# Bharath
## INSTITUTE OF HIGHER EDUCATION AND RESEARCH
(Declared as Deemed-to-be University under section 3 of UGC Act, 1956)
(Vide Notification No. F.9-5/2000 - U.3, Ministry of Human Resource Development, Govt. of India, dated 4th July 2002)

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*173, Agaram Road, Selaiyur, Tambaram,*
*Chennai - 600 073. Tamil Nadu.*

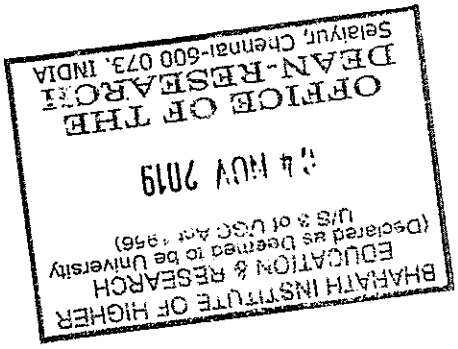

Ref No.SMS-2018-O-25 Date: 04/11/2019

TO

Mr. Dr. G. Gurumoorthy,

Associate Professor/ Chemistry,

BIHER.




Thro: Concern Head of the Department

Greetings!!!

We are happy to announce that the Research Advisory Committee has approved your proposal for Seed Money Scheme-2018 which was presented by you. You are requested to complete the proposal and send the progress report to the Dean Research in the prescribed time period.

**Title of the Project: Synthesis and Characterization of Metal dithiocarbamates and their Utilization of Anion Sensing: Preparation of Metal Sulphide and their Applications**

**Seed Money Amount: Rs.1, 00,000/- (Rupees One Lakh Only)**

**Approved on: 02/11/2019**

**Payment details:**

**Voucher No.25** **Dated: 08/11/2019**

With Regards

Dean-Research

# Bharath University

SELAIYUR, CHENNAI - 600 073, TAMIL NADU, INDIA.

**CASH / PAYMENT VOUCHER**

Date 08/11/19

V.No. 025.

Debit _____ Amount

**Rs.** 1,00,000/-

PAID TO Mr. G. Gurumurthy.

RUPEES One Lakh only

TOWARDS Seed Money Scheme

**Authorised by** | **Finance Manager** | **Cashier/Accountant** | **Payee's Signature**

## FORMAT FOR PROPOSAL SUBMISSION

**1. Details of Principal Investigator**

| | |
|---|---|
| Name | : Dr. G. GURUMOORTHY |
| Designation | : Associate Professor |
| Highest Qualifications | : Ph.D., |
| Department | : Chemistry |
| E-mail | : gurugovindchem@gmail.com |
| Contact no | : 8608804421 |
| Date of Joining | : 30/07/2019 |

**2. Details of Co-Principal Investigator**

| | |
|---|---|
| Name | : Dr. T. EZHILRASAN |
| Designation | : Associate Professor |
| Highest Qualifications | : Ph.D., |
| Department | : Chemistry |
| E-mail | : ezhilkongu@gmail.com |
| Contact no | : 9994958844 |
| Date of Joining | : 16/09/2019 |

## Technical details

### 1. Introduction

There has been a prodigious upsurge of knowledge in the chemistry of transition metal complexes with sulphur donor ligands. A major class of sulfur containing ligands is obtained by the general reaction of carbon disulphide with various nucleophiles. Carbon disulphide enters into reaction with a variety of nucleophiles. Its reaction with nucleophiles RO-, RNH- and R2Nare of considerable interest; the products in these cases are o-alkyldithiocarbonates (xanthates), N-monoalkyldithiocarbamates and N,N-dialkyldithiocarbamates respectively. Dithiocarbamate anions are strong complexing agents and give rise to a large number of chelate complexes with metal ions. Dithiocarbamates have considerable industrial and technological significance and have a variety of uses. Organic dithiocarbamate have received much attention due to their pivotal role in agriculture 1 and their intriguing biological activities 2 . Recently they are used in the synthesis of ionic liquids3. Their chelating properties allow them to be used as antidotes against nickel and copper poisoning (Wilson's disease) 4, in analytical determination of heavy metals, in waste water treatment and as rubber vulcanization accelerators. In the field of medicine these compounds also find application in the treatment of chronic alcoholism5 and in fungi and bacteria related diseases, and they have also received some attention as potential auxiliaries in oncological chemotherapy and in the prevention of arteriosclerosis. Diethyl dithiocarbamate are known to inhibit the activity of Cu/Zn-superoxide dismutase (SOD) through the withdrawal of copper from the protein both in vivo and invitro6 , and their chelating property with copper has made them strong inhibitors of NF-κB signalling pathway7 . Some dialkyl-substituted dithiocarbamates have proved to be an efficient anti-alkylating, anti-HIV and froth-floatation agents 8 Therefore, there is a continuing interest in the synthesis of new dithiocarbamates and their complexes.

