Synthesis and characterization of copper and silver complexes stabilized by Dithiocarbazate

Project work submitted to the Central University of Punjab

For the award of
Master of Science
In
Chemistry

BY
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May, 18

DECLARATION

I declare that the thesis entitled **“Synthesis and Characterization of copper and silver complexes stabilized by Dithiocarbazate”** has been prepared by me under the guidance of Dr. Rajendra Singh Dhayal, Assistant Professor, Department of Chemical Sciences, School of Basic and Applied Sciences, Central University of Punjab. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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Name and signature of candidate

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Date:

CERTIFICATE

I certify that Sambit Shashanka Sekhar Rout has prepared his thesis entitled **“Synthesis and Characterization of copper and silver complexes stabilized by Dithiocarbazate”** for the award of M.Sc. degree of the Central University of Punjab, under my guidance. He has carried out this work at the Department of Chemical Sciences ,Central University of Punjab.

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ABSTRACT

“Synthesis and Characterization of copper and silver complexes stabilized by Dithiocarbazate”

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Degree for which submitted : Master of Science

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Key words : Dithiocarbazate, Schiff base, clusters, Copper, Silver

ABSTRACT

Metal complexes of Dithiocarbazoic acid, it’s esters and their Schiff bases have been considered for the potential of anticancer, antibacterial, antifungal, antiamoebic and insecticidal activities. S-methyldithiocarbazate, S-benzyldithiocarbazate and it’s Schiff bases were already reported. We synthesize copper(I)/silver(I) complexes using of dithiocarbazate and it’s Schiff base. We also isolated heteroatomic (copper and silver) complexes stabilized by dithiocarbazate. All the complexes are characterised by SEM (Scanning Electron Microscope), EDS (Energy dispersive X-ray Spectroscopy), Elemental mapping and NMR (Nuclear Magnetic Resonance). Further, we synthesize hetero clusters by the use of copper and silver, which can be utilized for making of nanoparticles and nanomaterials in near future.

Name and signature of student

Name and signature of supervisor

To my parents …

ACKNOWLEDGEMENTS

This project is the end of my journey in obtaining my M.Sc. I have not traveled in a vacuum in this journey. This project has been kept on track and been seen through to completion with the support and encouragement of numerous people including my well-wishers, my friends, and colleagues.

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Name and signature of student

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LIST OF ABBREVIATIONS

Full Form	**Abbreviations**
Dithiocarbazate	**DTC**
S-methyldithiocarbazate	**SMDTC**
S-benzyldithiocarbazate	**SBDTC**
Deoxyribonucleic Acid	**DNA**
Nitrogen- Sulphur	**N-S**
Non Linear Optical	**NLO**
Nuclear Magnetic Resonance	**NMR**
Melting Point	**M.P**
Percentage	**%**
Gram	**Gm**
Milligram	**Mg**
Degree Celsius	**^{0}C**
Milimole	**Mmol**
Chemical shift	**δ**
Scanning Electron Microscope	**SEM**
Energy dispersive X-ray spectroscopy	**EDS**
Dichloromethane	**DCM**

CHAPTER 1

INTRODUCTION

1.Introduction:

The characterisation and synthesis of Dithiocarbazate (DTC) and it's derivatives have been studied several times. First,In 1974,Chemistry of nitrogen-sulphur (N-S) ligands was studied under Ali and Livingstone. From that, many more project work has been published about Dithiocarbazate and it's coordination with metal complexes. The main part of the work centred upon Dithiocarbazates, it's methyl and benzyl derivatives, Dithiocarbazate Schiff bases and their complexes, while other substituted derivatives have been reviewed in figure 1.a. Metal complexes of Dithiocarbazoic acid and it's esters and their Schiff bases have been considered mainly for the potential of anticancer, antibacterial, antifungal, antiamoebic and insecticidal activities (Chew et al.,2004), In recent years it has been has enthusiasm that the Schiff bases of Dithiocarbazates as a ligand deprotonated by the non-linear optical (NLO) properties of complexes; For the extended p-conjugation of the deprotonated ligands,the hyperpolarisability of these complexes was highly second order. Some of the metal complexes with Dithiocarbazate ligand are expected to be naturally active complexes. Otherwise, the carcinostatic activities have been found for some metal complexes of Dithiocarbazic acid and some Schiff bases derived from it's ester (Majumder et al., 1998). The synthesis of these metal complexes continues to be a enthusiasm for the assess of the coordination chemistry and their potential to be an anti-microbial and anti-cancer character.

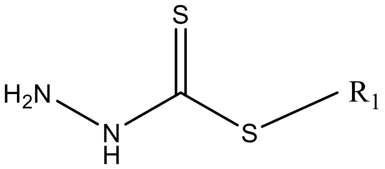
Dithiocarbazates are not examine by a single source precursors to synthesis of a semiconductor metal sulphide; although they are around a significant class of sulphur-nitrogen (N-S) chelating agents with the soft sulphur(S) and nitrogen(N) donor atoms in their structural backbones, also the capacity of reacting with both the transition metal and some of the main group metal ions from the air-stable complexes (Chan *et al.,*2008) (Mohammad Akbar Ali *et al.,*2008). Schiff bases ligands and the complexes of their metal have variety of applications in the biological, analytical, industrial and clinical fields (Kumar *et al.,* 2009; Gupta and Sutar, 2008). The Schiff bases, i.e. {Dithiocarbazate $NH_2NH_2CS_2$ (DTC)} and it's substituted derivatives, have been synthesized and studied in recent decades and the main purpose of study for the following foremost reasons are:

(a) They provides the arrangement of the ligands whose properties can be changed and presenting by the organic substituents, and thereby causing a difference in the donor properties of the ligand.

(b) The relations between the donors and the metal ions provides a different structure and properties to the complexes.

(c) The complexes are potentially useful biological activities.

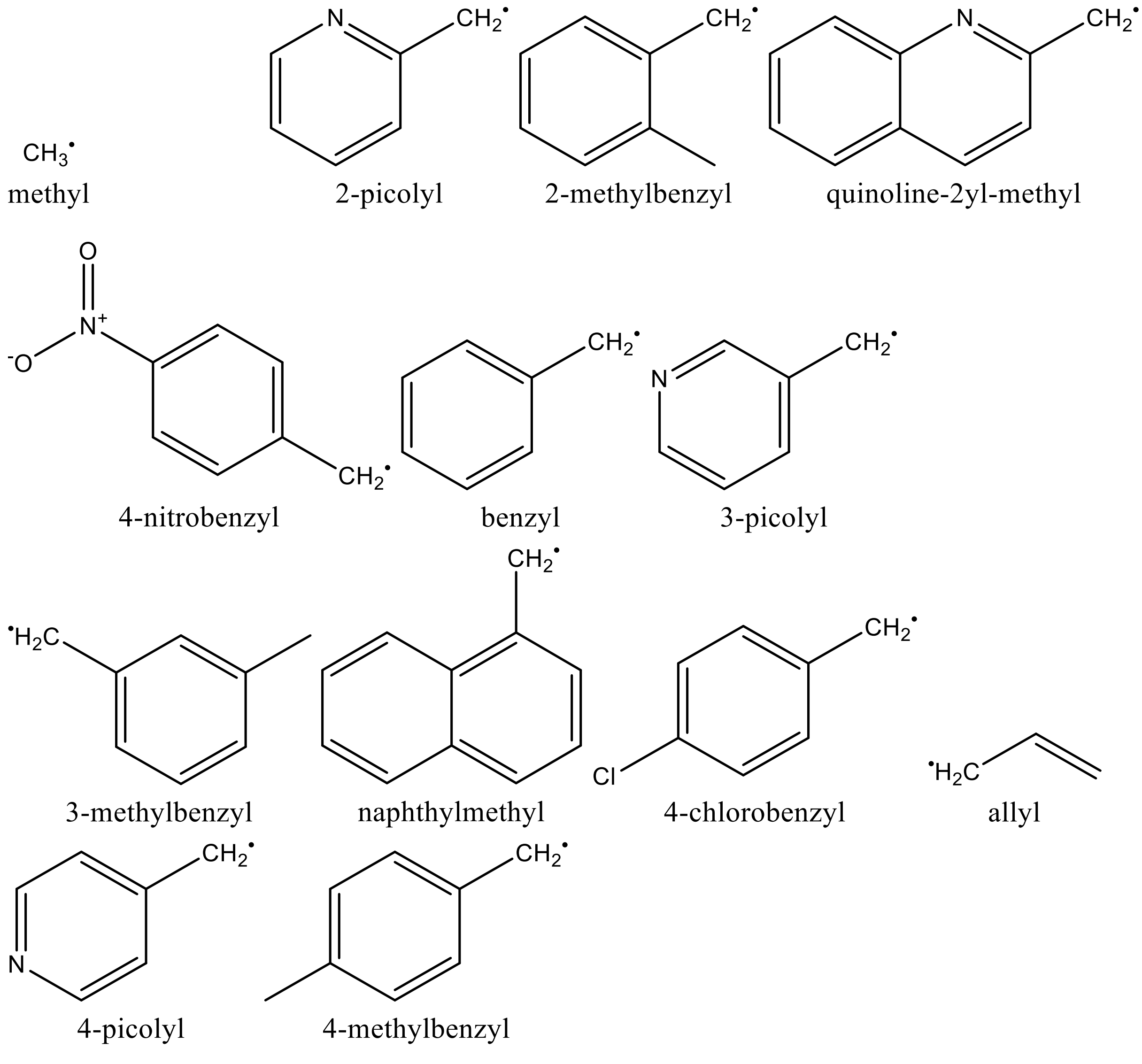
The nature of the metal centres, characteristic coordination modes and easy to get the redox states and it's tunable thermodynamics and kinetic properties are permit the metal complexes to offer the potential advantages over the organic substituents (Van Rijt and Sadler,2009). Again, Sadler stated that the nature of interactions, the biological target sites and the protein receptors of the deoxyribonucleic acid(DNA) was managed by the reactivity of the metals with the ligands (2009, p. 10647). The research in the coordination chemistry, having nitrogen(N) and sulphur(S) containing ligands like Schiff bases which were derived from the dithiocarbazate(DTC) has so many research works during recent years (M Akbar Ali and livingstone ,1974; Pelosi, 2010; Beraldo and Gambinob,2004). Schiff bases formed from the S-alkyl esters of dithiocarbazic acid and was a class of nitrogen(N)-sulfur(S) chelating group contain both the soft sulphur and nitrogen donor intermediates, which were capable of reacting with transition and with some main group metal ions. Both formed stable complexes having physico-chemical properties (M Akbar Ali *et al.,*2008). Schiff bases have frequently used as chelating ligands for the formation of complex compounds, which are useful as catalysts, dyes and polymers. The classes of ligands having both hard nitrogen(N) and soft sulphur(S) donor atoms. Both imino and thioamino groups are present in their Schiff base structures(Tarafder, Islam, Crouse,Chantrapromma ,and Fun, 2008). Coordination of such compounds with metal ions upgrades with their activities (Lobana, *et al.,*2009).



S-substituted dithiocarbazate

Figure 1(a): S- substituted dithiocarbazate

Where R_1 may be:



methyl 2-picolyl 2-methylbenzyl quinoline-2yl-methyl

4-nitrobenzyl benzyl 3-picolyl

3-methylbenzyl naphthylmethyl 4-chlorobenzyl allyl

4-picolyl 4-methylbenzyl

Figure 1(b): R-substituted compound

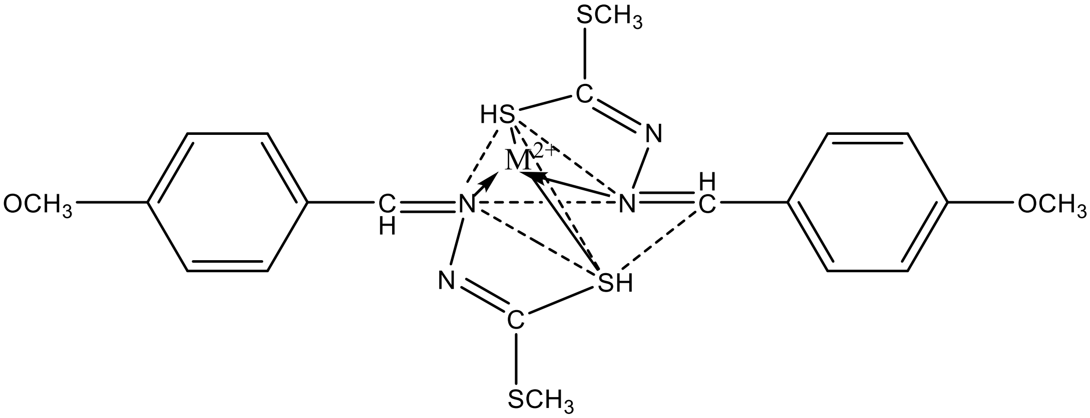


Figure 1(c): Tetrahedral geometry of M^{2+} complex; M^{2+} = Pb(II), Zn(II)

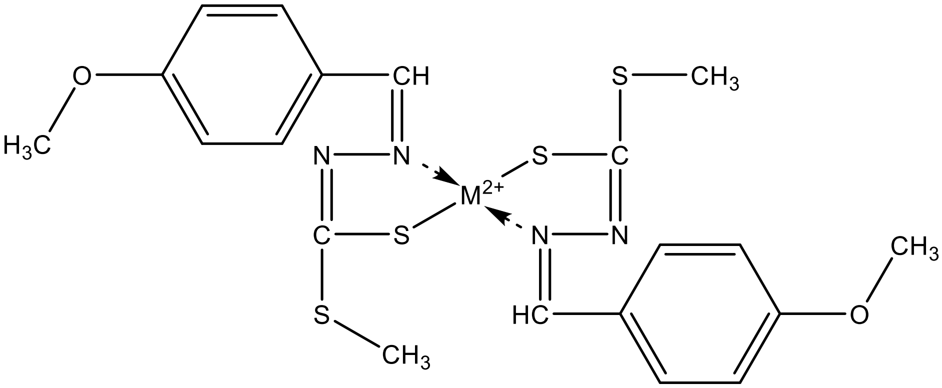


Figure 1(d): Square planar geometry of the M^{2+} complexes; i.e. Cu(II), Ni(II)

CHAPTER 2

REVIEW OF LITERATURE

Review of literature:

Schiff base ligands [Figure 2.1(a)] formed by the condensation of an aldehyde or a ketone having carbonyl carbon with the Dithiocarbazates. Figure 2.1(b), Carbonyl compounds used for the preparation of the ligand in the condensation process at position R_2. The Schiff bases and the Schiff base metal complexes of the examples of alkyl ,aryl and heteroatom carbonyl compounds are biological activity compound. From the variety of S–substituents, the modifications at N_1 atom of the derivatives of Dithiocarbazate have also been reported [Figure 2.1(c)]. Dithiocarbazate and bis(dithiocarbazate) ligands are open chain and macro acyclic metal complexes upon in the complex formation.

