

UGC MAJOR RESEARCH PROJECT FINAL REPORT

(F.No.: 42-341/2013(SR) dated 22.03.2013)

Acyclic and macrocyclic transition metal complexes for the electrochemical sensing of anions and synthesis of bimetallic sulfide nanoparticles

Principal Investigator : **Dr. S. Thirumaran**
Associate Professor
Department of Chemistry
Annamalai University
Annamalainagar – 608 002
Tamil Nadu, India

Co-investigator : **Dr. B. Arul Prakasam**
Assistant Professor
Department of Chemistry
Annamalai University
Annamalainagar – 608 002
Tamil Nadu, India

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002**

**PERFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE
FINAL REPORT OF THE WORK DONE ON THE MAJOR RESEARCH PROJCT**

1.	Title of the Project	Acyclic and macrocyclic transition metal complexes for the electrochemical sensing of anions and synthesis of bimetallic sulfide nanoparticles
2.	Name and Address of the Principal Investigator	Dr. S. THIRUMARAN Associate Professor Department of Chemistry Annamalai University Annamalainagar-608 002
3.	Name and Address of the Institution	Annamalai University, Annamalainagar-608 002.
4.	UGC Reference No. & Date	F. No: 42-341/2013 (SR) dated 22.03.2013
	U.G.C. Extension Letter No and Date	F. No: 42-341/2013 (SR) dated 09.03.2016
5.	Date of implementation	01.04.2013
6.	Tenure of the project	01.04.2013 to 31.03.2017
7.	Total Grant Allocated	Rs.11,42,733.00/-
8.	Total Grant Received	1 st Instalment : Rs. 6,66,800/- 2 nd Instalment : Rs.3,53,440/- Total: Rs. 10,20,240/-
9.	Final Expenditure	Rs. 10,16,976/-

10. Brief Objectives of the Project:

It is proposed

- 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, UV-vis 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.
- 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.

11. **Whether Objectives Were Achieved:** YES

12. **Achievements from the projects:**

- 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 crystal X-ray diffraction. Complexes displayed various intra- and intermolecular interactions. Particularly, C–H \cdots 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.

13. Summary of the findings:

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 (ν_{C-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 \cdots 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 displayed C-H \cdots π (chelate, MS_2C) interactions. Weak intermolecular C-H \cdots S, C-H \cdots π (chelate), C-H \cdots π , and

N-H $\cdots\pi$ 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 X-ray 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⁻, I⁻ and 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 F⁻ and 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.

14. Contribution to the Society

- Binding studies show that metal dithiocarbamate complexes are useful in the electrochemical 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 various phases 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 present study 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.

15. Whether any Ph.D. Enrolled/Produced out of the Project:

Ph.D. Produced : YES

Candidate Name : G.Gurumoorthy

Awarded on : 12-5-2017

16. List of Publications

1. G. Gurumoorthy, **S. Thirumaran***, and S. Ciattini, Synthesis and characterization of copper(II) dithiocarbamate complexes involving pyrrole and ferrocene moieties and their utility for sensing anions and preparation of copper sulfide and copper-iron sulfide nanoparticles, *Appl. Organomet. Chem.*, 2018; e4363. <https://doi.org/10.1002/aoc.4363> .
2. 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, *Inorg. Chim. Acta*, **2017**, 455, 132-139.
3. 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.
 4. 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.
 5. 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.
 6. P. Jamuna Rani, **S. Thirumaran*** and S. Ciattini, Synthesis and characterization of Ni(II) and Zn(II) complexes of (furan-2-yl)methyl(2-(thiophen-2-yl)ethyl)dithiocarbamate (ftpedtc): X-ray structures of [Zn(ftpedtc)₂(py)] and [Zn(ftpedtc)Cl(1,10-phen)], *Spectrochim. Acta, A*, 137 (2015)1164-1173.
 7. E. Sathiyaraj, P. Valaramthi, **S. Thirumaran***, S. Ciattini, V.K. Gupta and R.Kant, Effect of N-bound organic moiety in dithiocarbamate ($R_2NCS_2^-$) and *trans* influence of triphenylphosphine on NiS₂PN chromophore, *Phosphorus, Sulfur and silicon*, 2015, 190, 1127-1137.