It is not clear when dithiocarbamate was first synthesized, but certainly they have been known for at least 150 years, Debus reported the synthesis of dithiocarbamic acids as early as 1850. The first synthesis of transition metal dithiocarbamate complex is also unclear, however, in a seminal paper in 1907, Delepine reported on the synthesis of a range of aliphatic dithiocarbamate and also salts of di-iso-butyl dithiocarbamate with transition metals including chromium, molybdenum, iron, cobalt, nickel, zinc and gold. He also noted that while dithiocarbamate salts of alkali and alkaline

earth metals are water soluble, those of transition metals, p- block metals and lanthanides were precipitated from water to give salts soluble in ether and chloroform and even in some cases in benzene and carbon disulphide.

**Keywords:** 1.Novel synthesis, 2.Anion sensing, 3.Metal sulfide, 4.Photodegradation.

## 2. Review of status of Research and Development in the subject

Acyclic and macrocyclic Co(III), Ni(II), Cu(II) and Zn(II) complexes containing pyrrole and ferrocenyl based dithiocarbamates (1-53) were prepared and characterized by elemental analysis, IR, UV-vis and NMR spectroscopy. Elemental analyses are consistent with proposed formulae. The important stretching mode characteristic of the thioureide bond (vC-N (thioureide)) occurs in the region 1448- 1527 cm-1 for all the complexes. Electronic spectral studies suggest an octahedral environment around Co(III) and the square planar environment around Ni(II) and Cu(II) centres in their respective dithiocarbamate complexes. Single crystal X-ray structural analysis was carried out for seventeen complexes. Unusual intramolecular C-H ...Ni anagostic interactions were observed in nickel complexes. Complexes with anagostic interactions are important due to their possible involvement in the C-H bond activation in the organic synthesis. Crystal structures of some complexes displayedC-H··· (chelate, MS2C) interactions. Weak intermolecular C-H···S, C-H··· (chelate), C-H··· , and N-H··· interactions observed in various complexes lead to the supramolecular aggregation. Geometry optimization, geometrical parameters, molecular electrostatic potential maps and frontier molecular orbital analyses of some complexes were carried out by DFT methods and compared with experimental Xray diffraction. Molecular electrostatic potential diagrams reveal that the negative charge on S atoms and positive charge on N atoms of NCS2 support the partial double bond character of C-N (thioureide) bond. The anion (F- , Cl- , Br- , Iand benzoate ions) binding studies with thirteen complexes were carried out using cyclic voltammetry. Generally, nickel complexes containing pyrrole and ferrocene moieties prefer to bind with I- , whereas pyrrole and ferrocene based Zn(II) complexes exhibit affinity for Fand Br- , respectively. Macrocyclic pyrrole based Ni(II) and Cu(II) complexes show marked electrochemical change to F- . This study indicates that transition metal dithiocarbamate complexes containing pyrrole and ferrocene moieties can be used for sensing anions. Monometallic sulfide (cobalt sulfide, nickel sulfide, copper sulfide and zinc sulfide) nanoparticles were prepared from homoleptic metal complexes with pyrrole based