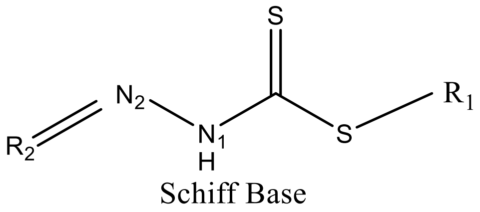
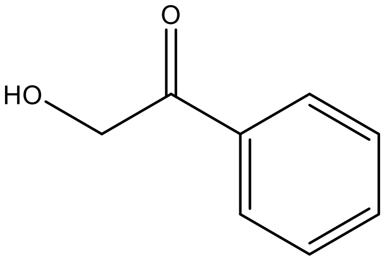
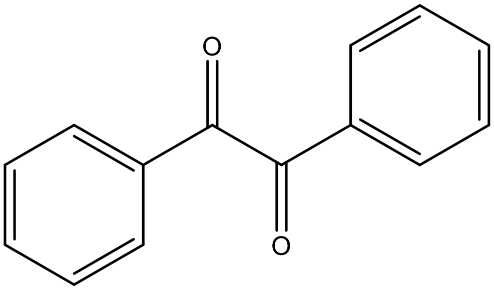


Figure 2.1(a): Schiff base

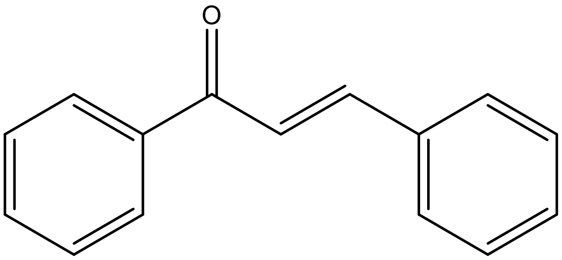
(I) Alkyl and Aryl series



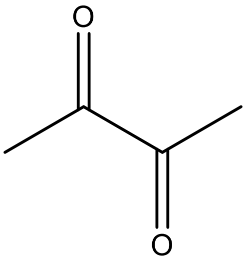
2-hydroxyacetophenone



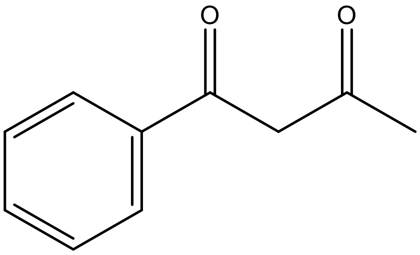
benzil



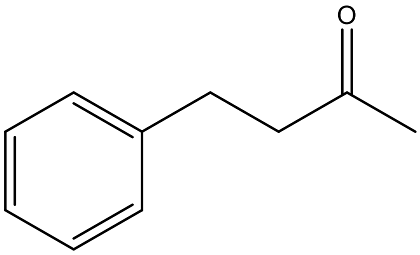
chalcone



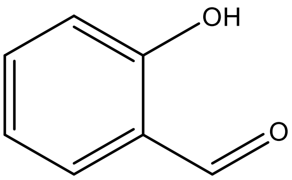
2,3-butanedione



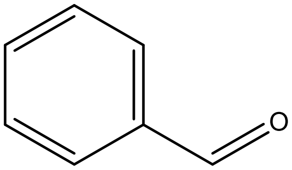
4-phenyl-2,4-butanedione



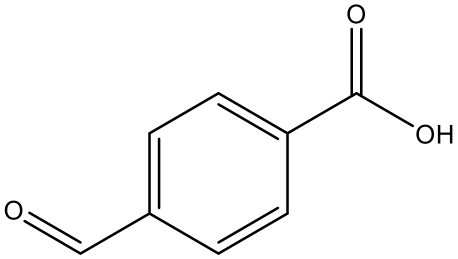
benzyl acetone



salicylaldehyde



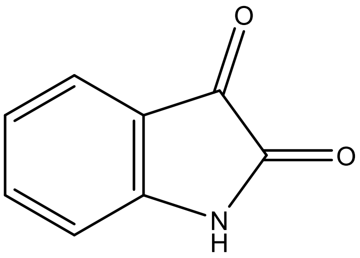
benzaldehyde

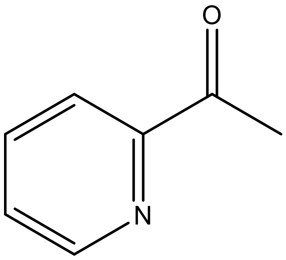


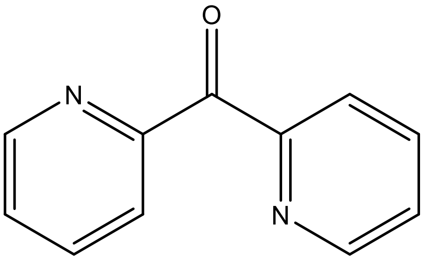
4-carboxybenzaldehyde

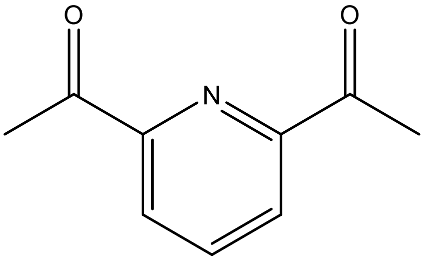
Figure 2.1(b): Alkyl and Aryl halide

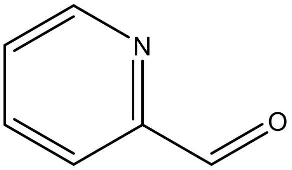
(II) Heteroatom series:

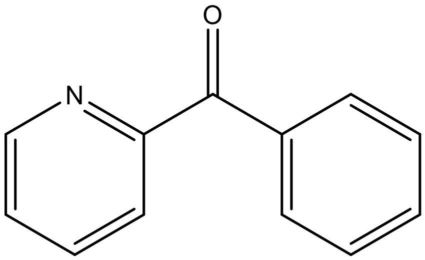

isatin

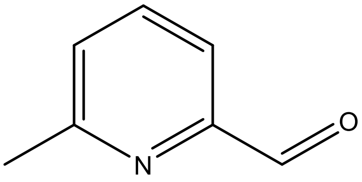

2-acetylpyridine

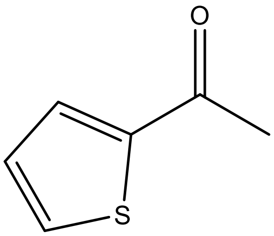

di-2-pyridylketone

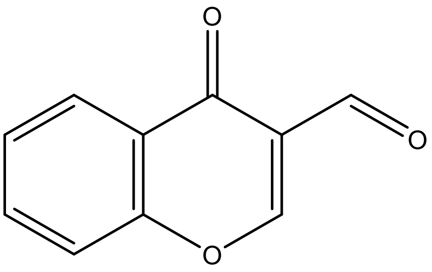

2,6-diacetylpyridine

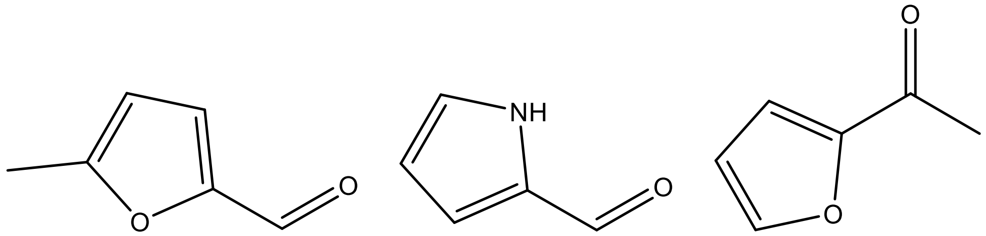

2-pyridinecarbaldehyde


2-benzoylpyridine

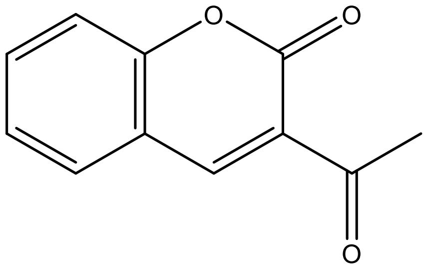

6-methyl-2-formylpyridine


2-acetylthiophene


3-formylchromone



5-methyl-2-furaldehyde pyrrole-2-carboxaldehyde 2-acetylfuran

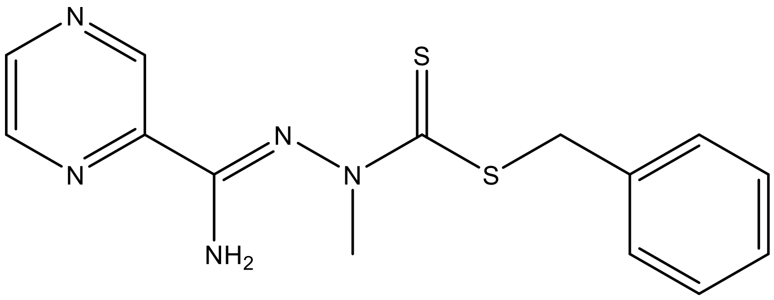


3-acetylcoumarin

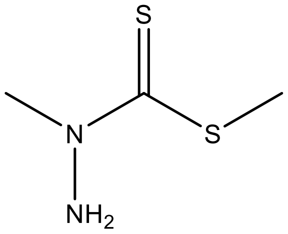
Figure 2.1(c): Heteroatom series

Examples of carbonyl compounds which are used for the formation of Schiff base with dithiocarbazate ligands (a) alkyl and aryl series; (b) heteroatom series.

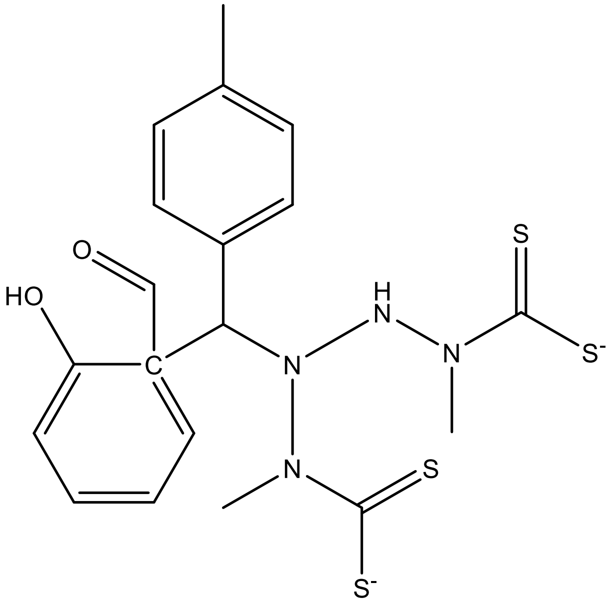
2.2 Other derivatives at N_1 atom of the Schiff base:



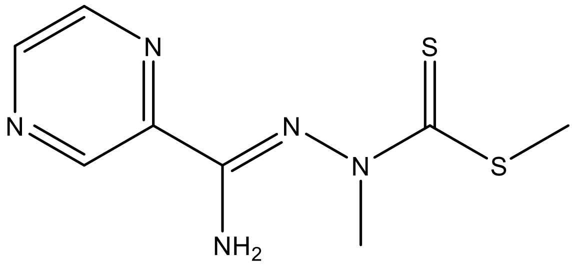
benzyl-3-[amino(pyrazin-2-yl)methylidene]-2-methyldithiocarbazate



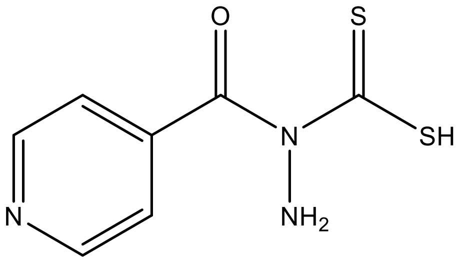
N-methyl-S-methyl dithiocarbazate



salicylaldehyde-a,a'-xylene-bis(N-methyldithiocarbazate)



methyl-3-[amino(pyrazin-2-yl)methylidene]-2-methyldithiocarbazate



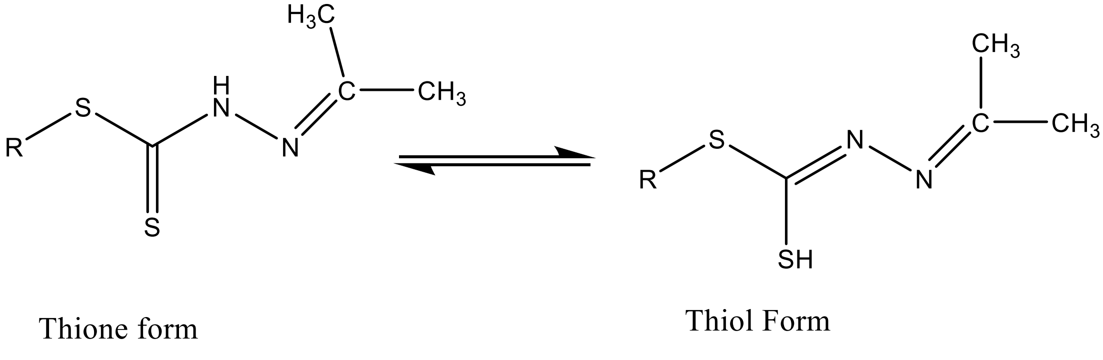
isonicotinoyldithiocarbazic acid

Figure 2.2 : N_1 atom of the Schiff base

Examples of different dithiocarbazate derivatives at N_1 atom

Dithiocarbazate connected compounds could exist differently, by their structural demonstrate was E or Z diastereoisomers compare to C=N bond in azomethine. The conformations form thiol-thione tautomers and ,if a hydroxyl functional group is there , than thiocarbonyl group affected by C=S or S=C conformation either towards (Lanfredi, *et al.,1977)* or away from the intermolecular hydrogen bonding (Figure 2.4) (Krasowska, *et al.,* 2010). Schiff bases,in the solid state exist in thioketo tautomeric form which trans to the thione sulphur atom with the azomethine nitrogen atom (M Akbar Ali *et al.,*2008). Dithiocarbazate derivative compounds crystallize in trans-cis configuration of the C=S bond in both the S-alkyl/aryldithiocarbazate and it's dithiocarbazate Schiff base ligands. They form intermolecular bonds between the NH-S hydrogen bonding and CH-S interactions between in the S-alkyl/aryldithiocarbazates and it's dithiocarbazate Schiff base ligands. In square planar, tetrahedral, square pyramidal and octahedral structure; number of bonding modes and geometries reviewed for the dithiocarbazate derivatives with the actinides and with the transition, non-transition and heavy metals.

