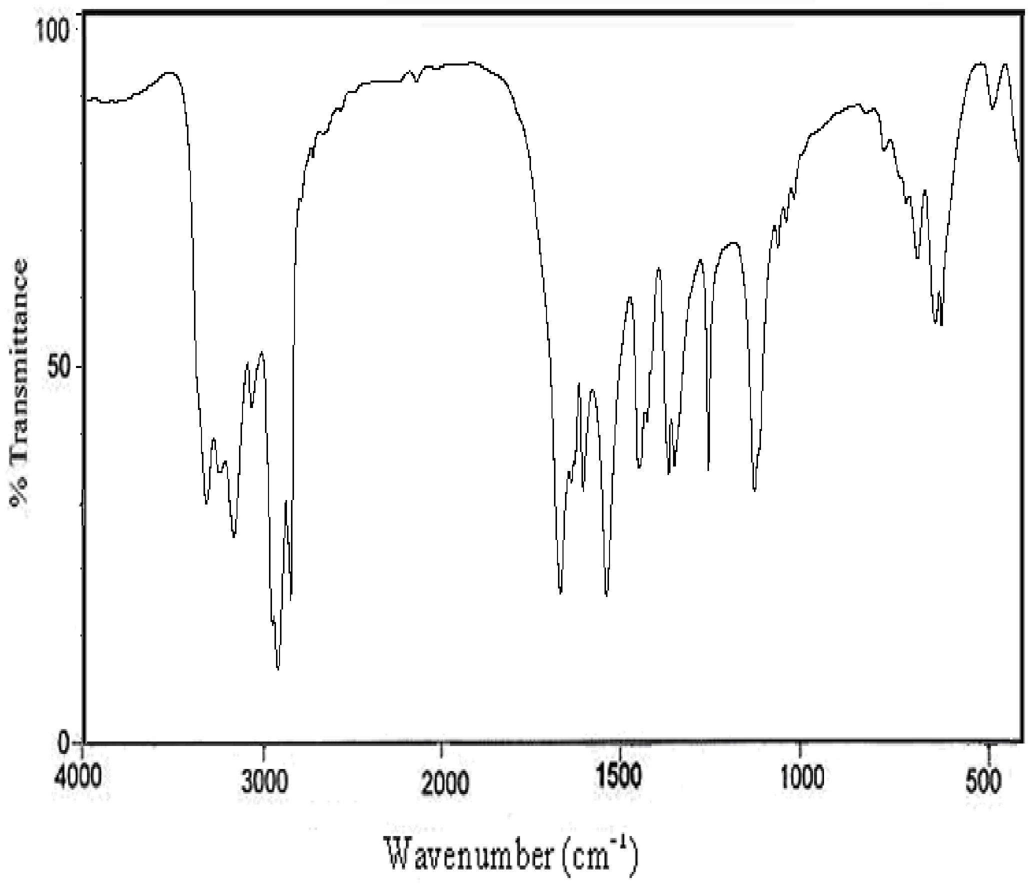


Fig. 1 Infrared spectrum of ligand TBSC

IR spectrum of the complex [Cu(TBSC)$_2$SO$_4$]

The tentative assignments of the IR spectral bands useful for determining the ligand’s mode of coordination are presented in Table 2 and the spectrum of the complex is shown in Fig. 2. The spectrum of the ligand exhibit a band at 3324 cm^{-1} which is assigned to ν(^{4}NH) vibration. A band at 3172 cm^{-1} in the free ligand due to ν(^{2}NH) vibration indicates that the ligand remains in the keto form in the solid state. The presence of this band in the complex indicates that there is no enolization and deprotonation of the ligand and the semicarbazone is coordinated in the neutral form. A band at 1684 cm^{-1} in the ligand is shifted to lower frequency in the complex showing the involvement of C=O oxygen in coordination. The presence of band 1662 cm^{-1} for complex supports the keto form of ligand in the complex. A sharp band at 1619 cm^{-1} in the semicarbazone can be attributed to the characteristic >C=N– group. This band shift slightly towards lower frequencies in the complex, indicating the coordination of azomethine nitrogen to metal. It is further supported by the appearance of new bands at 411 cm^{-1} assignable to ν(Cu–N) for the complex. The ν(N–N) band of semicarbazone is observed to 1035 cm^{-1}. The increase in the ν(N–N) value in the spectrum of the complex is due to the increase in double bond character, off-setting the loss of electron density *via* donation to the metal and it is a confirmation of the coordination of the ligand through the azomethine. In complex $[Cu(TBSC)_2SO_4]$**,** the spectral data indicates the bidentate nature of the sulphate anion (Kala *et al*., 2007).