dithiocarbamates. Cobalt(III), nickel(II), copper(II) and zinc(II) complexes with ferrocenyl based dithiocarbamates were used as single source precursors for the preparation of bimetallic sulfide (cobalt-iron sulfide, nickel-iron sulfide, copper-iron sulfide and zinc-iron sulfide) nanoparticles. The as-prepared nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDAX), IR, UV-vis and fluorescence spectroscopy. XRD and TEM studies demonstrate that the metal-dithiocarbamate complexes were found to be effective single source precursor for the preparation of various phases, shapes and sizes of monometallic and bimetallic sulfide nanoparticles. IR spectral studies confirm the presence of capping agent (triethylenetetraamine) and the absence of dithiocarbamate ligands in monometallic and bimetallic sulfide nanoparticles. Photocatalytic activities of as-prepared monometallic sulfides and bimetallic sulfides were assessed by decolourisation of methylene blue and rhodamine-B in aqueous solution under ultraviolet light. This study indicates that in general, bimetallic sulfide nanoparticles are found to be more efficient photocatalysts than monometallic sulfide nanoparticles.

## 2.1 International Status

Binding studies show that metal dithiocarbamate complexes are useful in theelectrochemical sensing of anions. As a consequence of the fundamental roles played by negatively charged species in a range of biological, chemical, medical and environmental processes, the receptors to recognize and sense anions are useful to the society. Monometallic sulfide and bimetallic sulfide nanoparticles with variousphases and morphologies were prepared using metal dithiocarbamate complexes as single source precursors. Single source precursors are usually safer and more stable than the dual precursor systems. The properties studied of various metal sulfide nanoparticles in the presentstudy can help to provide their use in near future as photovoltaic and thermoelectric devices. The prepared nanoparticles showed effective photocatalytic activity towards the degradation of methylene blue and rhodamine–B which indicates their probable application in waste water treatment.

## 2.2 National Status

It has always been a challenge to synthesise pure solid mixed ligand complexes containing dithiocarbamato ligands, as their structural, electronic and magnetic properties are expected to be

distinct from those of the simple dithiocarbamate complexes. The main objective of the present investigation is to synthesise mixed ligand complexes of copper(II) and nickel(II) containing the dithiocarbamate ligand and the Schiff base The following strategies were adopted for the synthesis: _ Reaction of simple dithiocarbamate complexes of nickel (II) with SAAP. _ Reaction of simple SAAP complexes of nickel(II) with dithiocarbamate ligand derived from various aminoacid _ Reaction of bis(dithiocarbamato)-μ-dichlorodicopper(II) with VAAP and VAAPy

**2.3 Importance of the proposed project in the context of current status including scientific objective**

The present work is proposed Acyclic and macrocyclic transition metal dithiocarbamate complexes containing ferrocene and pyrrole moieties were successfully prepared and characterized by various spectral techniques. Structures of seventeen complexes were determined by single crystalX-ray diffraction. Complexes displayed various intra- and intermolecular interactions. Particularly, C–H···Ni anagostic interactions observed in some synthesized nickel complexes containing phosphine ligands are important due to their possible involvement in the C–H bond activation in the organic synthesis. Some of the as-prepared metal dithiocarbamate complexes are suitable receptors for anion sensing. Various phases and shapes of monometallic (M=Co, Ni, Cu, Zn) and bimetallic (Fe-M (M=Co, Ni, Cu, Zn)) sulfide nanoparticles were prepared from metal dithiocarbamate complexes. Metal (monometallic and bimetallic) sulfide nanoparticles were used as photocatalyst for degradation of toxic dyes.

**3. Progress/achievement so far,**

a) To synthesize pyrrole based acyclic and macrocyclic transition metal dithiocarbamate complexes (M = Co, Ni, Cu, Zn) which are designed to coordinate anions via their pyrrole NH groups, precluding direct metal ion coordination to the deprotonated pyrrole nitrogen atom.

b) to synthesize certain novel acyclic transition metal dithiocarbamate complexes (M = Co, Ni, Cu, Zn) containing ferrocene moiety.

c) to characterize the new complexes using elemental analysis, FT-IR, UVvis and NMR spectroscopy and X-ray crystal structure determination.

d) to investigate the anion (F— , Cl— , Br— , I— and benzoate) sensing properties of synthesized complexes using cyclic voltammetry. e) to synthesize bimetallic (Fe-M (M = Co, Ni, Cu, Zn))

sulfide nanoparticles from the synthesized ferrocenyl based complexes.