(a)



(b)

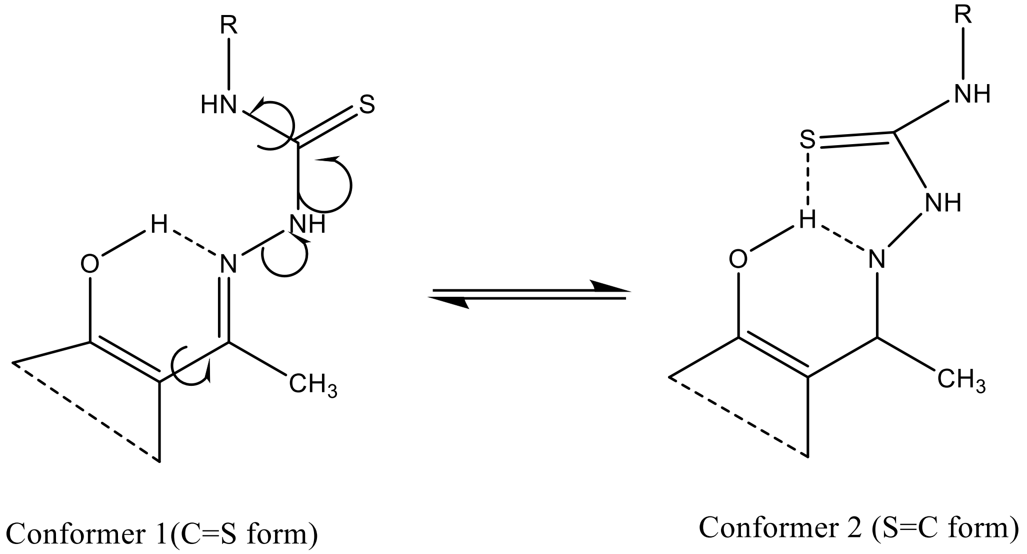


Figure 2.4(a) Thiol - Thione tautomeric form of Schiff base (Ali et al.,2008) (b) C=S and S=C conformers (Krasowska et al.,2010)

Transition metal complexes containing sulphur – nitrogen (S-N) chelating agents were derived from the dithiocarbazic acid ,it's alkyl/aryl esters and their Schiff bases studied in coordination chemistry (Chew *et al.,*2004). The derivative complexes from Schiff bases of dithiocarbazates were show:

(a) Due to the extended p-conjugation of the Schiff base dithiocarbazate deprotonated ligands, it show high second order hyperpolarisability .
(b) Non linear optical (NLO) properties

Due to the transition metal complexes, NS donors show wide Lewis acid properties in spite of their coordination geometries (Cases, *et al.,2000)*.

The isomeric Schiff bases,(NS) and (NS') formed from the condensation of methylketone and furalaldehyde with SMDTC. Bidentate Schiff base ligands prepared with Cd, Sn, Co, Pb and Fe (Chew *et al.,*2004).

In Schiff bases, the aldehyd/ketones replaced by imine or azomethine group then it was widely used for biological activities such as antibacterial, antiviral, antimalerial and antifungal Schiff bases and also used for industrial purposes (Silva *et al.,*2011).

To study about the drug for the treatment of anti-tuberculosis therapy synthesized from the compounds based on dithiocarbazates, thiosemicarbazones, semicarbazones and hydrazones compounds (Pavan *et al.,*2010).

All dithiocarbazate complexes show a planar fourfold environment around the metal M(II) center. These dithiocarbazate complexes exhibited biological activity with the intracellular forms of Trypanosoma cruzi, which was time and concentration dependent (Maia *et al.,*2010).

Poor reviews for main group element was due to the low solubility of the main group element complexes with the non-coordinating solvents. Due to air-stable, nontoxic and easy to handle properties they consolidate all the elements to synthesize the product. The bulkiness of the single source metal complexes of the ligands such as dithiocarbamates, dialkyldiselenophosphinate, dichalcogenoimidophosphinate, ionic dialkyldiselenophosphinate (Fan *et al.,*2007; Kedarnath *et al.,*2007). Copper complexes are subjected to research because of their heavy potential therapeutic applications (Duncan and White, 2012) mainly in valuable antitumor (Afrasiabi *et al.,*2003;Chakraborty *et al.,*2010) and antibacterial agents. In cell destruction thiosemicarbazone copper complexes are active and inhibition of DNA synthesis (Ferrari, *et al.,* 2002). Copper complexes with multidentate Schiff base ligands are rich in spectroscopic and magnetic properties. Different oxidation state of copper provide biological metalloenzymes and metalloproteins (Balamurugan, *et al.,*2006). Single source of molecular precursors in metal complexes used by synthetic chemistry of MS semiconductor nanocrystals(Fan,*et al.,*2007); Jun,*et al.,* 2001).

Hugo Schiff was first reported Schiff's base which was an important class of organic compounds in 1864 and the azomethine group (-CH=N-) containing compounds are formed by the condensation of primary amines and carbonyl compounds. The azomethine group (RCH = N-R^1), (where R and R^1 are alkyl, aryl, cycloalkyl, or heterocyclic groups) (Hussain, *et al.,*2014).

Schiff bases bi- or tri- dentate ligands are capable of forming stable complexes with the transition metals. Aromatic aldehydes with the conjugation system are more stable compared to the aliphatic aldehydes (Arulmuruga, *et al.,*2010).

Schiff bases formed by the condensation of dithiocarbazate derivatives.

We have interested to synthesize air stable copper (I) and silver(I) complexes, from a stable secondary ligand like dithiocarbazate derivative to form nanoparticles. We also tried to form homoatomic and heteroatomic dithiocarbazate cluster complexes for the further formation of different types of clusters and nanoparticles.

Choice of metal:

Complexes which are based on copper have various biological activities like antiviral (Manan *et al.,*2011), anticancer (Patitungkho, *et al.,*2011), antimicrobial (Manan *et al.,*2011) and anti-inflammatory agents (Hoonur *et al.,*2010).

The condensation of SBDTC and acetophenone form a bidentate Schiff base which on further reaction with copper(II), synthesize a bis-chelated inner complexes(CuL_2). The ligand characterized by the physico-chemical techniques. CuL_2 Complex showed analgesic activity compared to Diclofenac sodium, all the compounds displayed good anti-inflammatory activity than the Indomethacin drug (Zangrando *et al.,*2015).

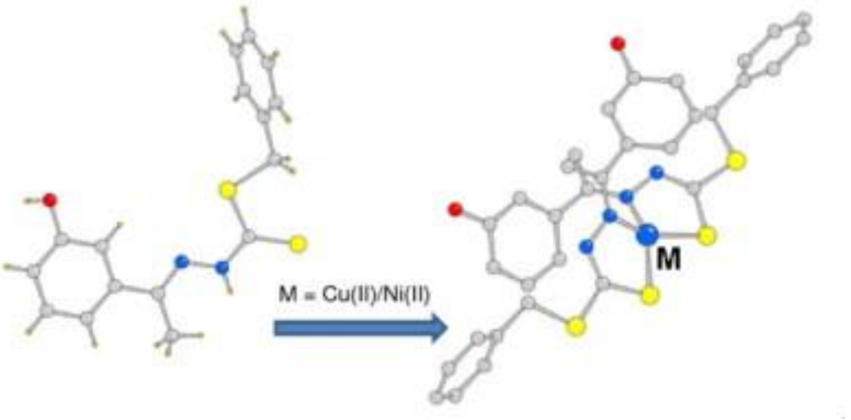


Figure 2.5: copper bis-chelated

Analogues of Bis(thiosemicarbazone) with Cu(II) are biological revolution as radiopharmaceuticals (Paterson and Donnelly,2011). Further, Nitrogen atom replaced by the sulphur atom results for the exploration into dithiocarbazate compounds.

CHAPTER 3

METHODS AND MATERIALS

Methods and materials

Reagents:

All the chemicals which were used for the preparation of the ligands and the complexes, were of analytical grade and that were used without further purification. $Cu(PPh_3)_2NO_3$, Potassium hydroxide (KOH), Hydrazine hydrate (NH_2NH_2, H_2O, 90%) , Carbon disulfide (CS_2), $Ag(PPh_3)_2NO_3$, Ethanol, Acetonitrile, n-Hexane, Diethyl ether, chloroform, Dichloromethane (DCM) was obtain from Loba chem, Methanol obtained from fisher chemicals and Tetrahydrofuran(THF) obtained from the spectrochem. Double distilled water was also used for the preparation of chemicals and reagents.

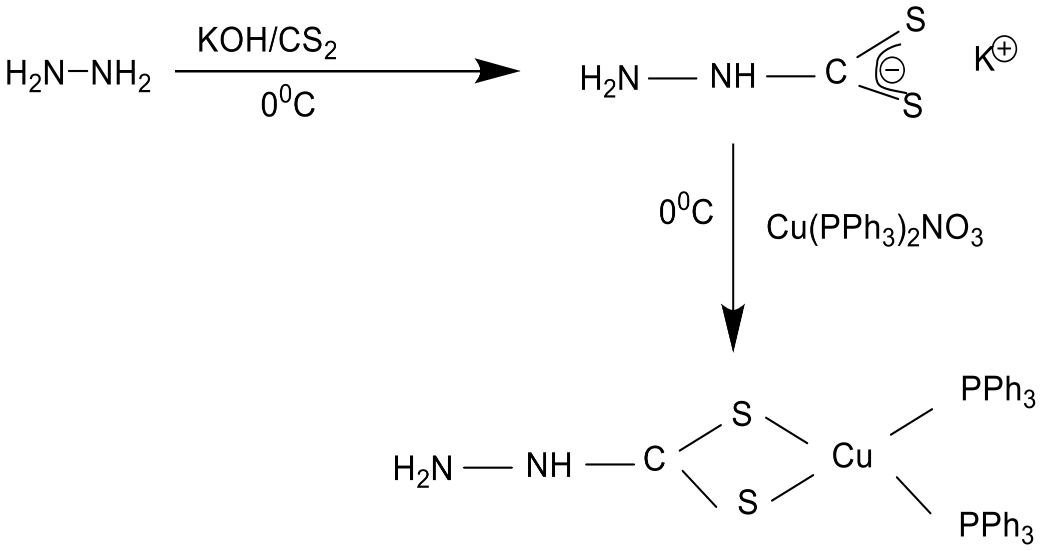
Instruments Used:

Swiss made weighing balance used for weigh for all reagents and chemicals . The Characterisation of the ligand and it's derivatives done by the Nuclear Magnetic Resonance (NMR). ^{1}H NMR and C^{13} NMR data used for the characterisation. Ligand and it's derivatives also characterised by Field Emission Scanning Electron Microscope (FESEM) (by ZEISS sigma family electronics). EDS (Energy Dispersive X-ray spectroscopy) used for the chemical characterisation or the elemental analysis of the dithiocarbazates. SEM (Scanning electron microscope) used for the image of the surface of the compound.

Synthesis of dithiocarbazate:

0.573 gm of KOH is dissolved in 90% ethanol (10 ml).after stirring , Hydrazine hydrate (498 μl)is added to it. The reaction is cooled in ice by keeping the temperature 0 ^{0}C . After 15 minutes of stirring ,CS_2 (616 μl)is added through additional funnel. The reaction is continue in 0 ^{0}C . After the total addition of CS_2 ,a white colour turbid liquid formed. After 2.30 hours of stirring a yellow colour has been appeared. Then after stop stirring ,two layer appear. The lower heavy layer as yellow colour ,the upper layer has been discarded.

Then after drying the yellow colour precipitation , 22.4 mg of the yellow colour added to THF . then 100 mg of $Cu(PPh_3)_2$ NO_3 ,which added to THF is added to the yellow colour precipitation through cennula. Then a dark yellow colour solution formed. After drying the solution a greenish dark yellow colour precipitation formed. After washed out with DCM ,yellow precipitation formed.