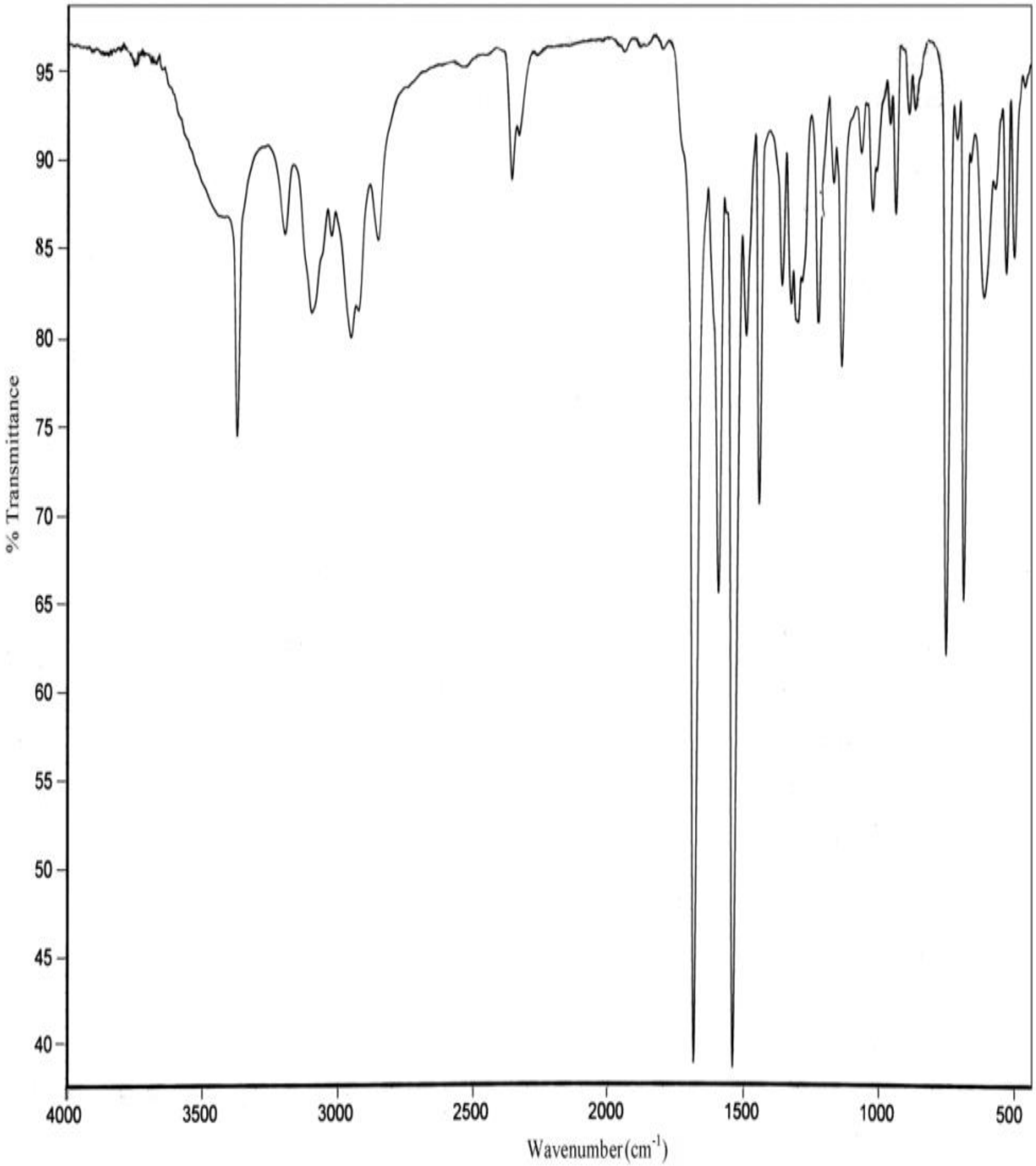


Fig. 2 Infrared spectrum of complex [Cu(TBSC)$_2$SO$_4$]

Table 2

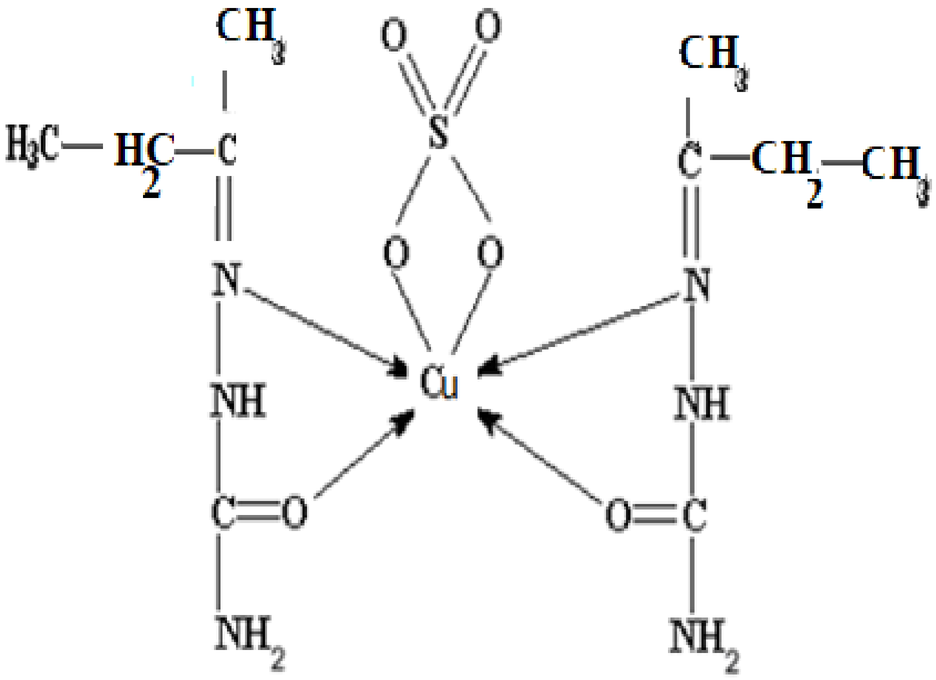
Selected IR spectral assignments (cm^{-1}) of TBSC and its Cu(II) complex

Compound	ν(C=O)	ν(C=N)	ν(^{2}NH)	ν(^{4}NH)	ν(N–N)	ν(Cu–N)
TBSC	1684	1619	3172	3324	1035	-
[Cu(TBSC)$_2$SO$_4$]	1662	1600	3085	3364	1063	411

CONCLUSION

2-butanonesemicarbazone (TBSC) was synthesized in methanol solution by the condensation of 2-butanone and semicarbazide in acid medium where TBSC stands for the ligand 2-butanonesemicarbazone. The ligand and complex were characterized by elemental analyses, conductivity measurements and IR spectral studies. Elemental analyses data are consistent with the empirical formula of ligand. The IR data suggests that the ligand TBSC and its complex $[Cu(TBSC)_2SO_4]$ exist in the keto form in the solid state.

The complex was found to be non-electrolyte. IR spectral data shows the neutral bidentate behaviour of the ligand in the complex coordinating through the carbonyl oxygen and azomethine nitrogen. In the complex, the semicarbazone is coordinated as neutral bidentate ligand. Based on elemental analyses, conductivity measurement and infrared spectral data the following tentative structure is given for complex.



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