**4. Work Plan:**

This proposed project is visualize with the following objectives

- f) to synthesize metal (MS (M = Co, Ni, Cu, Zn)) sulfide nanoparticles from the synthesized pyrrole based dithiocarbamate complexes.
- g) to characterize the nanoparticles using FT-IR, PXRD, SEM/ TEM/HRTEM and EDS. h) to study the optical properties of the nanoparticles using UV-vis and fluorescence spectroscopy

**4.1 Methodology:**

Sodium salt of diethyldithiocarbamate (Et2dtc) and morpholine-N-carbodithioate (mordtc) was prepared by the general procedure given below: A 500 ml three-necked flask was equipped with a separating funnel, electric stirrer and air condenser. An aqueous solution of NaOH (20g, 0.5 moles) and 0.5 mole of amine were taken in the flask. This was cooled in a freezing mixture of ice and salt.CS2 (31 ml, 0.5 moles) was added drop wise from the separating funnel and the mixture was stirred for about 2 hours. The solid separated out was washed several times with petroleum ether and recrystallised from water.

The dithiocarbamato derivatives of α-amino acid such as glycine, alanine and methionine have been synthesized following a method similar to that described by Musil and Irgolic75 . The amino acid(50mmole) was reacted with an aqueous solution of Ba(OH)2.8H2O (55mmole) and the resulting suspension was magnetically stirred until total solution is achieved. In order to overcome the precipitation of barium carbonate, the presence of air was 22 avoided. Acetone (50ml) was then added followed by carbon disulphide(60mmole) dropwise. Formation of the barium salt occurs according to the reaction.

$$RHNHC(R')CO2H + M(OH)2 + CS2 \rightarrow Ba(S2CNRHC(R')CO2) + 2H2O$$

The solution was kept at 0o c for 12 hours. Addition of ethanol resulted in a white precipitate, which was filtered and washed with diethyl ether. The product was further purified by dissolving it in water and reprecipitating with ethanol.

## 4.2 Time Schedule of activities giving milestones through BAR diagram.

| S. NO | ACTIVITIES | 1st 4 (month) | | 2nd 4 (month) | | 3 rd 4 (month) | |
|---|---|---|---|---|---|---|---|
| 1 | Literature survey | | | | | | |
| 2 | Recruitment and Purchase of chemicals | | | | | | |
| 3 | Design synthesis of novel dithiocarbamate complexes | | | | | | |
| 4 | **Anion Sensing study** | | | | | | |
| | **Characterization of metal complexes** | | | | | | |
| 5 | Biological Studies | | | | | | |
| 6 | Compilation of results, submission of papers & report preparation Efforts towards are commercialization of developed product | | | | | | |

## 4.3 Expected outcome within the time period of Seed Money Scheme

- The novel synthesis and sensor methodology that will be obtained through this proposed project may be potential for biological applications in near future.
- The resultant sensing methodology of this project could be nationally as well as internationally patented.
- The completed project work could be commercialized towards the large scale development of product.
- The results of our project work will be consolidated, published in highly reputed journals.
- A group of full time research scholars working under the guidance of PI will be highly benefited and will be trained to carry-out an independent research in this field.

5. **Suggested Plan of action stating the name of funding agency where the project will be communicated for financial support within the time period of project.**

**NIL**

6. **Bibliography:**

**NIL**

7. **List of Projects submitted/implemented by the Investigators (Separate for Pi and Co-PI)**

**NIL**

## 7.1 List of Projects submitted to various Funding Agencies:

| SI. No | Title | Cost in lakhs | Month of Submission | Role as PI/Co-PI | Agency | Status |
|---|---|---|---|---|---|---|
| | NA | NA | NA | NA | NA | NA |

## 7.2 Details of Projects under Implementation:

| SI. No | Title | Cost in lakhs | Month of Submission | Role as PI/Co-PI | Agency |
|---|---|---|---|---|---|
| | NA | NA | NA | NA | NA |