Scheme 1: Synthesis of Dithiocarbazate

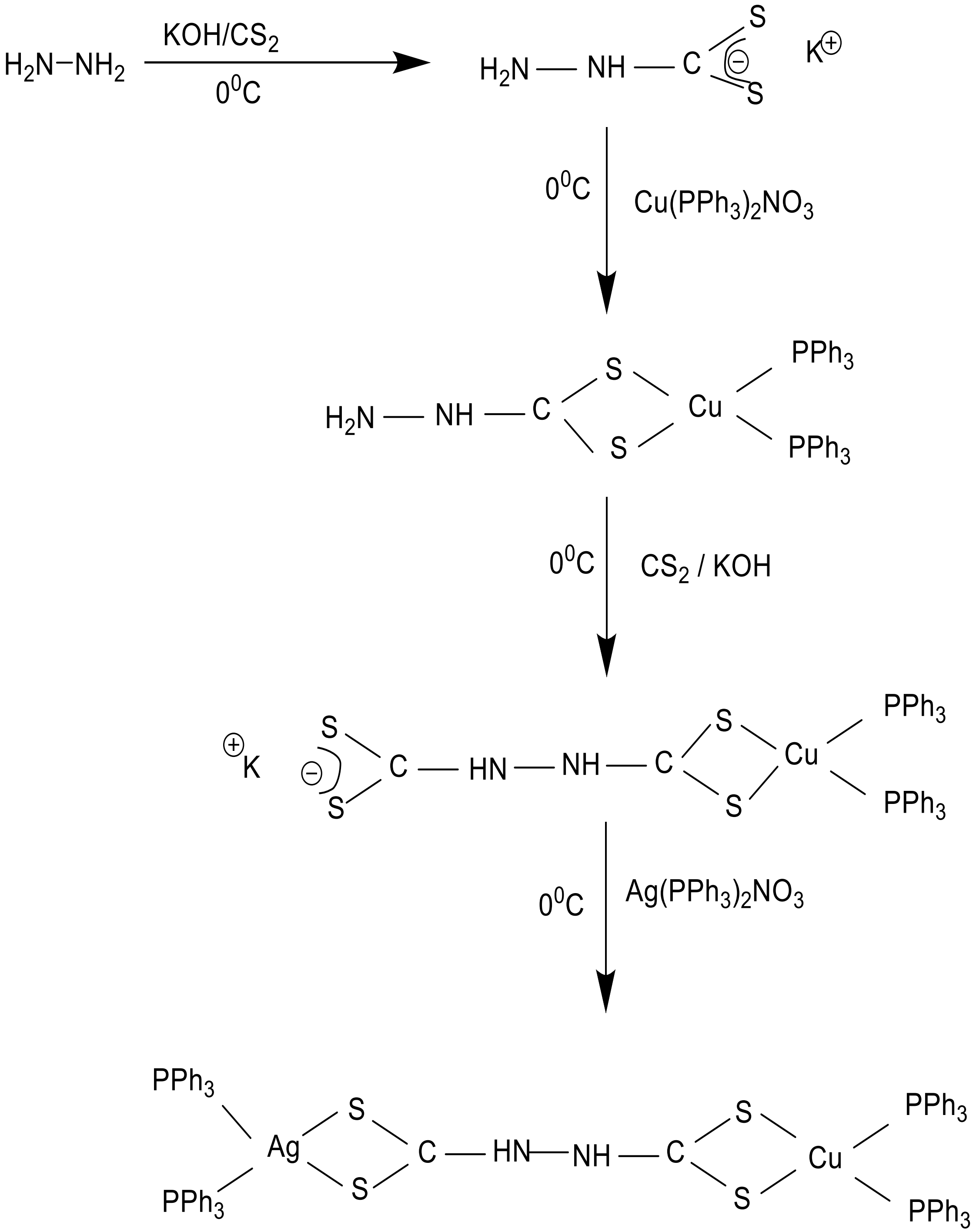
Preparation of $Ag(PPh_3)_2NO_3$:

A solution of PPh_3 (925 mg, 1.14 mmol) in 20 ml of MeCN was added to a solution of $AgNO_3$ (300mg, 0.57 millimole) in 10 ml of MeCN and stirred for about 30 minutes to obtain a precipitation of $AgNO_3(PPh_3)_2$.

$$AgNO_3 + 2PPh_3 \longrightarrow AgNO_3(PPh_3)_2$$

Synthesis of heteroatomic Bis(dithiocarbazate):

KOH (250mg,M.W=56.1056)was dissolved in 90% ethanol (5 ml) . After continuous stirring when it completely dissolved, Hydrazine hydrate (216 µl) having molecular weight 50.06 g/mol,0.00445 mole and density 1.025 g/cm^3 was added to it. The process is continue in 0^{0}C. This reaction was continue about 30 minutes. After 30 minutes CS_2 was added to it. About 268 µl of CS_2 having molecular weight=76.139 g/mol,0.00445 mol and density 1.26 was added drop wise through additional funnel. The ratio between KOH,CS_2 and NH_2NH_2,H_2O was 1:1:1 equivalent. After 2 hours of stirring 1 equivalent of $Cu(PPh_3)_2NO_3$ (2.89 gm) having molecular weight 650.1218 g/mol was added to the above solution. Again after 1 hour of stirring in argon atmosphere the solution was dried out. The compound was dissolve in DCM. The DCM dissolve part dried for the further reaction. Then 200mg of KOH (0.00356 mol) and the DCM dissolve part is dissolved in ethanol (10 ml). After complete dissolve 215 µl CS_2 was added to the solution drop wise through additional funnel. Again after 2 hours of reaction 153 mg of $AgNO_3(PPh_3)_2$ having molecular weight 694.440 g/mol was added. This is very less than 1 equivalent (I.e. 2.47 gm) but due to the shortage we add only 153 mg. After 3 hours of reaction ,the solution was dried out for expected result.

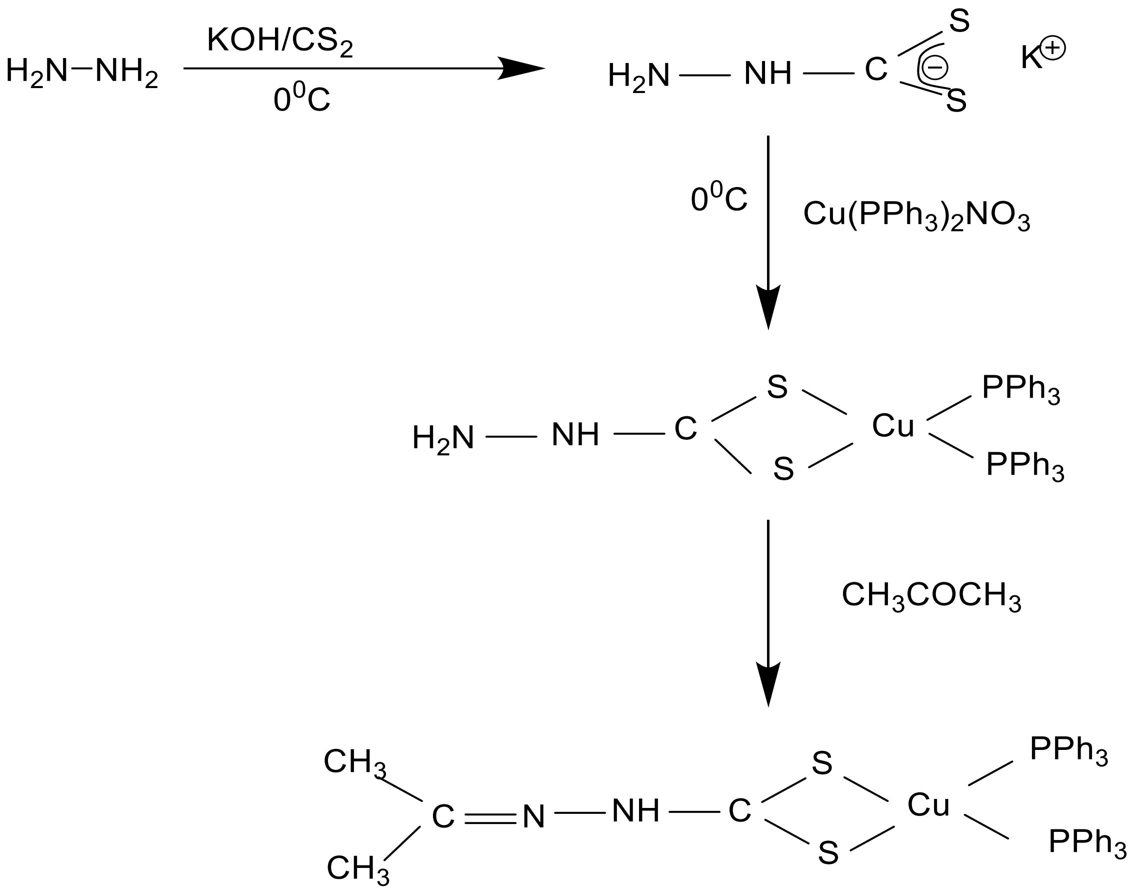


Scheme 2: Synthesis of heteroatomic Bis(dithiocarbazate)

Synthesis of Schiff base:

194 mg of KOH (0.00345 mol) dissolved in 90% ethanol (5 ml). After complete dissolved 167 µl of hydrazine hydrate (NH_2NH_2, H_2O,90%) was added to it through micro pipette. The reaction carried out through 0 – 6^0C. Then, after 30 minutes 207 µl of CS_2 added to it drop wise through additional funnel. All components are in 1 equivalent. Again after 2 hours of the reaction Dithiocarbazate was formed. This dithiocarbazate was dissolved in dry THF and 1.18 gm of $Cu(PPh_3)_2NO_3$ was dissolved in THF in a different conical flask. Then both the solutions added through cannula. After 2 hours of reaction, a greenish yellow colour compound was appeared.

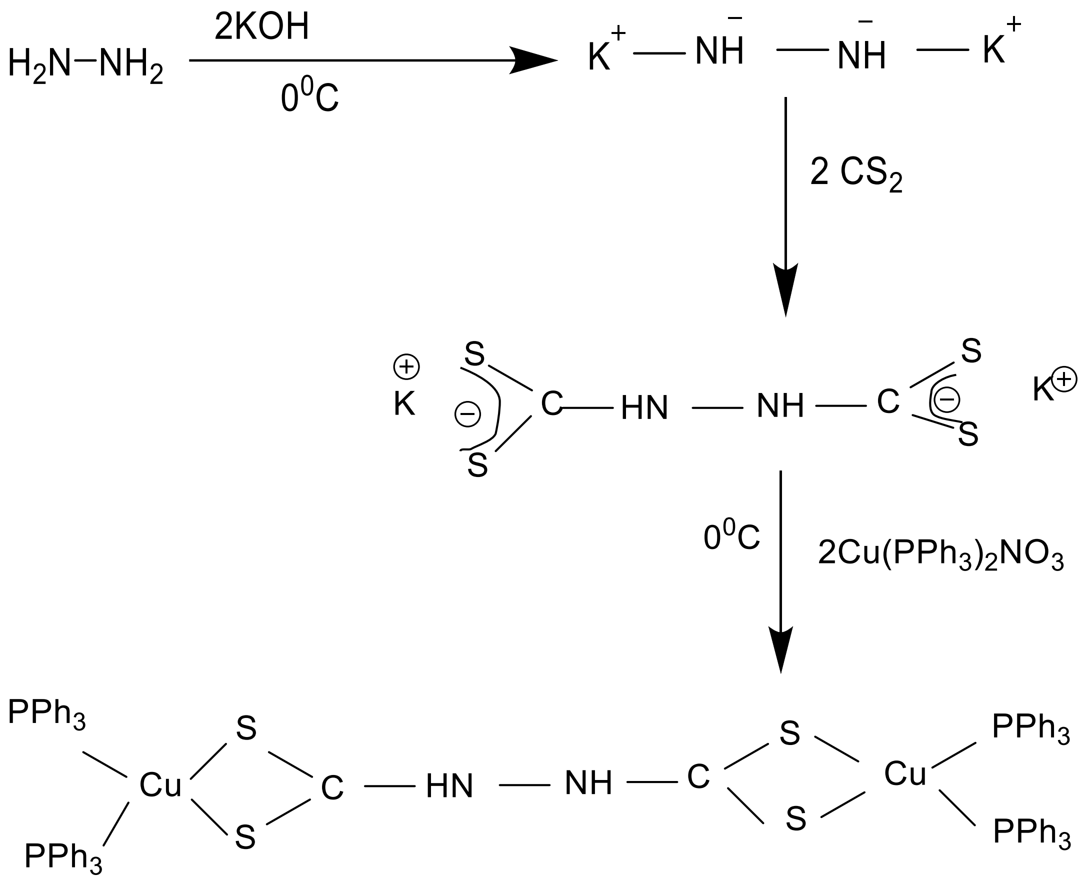
Further 200 mg of the greenish yellow compound (molecular weight=435.02 g/mol, 0.4597 millimole) was taken in a different flask which was dissolved in DCM. Then in an another flask, 34.02 µl of acetone (molecular weight=58.08 g/mol and density=0.7845 g/cm^3) was taken and dissolved in DCM. Then the two different solutions added through cannula. The reaction was about 40^0C and kept to reflux to complete the reaction. After the reflux from the condenser, the reaction was stopped. A yellow colour precipitation formed.



Scheme 3: Synthesis of Schiff base

Synthesis of bis(dithiocarbazate) with $[Cu(PPh_3)_2]^+$:

2 equivalent of KOH(43.13 mg, 0.769 millimoles) dissolved in 90% ethanol (5 ml). After complete dissolved 1 equivalent 18.77 µl of hydrazine hydrate (NH_2NH_2,H_2O) (0.3845 millimoles) was added to it through a micro pipette. The reaction carried out through 0^0 – 6^0C. then after 30 minutes, 2 equivalent of CS_2 (46.46 µl,0.769 millimoles) added to it drop wise through additional funnel. Again after 2 hours of the reaction Dithiocarbazate was formed. This dithiocarbazate was dissolved in dry THF. 2 equivalent of 500 mg of $Cu(PPh_3)_2NO_3$ (0.769 millimoles) was dissolved in THF in a different conical flask. Then both the solutions added through cennula. 2 hours of reaction a greenish colour compound was formed. Then it was dissolved in DCM. The DCM dissolved part carried out for further experiments.



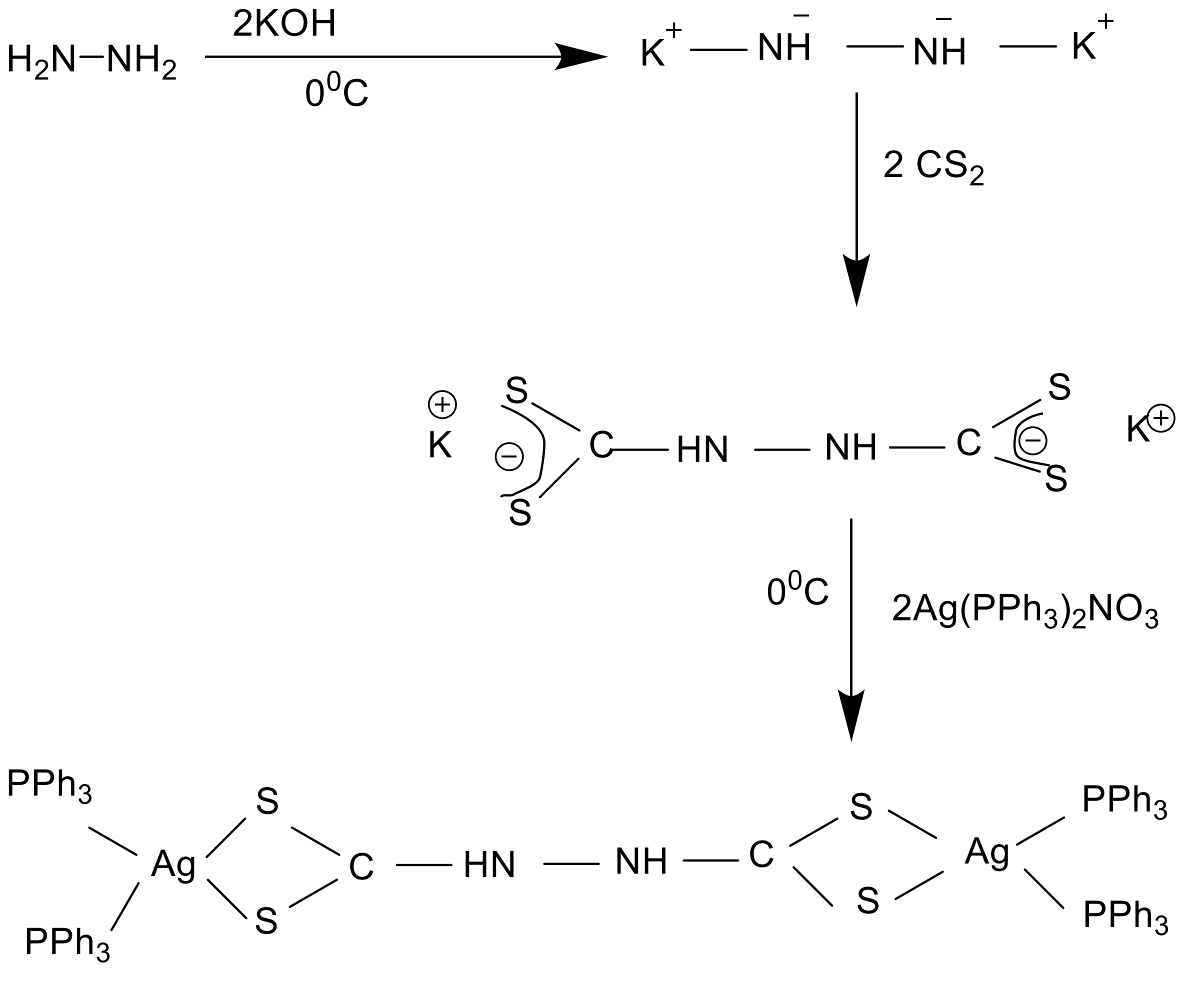
Scheme 4: Synthesis of bis(dithiocarbazate) with $[Cu(PPh_3)_2]^+$

Synthesis of bis(dithiocarbazate) with $[Ag(PPh_3)_2]^+$:

2 equivalent of KOH (32.31 mg,0.576 millimole) dissolved in 90% of ethanol (5 ml) completely. After KOH dissolved completely, 1 equivalent of hydrazine hydrate (NH_2NH_2,H_2O) (14.01 µl,0.288 millimole) was added to the KOH dissolved solution drop wise. After 30 minutes of reactions 2 equivalent of CS_2 (34.80 µl, 0.576 millimole) added to the solution through additional funnel drop wise. All the above reaction carried through 0^0 – 6^0C. after 2.30 hours of reaction, dithiocarbazate formed.

2 equivalent $Ag(PPh_3)_2NO_3$ (400 mg, molecular weight= 694.440 g/mol and 0.576 millimole) taken in a different flask. Both the $Ag(PPh_3)_2NO_3$ and

dithiocarbazate was dissolved in THF. Both the solutions were added through the cennula and kept for reaction about 2 hours. After 2 hours a slightly black colour solution formed.



Scheme 5: Synthesis of bis(dithiocarbazate) with $[Ag(PPh_3)_2]^+$

Set up distillation units for various solvents:

To avoid contamination, we use pure solvent during analysis. Steam distillation was the common process for distillation.

Distillation of tetrahydrofuran (THF):

Benzophenone-Sodium method was the best method for the production of THF (oxygen and peroxide free). The ketyl molecule {produced via the reaction between benzophenone and sodium(Na) metal} forms deep blue colour solution and reacts immediately with the peroxide, water and oxygen dissolved in THF. Sodium metal pieces placed into THF containing benzophenone. Pure THF collected from the collector.

Distillation of Acetone:

$KMnO_4$ method was the best method to produced moisture and oxygen free acetone (CH_3COCH_3). A Pinch amount of $KMnO_4$ was added to the LS grade of acetone and than heated. A purple colour appear and disappear; $KMnO_4$ was added till a colour persists. Pure acetone was collected by passing it over the anhydrous calcium sulphate from collector whenever required.

CHAPTER 4

RESULT AND DISCUSSION

Result and discussion:

Analysis of Dithiocarbazates:

SEM (Scanning Electron Microscopy):

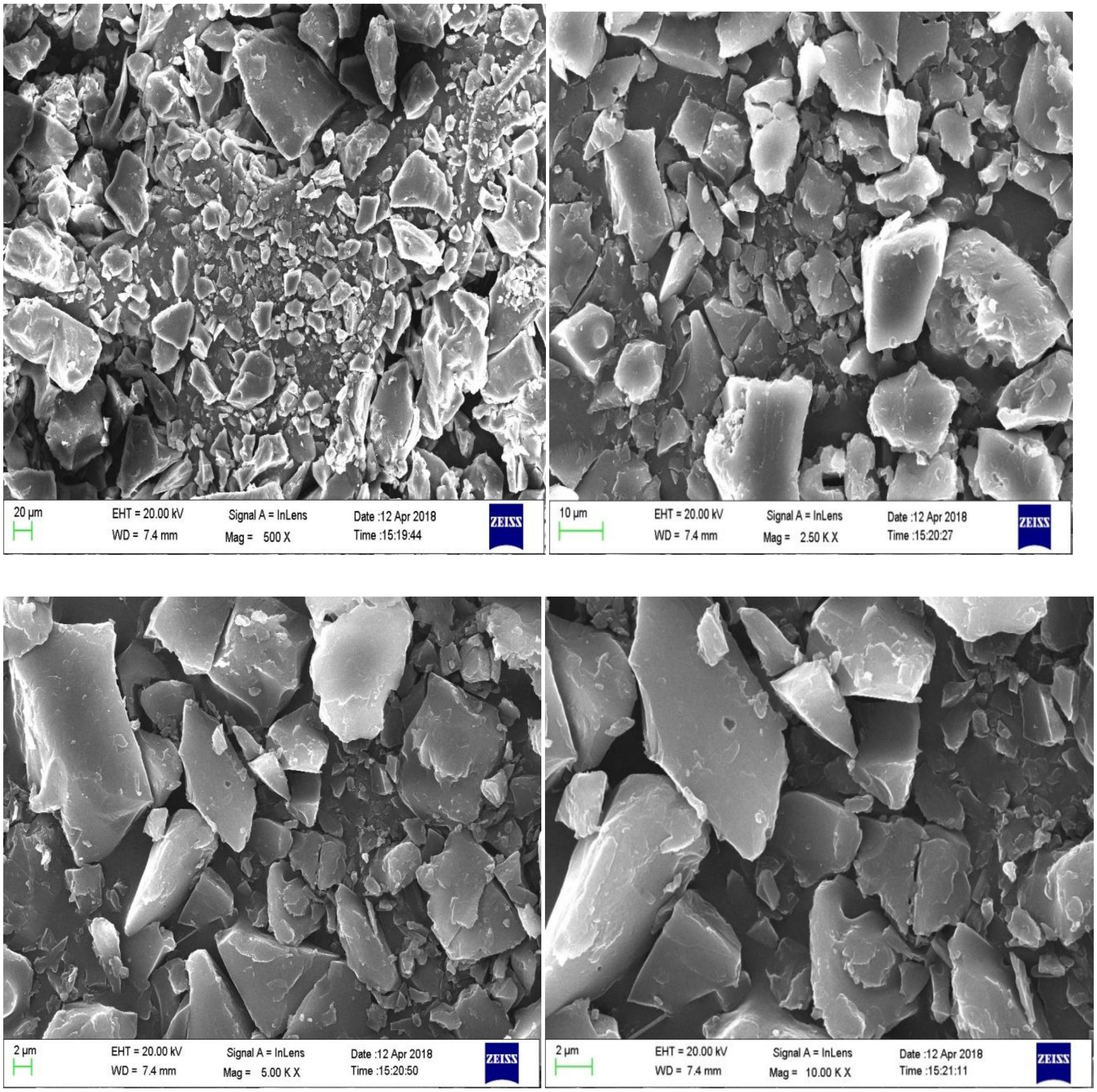
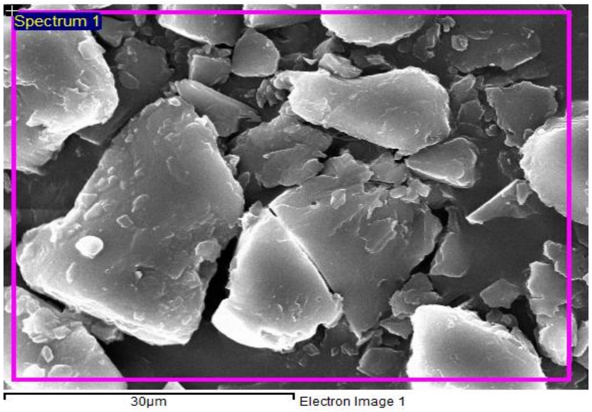


Figure 4.1 (a): SEM

EDS (Energy-dispersive X-ray spectroscopy):

Characterization of Dithiocarbazate complex by EDS, the elemental ratio of the complex is below the table,-

Element	Weight%	Atomic%
P K	41.40	46.84
S K	38.48	42.06
Cu K	20.13	11.10
Totals	100.00	



Element	Weight%	Atomic%
S K	60.85	75.49
Cu K	39.15	24.51
Totals	100.00	

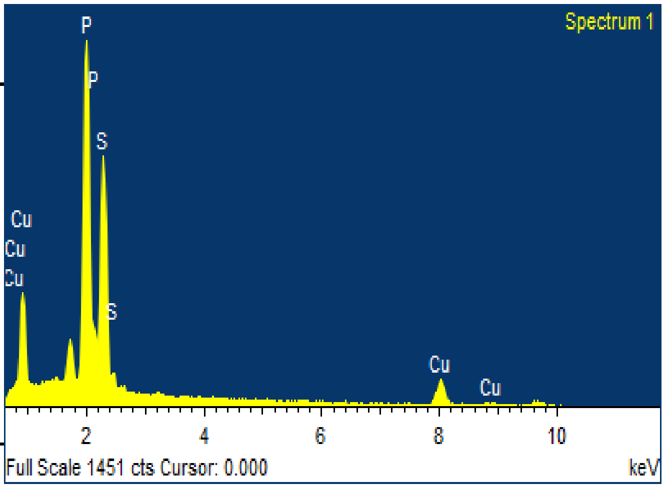


Figure 4.1 (b): EDS

Elemental Mapping:

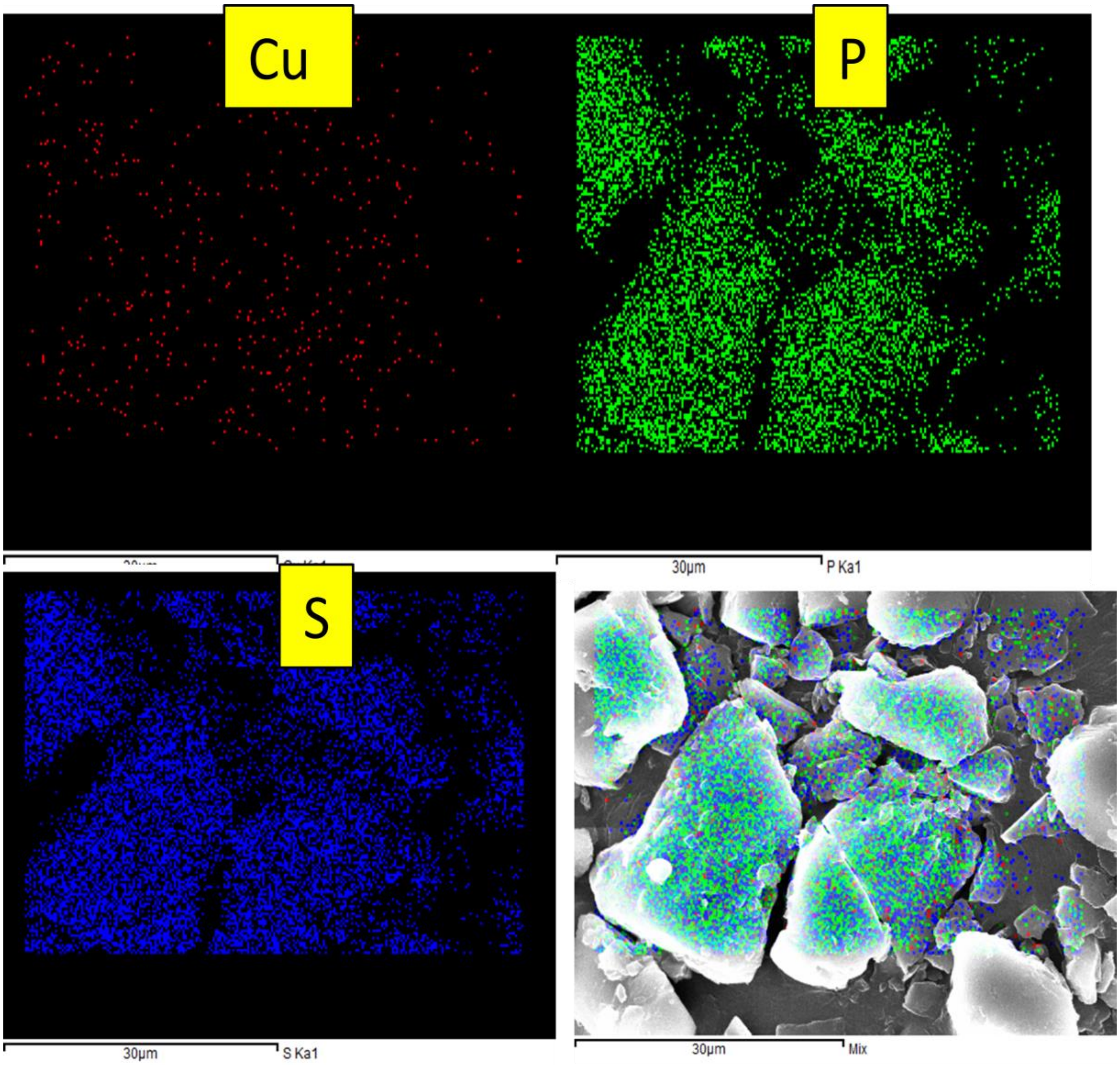
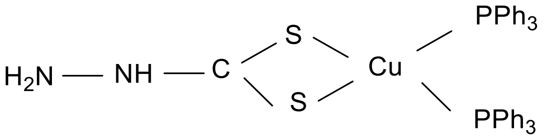