## 7.3 Details of Projects completed during the last 5 Years:

| SI. No | Title | Cost in lakhs | Month of Submission | Role as PI/Co-PI | Agency |
|---|---|---|---|---|---|
| | NA | NA | NA | NA | NA |

## 8. List of publications published by the Investigators

1. **G. Gurumoorthy**, S. Thirumaran and S. Ciattini, Unusual octahedral Hg(II) dithiocarbamate: Synthesis, spectral and structural studies on Hg(II) complexes with pyrrole based dithiocarbamates and their utility for the preparation of α- and β-HgS, *Polyhedron,* **2016**, 118, 143–153.
2. **G. Gurumoorthy** and S. Thirumaran, Synthesis, spectral, structural and DFT studies on nickel(II) complexes with pyrrole based dithiocarbamate and triphenylphosphine ligands, *Phosphorus Sulfur Silicon Relat. Elem.,* **2017**, 192, 330-337
3. **G. Gurumoorthy**, P. Jamuna Rani S. Thirumaran and S. Ciattini, Cobalt(III) dithiocarbamates for anion sensing and preparation of cobalt sulfide and cobalt-iron sulfide nanoparticles: photocatalytic degradation of dyes with as-prepared nanoparticles, *Inorganica. Chimica. Acta,* **2017**, 455, 132-139.
4. **G. Gurumoorthy,** S. Thirumaran and S. Ciattini, Synthesis of copper sulfide and copper-iron sulfide nanoparticles from copper(II) dithiocarbamate complexes involving pyrrole and ferrocene moieties: X-ray structure of bis(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamato-S,S')- copper(II), *Appl Organomet Chem.* 2018;**32**:e4363.
5. **G. Gurumoorthy,** and S. Thirumaran, Tris(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamato-S,S')cobalt(III) for anion sensing and preparation of cobalt-iron sulfide nanoparticles: A new photocatalyst for the degradation of dyes, https://doi.org/10.1080/10426507.2018.1539720.
6. E. Sathiyaraj, **G. Gurumoorthy** and S. Thirumaran, Nickel(II) dithiocarbamate complexes containing the pyrrole moiety for sensing anions and synthesis of nickel sulfide and nickel oxide nanoparticles, *New J. Chem.,* **2015**, 39, 5336-5349.
7. S. Tamilvanan, **G. Gurumoorthy**, S. Thirumaran and S. Ciattini, Synthesis, characterization, cytotoxicity and antimicrobial studies on Bi(III) dithiocarbamate complexes containing furfuryl group and their use for the preparation of $Bi_2O_3$ nanoparticles, *Polyhedron* **2017**, 121, 70-79.
8. S. Tamilvanan, **G. Gurumoorthy**, S. Thirumaran and S. Ciattini, Bismuth(III) furfuryl based dithiocarbamates: Synthesis, structures, biological activities and their utility for the preparation of $Bi_2S_3$ and $Bi_2O_3$ nanoparticles, *Polyhedron* **2017**, 123, 111-121.

**List of publications published by the Investigators**

1. T. Ezhilarasuand S. Balasubramanian, Synthesis, characterization, photophysical and electrochemical studies of Ru(II) complexes with 4'-substituted terpyridine ligands and their biological applications, *ChemistrySelect*,2018, *3*, 12039.
2. T. Ezhilarasu, A. Sathiyaseelan, P. T. Kalaichelvan and S. Balasubramanian, Synthesis of 4'-substituted-2,2';6',2"-terpyridine Ru(II) complexes

Electrochemical, Fluorescence quenching and antibacterial studies, *Journal of Molecular Structure*, 2017, *1134*, 265.