Figure 4.1(c): elemental Mapping

NMR analysis:

^{1}H NMR of Dithiocarbazate:



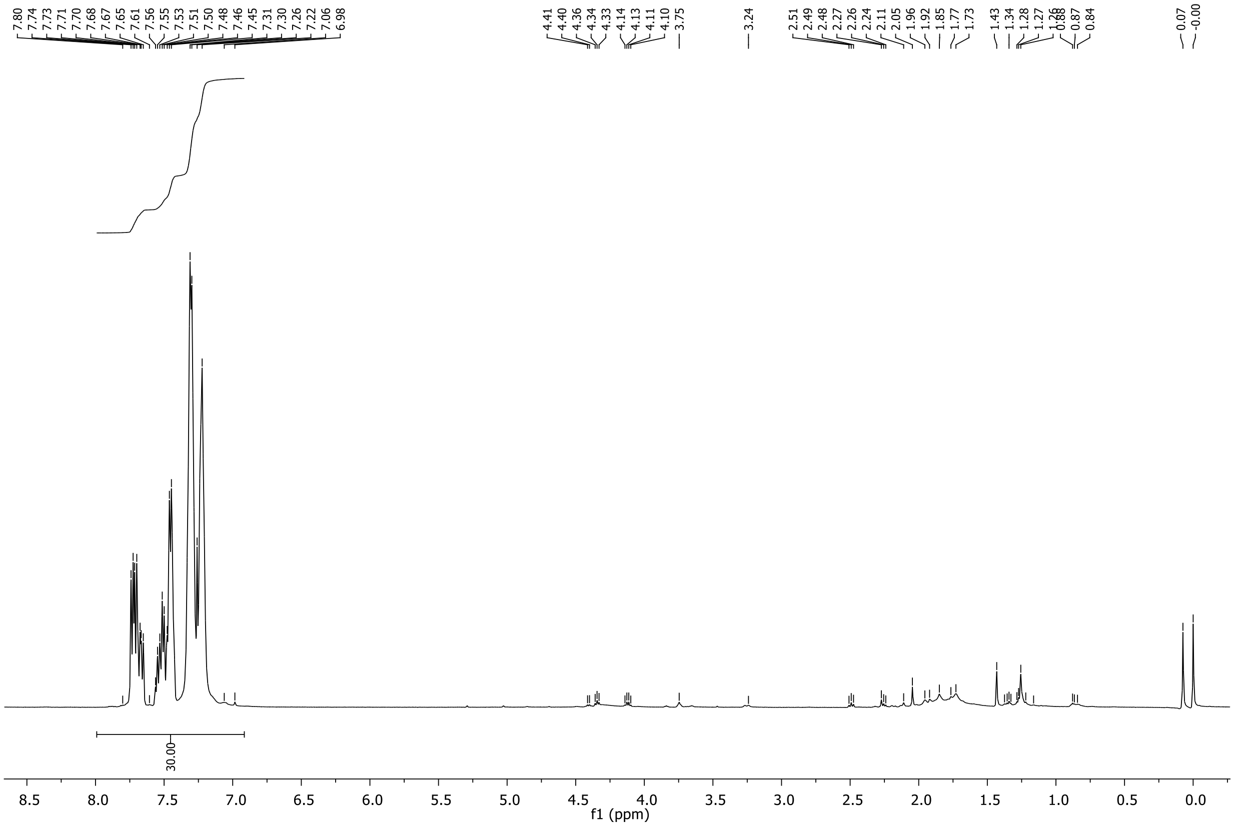
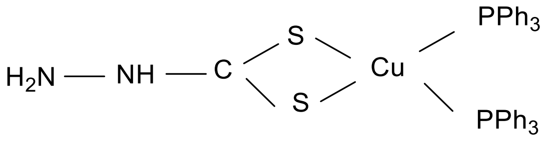


Figure 4.1(d)

As shown in Figure 4.1(d), the phenyl groups in the phosphine ligands appeared from shift 6.98 to 7.80 ppm in multiplate form. The proton of –NH- group, the chemical shift shows at 3.75 ppm and in $–NH_2$ group, it is 3.24 ppm. We use DCM to purify our ligand after synthesis and partial impurity of DCM show overlap in chemical shift.

^{13}C NMR of Dithiocarbazate:



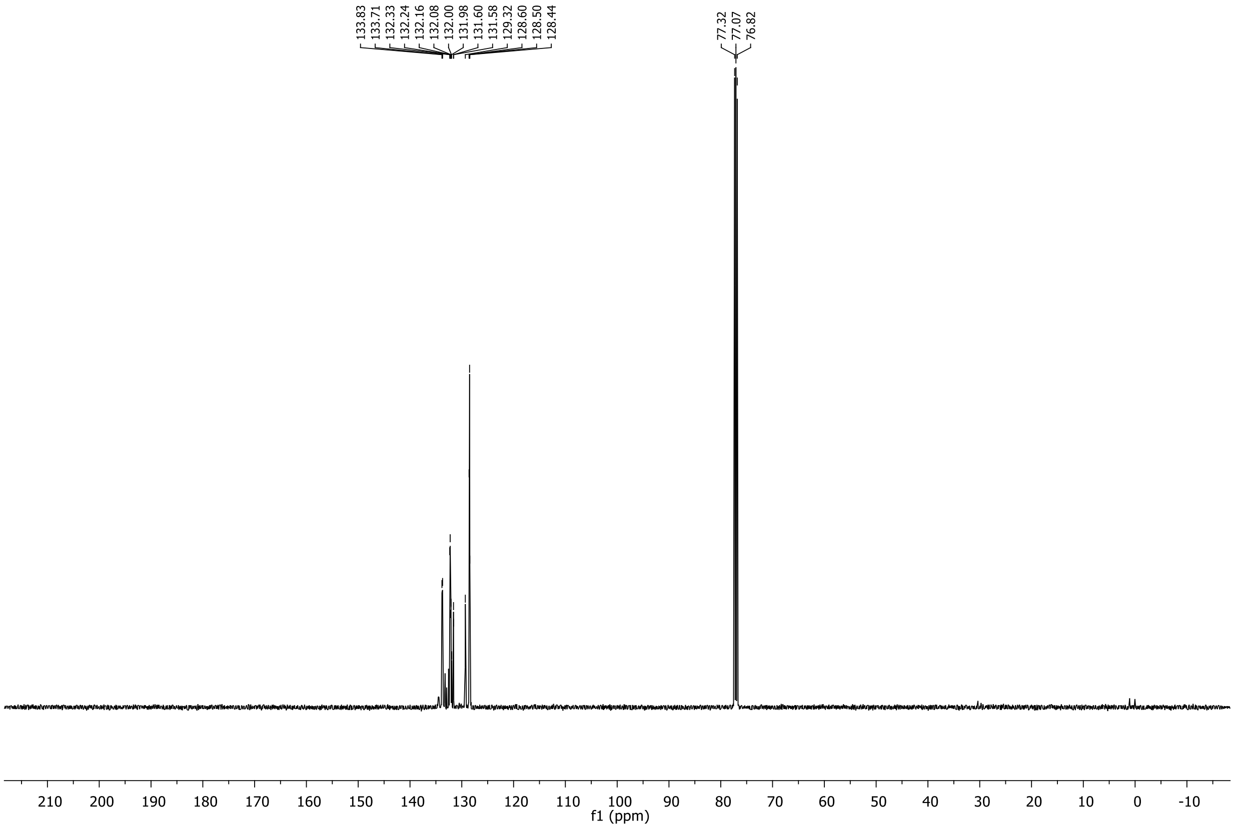


Figure 4.1(e)

In the NMR spectrum C-N and C-S group Carbon shows peak range between 76 to 77 ppm which is observed here. The data showing that the formation of complex with functional groups.

Analysis of heteroatomic bis(dithiocarbazate):

SEM (Scanning Electron Microscopy):

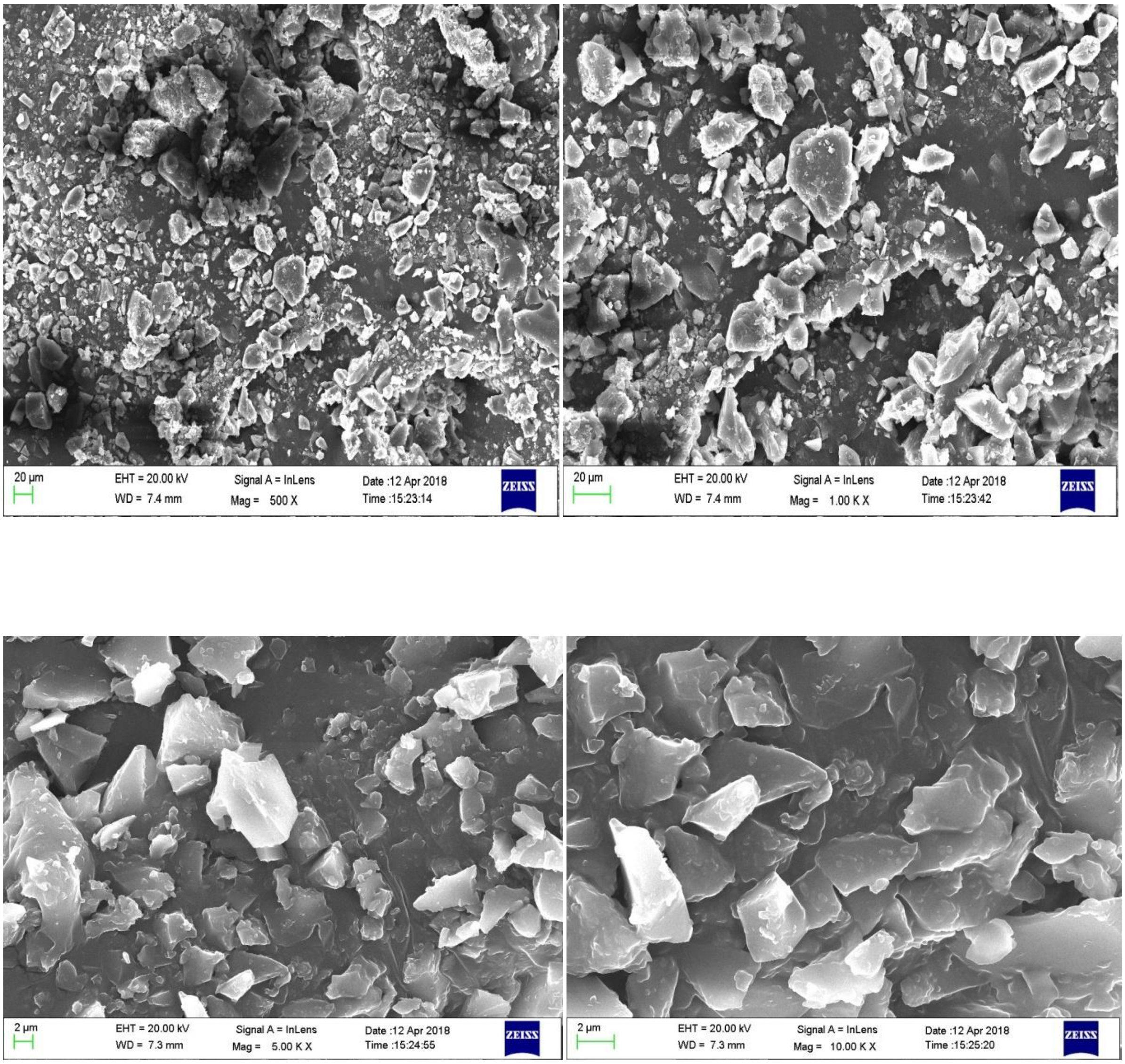
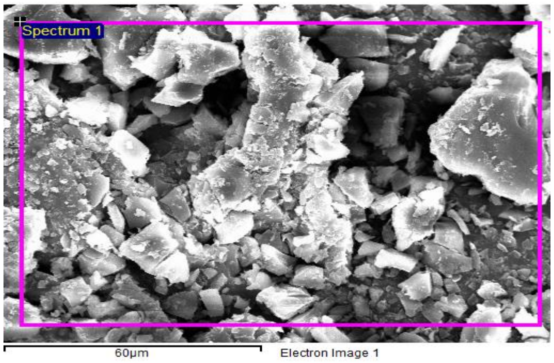


Figure 4.2(a): SEM

EDS(Energy-dispersive X-ray spectroscopy):

Characterisation of hetero atomic bis(dithiocarbazate) by EDS, the elemental ratio is -

Element	Weight%	Atomic%	Calculated%
P K	33.63	40.57	40
S K	36.38	42.39	40
Cu K	27.50	16.17	10
Ag L	2.48	0.86	10



Element	Weight%	Atomic%
S K	51.18	68.25
Cu K	44.84	30.18
Ag L	3.98	1.58
Totals	100.00	

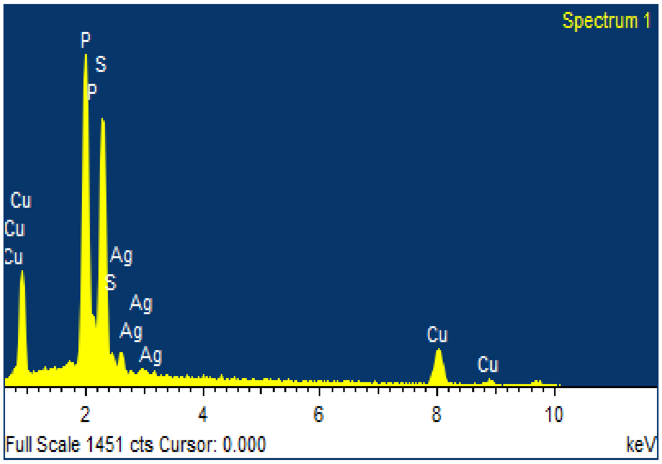
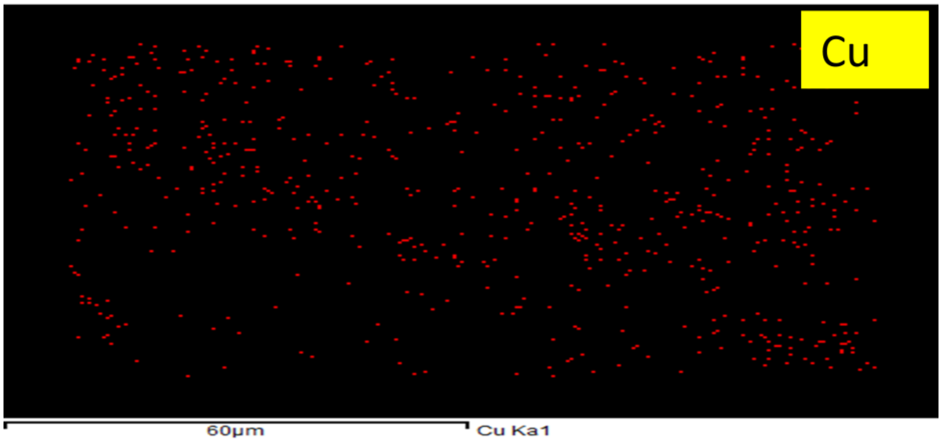
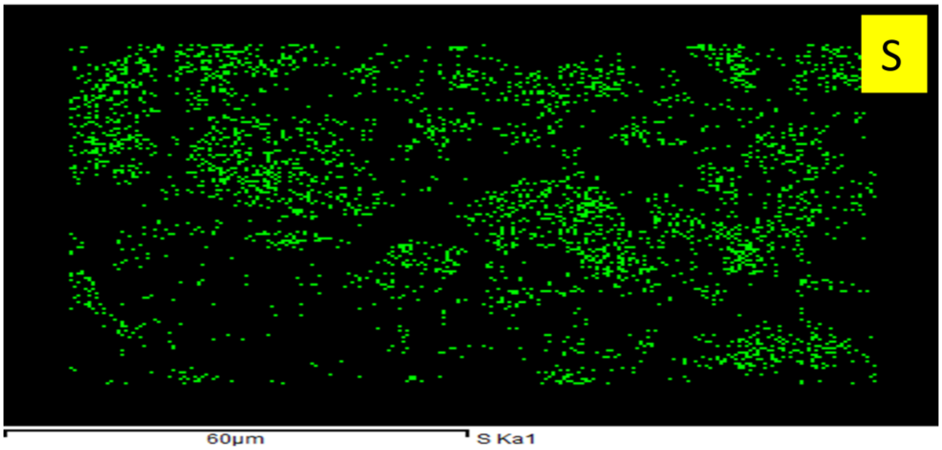
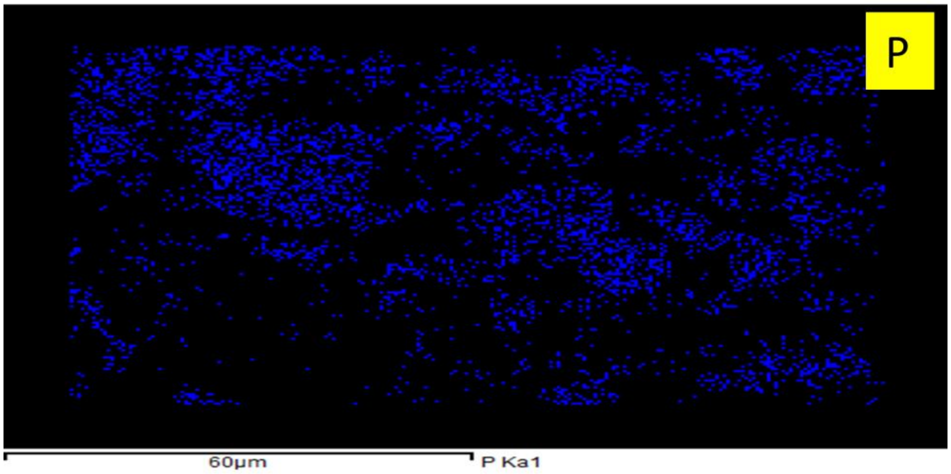


Figure 4.2(b): EDS

Mapping:







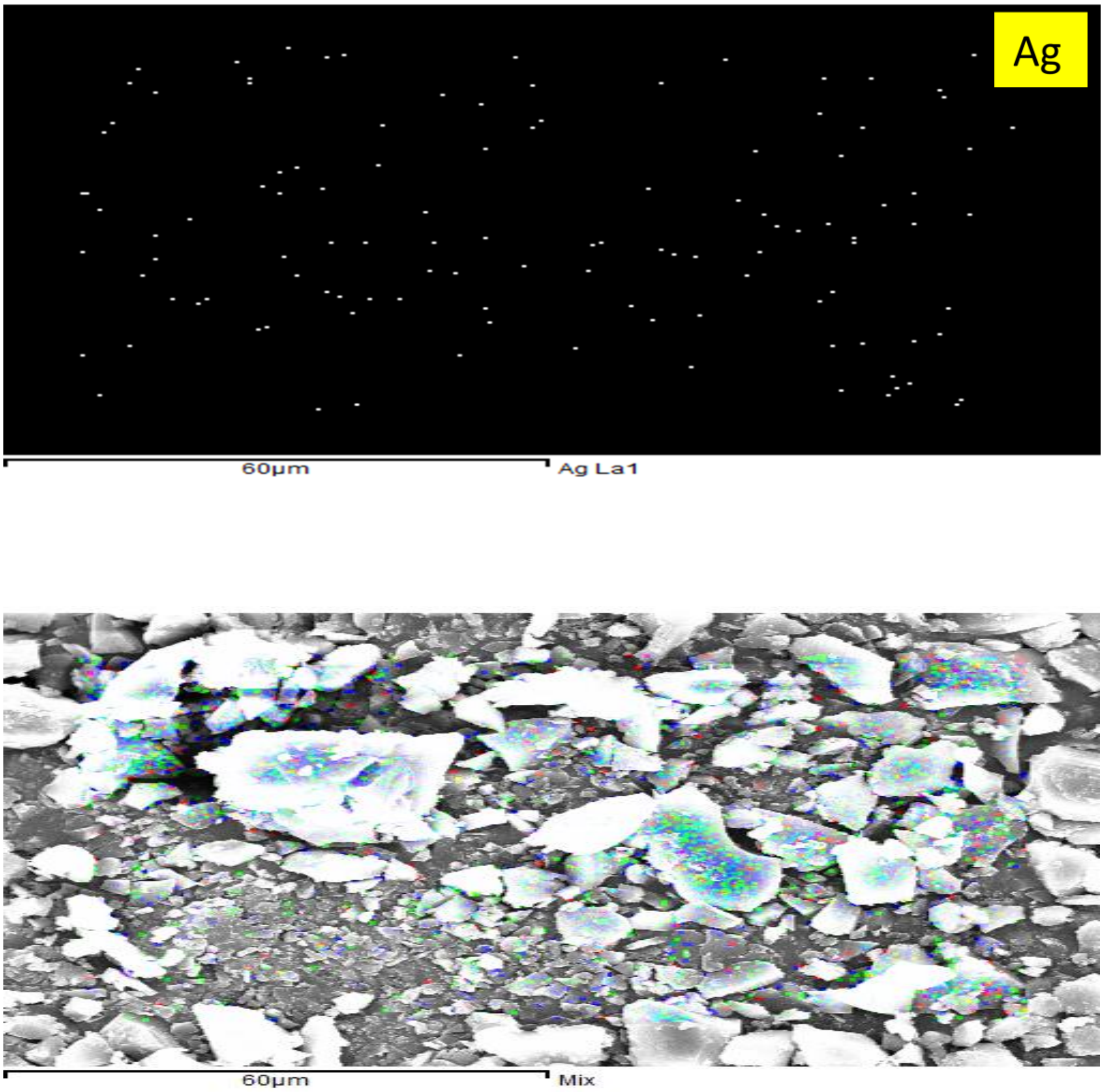
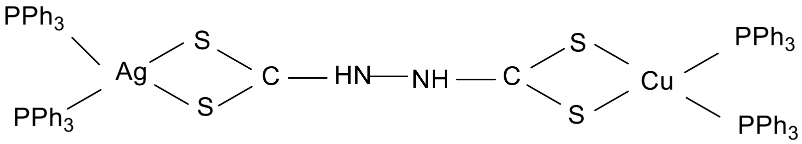


Figure 4.2(c): Mapping

^{1}H NMR of Heteroatomic bis(dithiocarbazate):



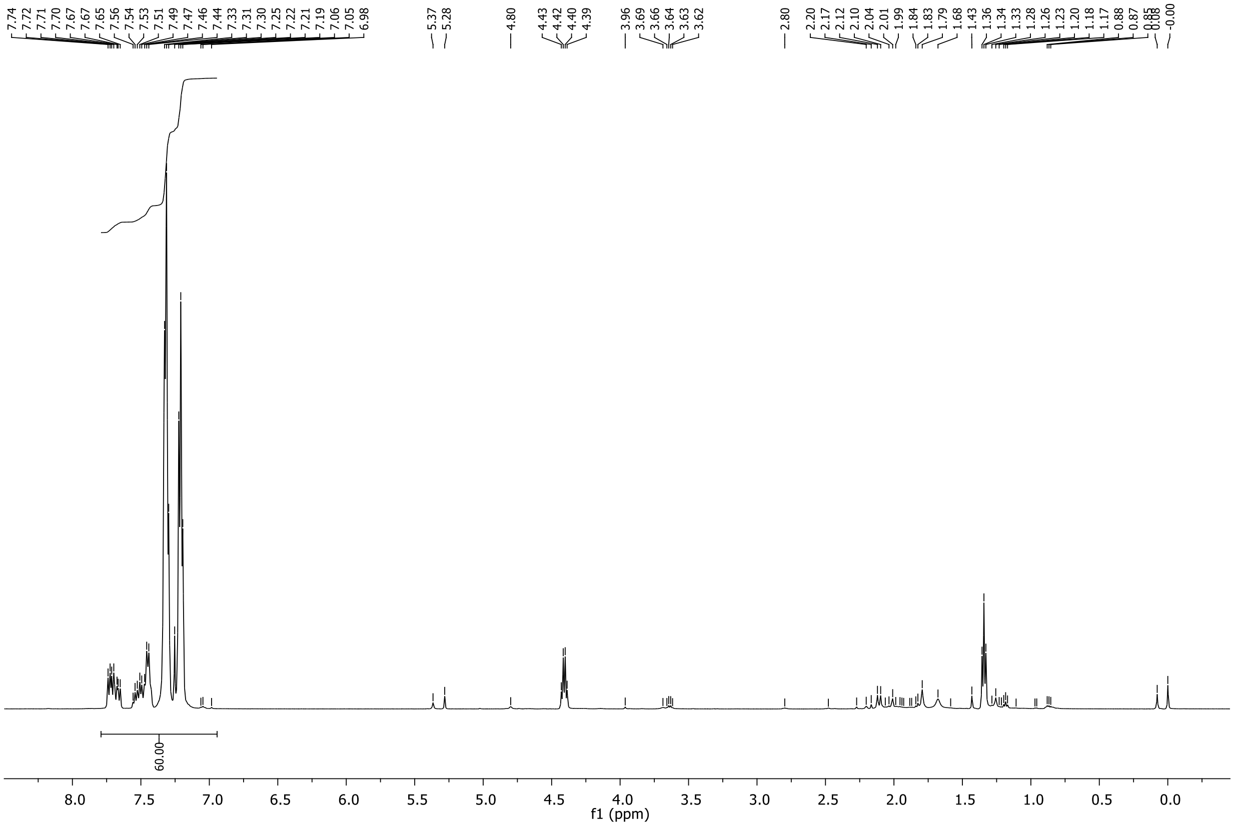
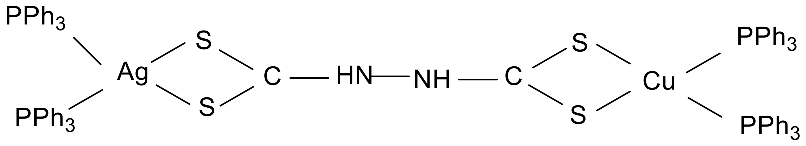


Figure 4.2(d): ^{1}H NMR

As shown in Figure 4.2(d), phosphine ligands having phenyl group is appeared from the chemical shift range 6.98 to 7.74 ppm in the form of multiplate. The proton of –NH- group peak should appear in the range 4.39 to 4.43 ppm doublet form with the overlap of partial impurity in DCM solvent, as we were washed our complex using DCM to purify after synthesis.