3. T. Ezhilarasu and S. Balasubramanian, 3-Methoxy-4-(prop-2-yn-1-yloxy)benzaldehyde, *IUCrData*, 2016, *1*, x161919.
4. S. Malathi, T. Ezhilarasu, T. Abiraman and S. Balasubramanian, One pot green synthesis of Ag, Au and Ag-Au alloy nanoparticles using isonicotinic acid hydrazide and starch, *Carbohydrate Polymers*, 2014, *111*, 734.
5. S. Malathi, V. Ramya, T. Ezhilarasu, T. Abiraman and S. Balasubramanian., Green Synthesis of novel jasmine bud shaped copper nanoparticles, *Journal of Nanotechnology*, 2014, Article ID 626523, 1.
6. T. Ezhilarasu, S. Malathi and S. Balasubramanian, Synthesis, characterization and electrochemistry of ruthenium terpyridine complex anchored to gold nanoparticle and its anticancer activity, *NanoBiomaterials*, 2012, 65. Bloomsbury Publishing India Pvt. Ltd, New Delhi, ISBN: 978-93-82563-37-2.

**9. Budget***

| **Sl. No.** | **Head** | **Amount in INR** |
|---|---|---|
| 2 | Borosil RMA Stirring Mantle, BLFHRMA250<br>AIE UV-C Chamber 33 WATTS UV-C (35 Liters Capacity) – DIGITAL<br>Consumables (Like ICs, application boards, chemicals, testing<br>charges, tools, etc.) | 11,000/-<br>12,000/-<br>60,000/- |
| 3 | Travel support for the purpose of research work. | 6,000/- |
| 4 | Contingency | 5,000/- |
| 5 | Others | 6,000/- |
| | **Total** | 1,00,000 |

**10. Name of at least two subject experts from the Institute and one from the outside Institute with their contact details:**

a) Dr. P. Paulraj – Associate professor, Dept. Of chemistry, BIHER, Chennai-600073

b) Dr. K. Kannan, Associate professor, Dept. Of chemistry, BIHER, Chennai-600073

## CERTIFICATE FROM THE INVESTIGATOR

Project Title:

**Synthesis and Characterization of Metal dithiocarbamates and their Utilization of Anion Sensing: Preparation of Metal Sulphide and their Applications**

**It is certified that**

1. I do hereby agree to submit a complete proposal for financial support to the external funding agency within the time period of SMS-2018
2. I undertake that spare time on equipment procured in the project will be made available to other users.
3. I agree to submit a certificate from Institutional Biosafety Committee, if the project involves the utilization of genetically engineered organisms. I also declare that while conducting experiments, the Biosafety Guidelines of Department of Biotechnology, Department of Health Research, GOI would be followed in to.
4. I agree to submit ethical clearance certificate from the concerned ethical committee, if the project involves field trails/experiments/exchange of specimens, human & animal materials etc.
5. I agree to abide by the terms and conditions of SMS-2018, BIHER,Chennai.

Name and signature of
Principal Investigator
Dr. G. GURUMOORTHY

Name and signature of
Co-Principal Investigator
Dr. T. EZHILRASAN

Date: 01/10/2019

Place: Chennai-73

Forwarded by Head of the Department

Signature of the Head

## PROJECT EVALUATION FORMAT

**Recommendation Sheet**

Name of the Investigator : Dr. G. Gurumoorthy

Name of the Co-Investigator : Dr. T. Ezhilrasan

Name of the Department : Chemistry

Title of project : **Synthesis and Characterization of Metal dithiocarbamates and their Utilization of Anion Sensing: Preparation of Metal Sulphide and their Applications**

Recommendation of the evaluation committee (Recommended/Revision/Not Recommended)

Financial allocation recommended

| Sl. No. | Head | Amount in INR |
|---|---|---|
| 1 | Borosil RMA Stirring Mantle, BLFHRMA250<br>AIE UV-C Chamber 33 WATTS UV-C (35 Liters Capacity) - DIGITAL | 11,000/-<br>12,000/- |
| 2 | Consumables (Like ICs, application boards, chemicals, testing charges, tools etc.) | 60,000/- |
| 3 | Travel support for the purpose of research work. | 6,000/- |
| 4 | Contingency | 5,000/- |
| 5 | Others | 6,000/- |
| | **Total** | 1,00,000/- |

**Name and Signature of the Research Advisory Committee members with date**

Dr. P. Naveenchandran

*BIHER, Chennai*

*Seed Money Scheme - 2018*