^{13}C NMR of heteroatomic bis(dithiocarbazate):



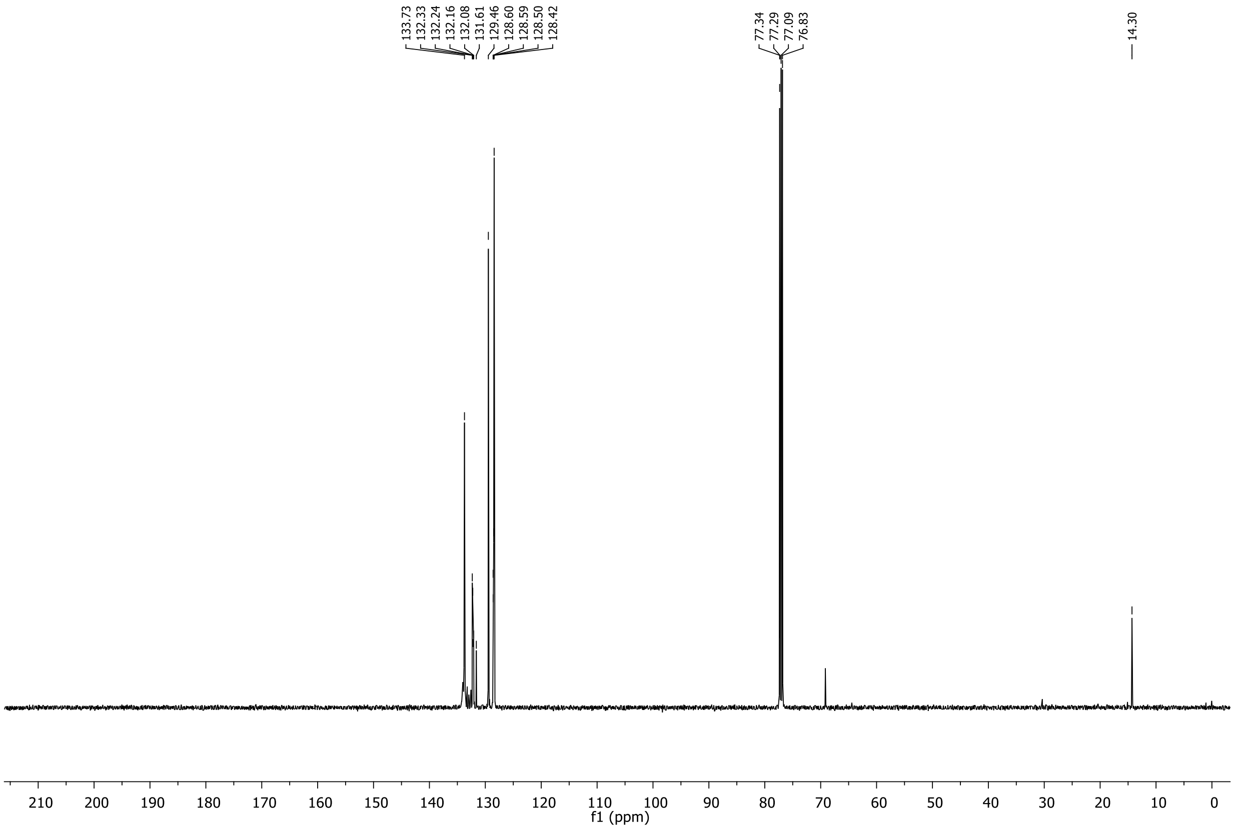


Figure 4.2(e)

In the NMR spectrum C-N and C-S group Carbon shows peak range between 76 to 77 ppm which is observed here. The data showing that the formation of complex with functional groups.

Analysis of Schiff base:

SEM (Scanning Electron Microscopy):

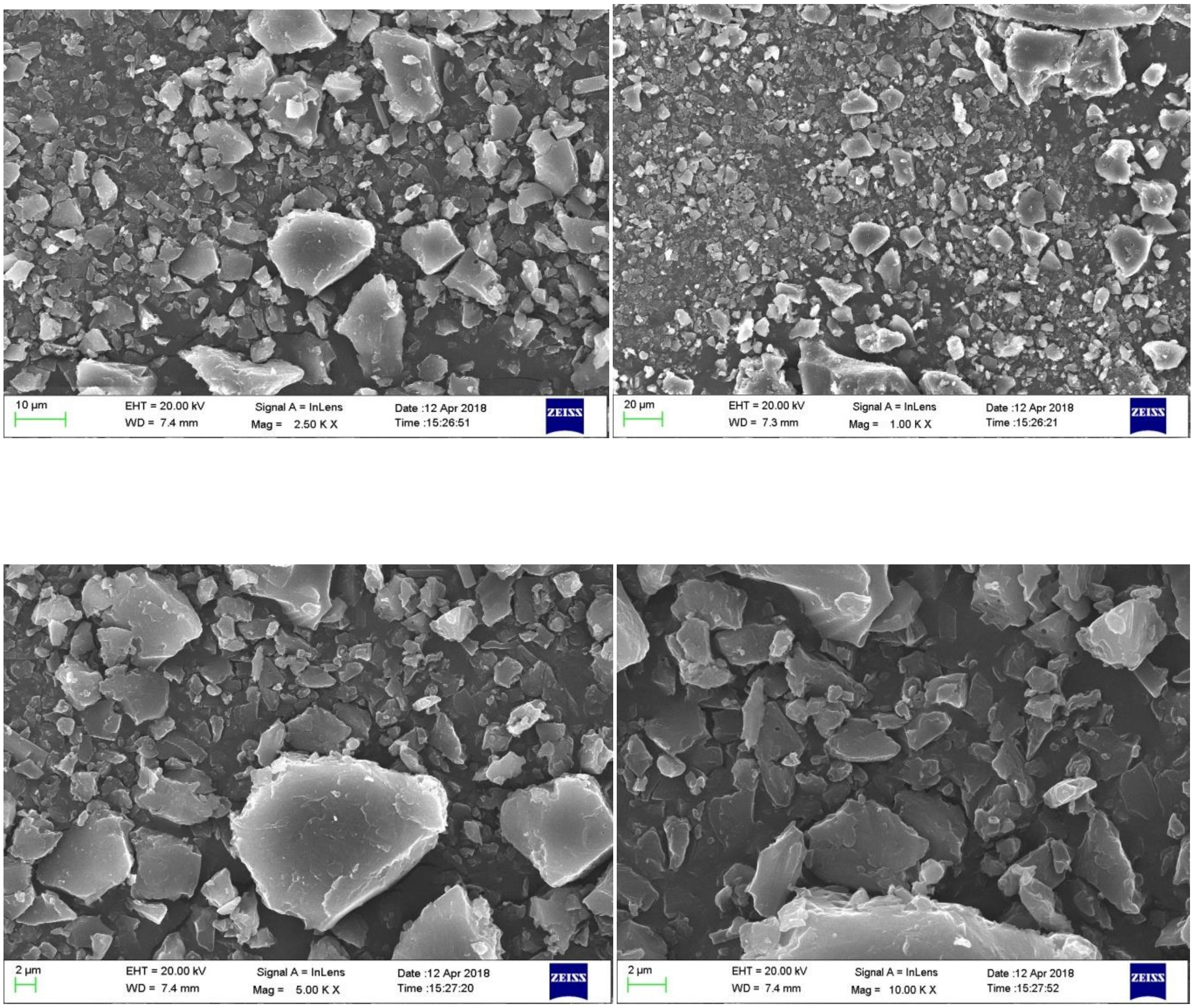
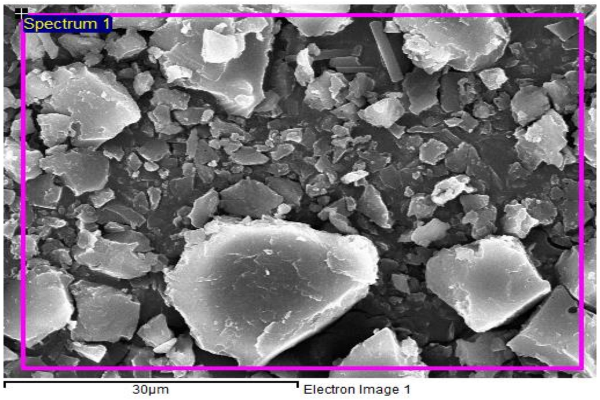


Figure 4.3(a)

EDS(Energy-dispersive X-ray spectroscopy):

Elemental ratio of Schiff base is

Element	Weight%	Atomic%	Calculated%
P K	34.08	40.54	40
S K	37.32	42.88	40
Cu K	28.60	16.58	20
Totals	100.00		



Element	Weight%	Atomic%	Calculated%
S K	52.81	68.92	66.6
Cu K	47.19	31.08	33.3
Totals	100.00		

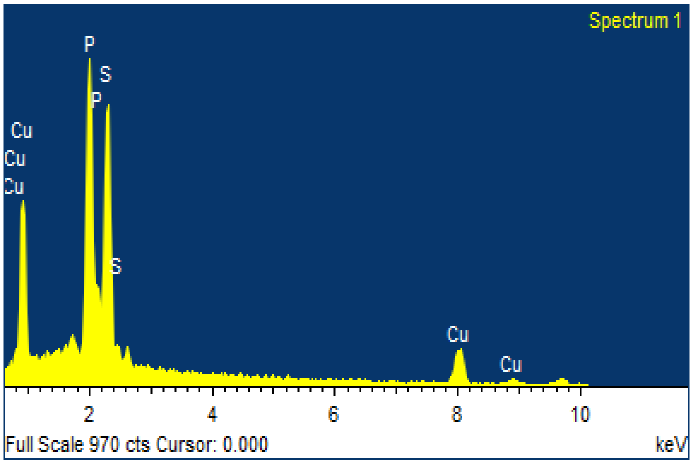


Figure 4.3(b)

Mapping :

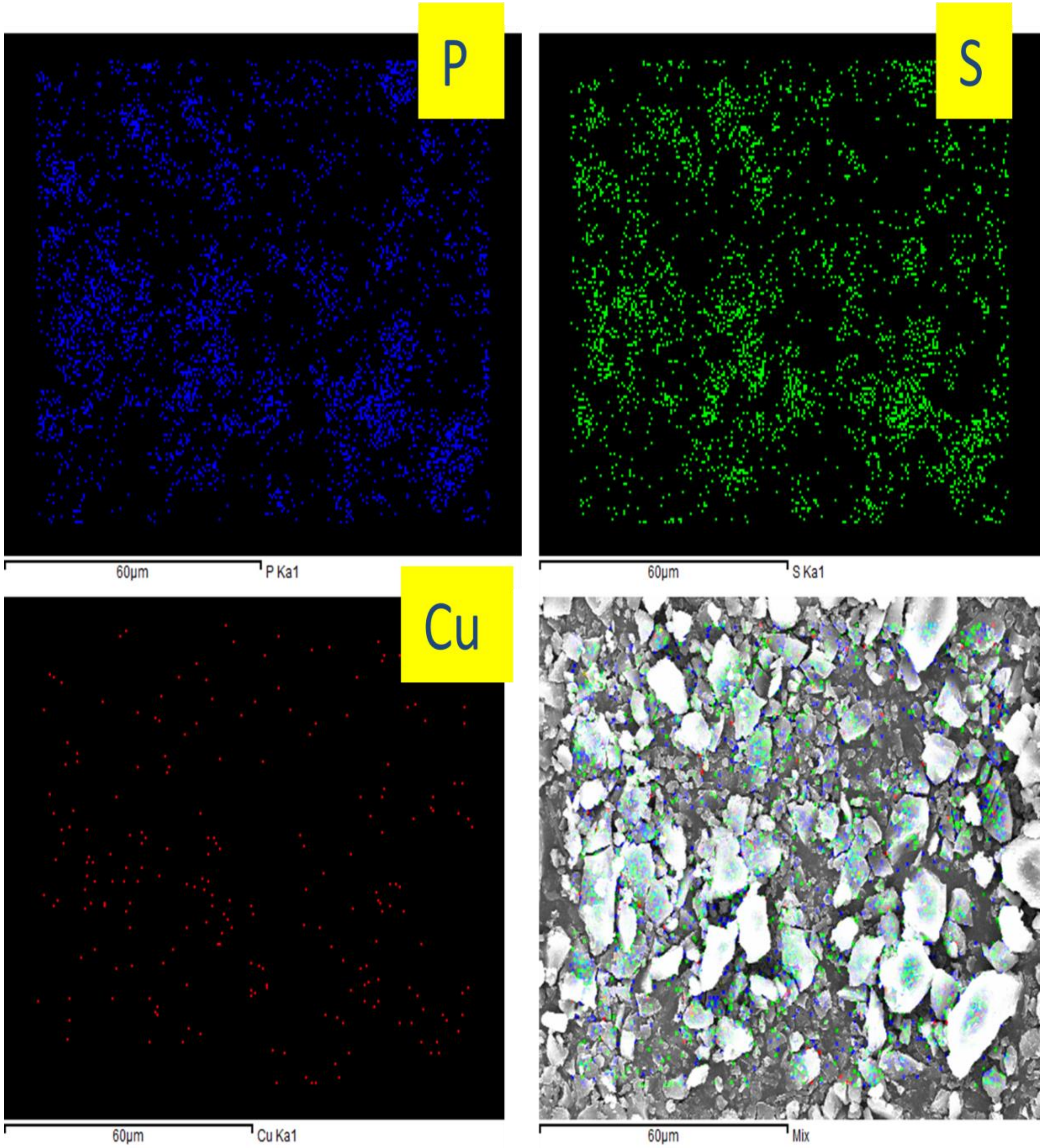
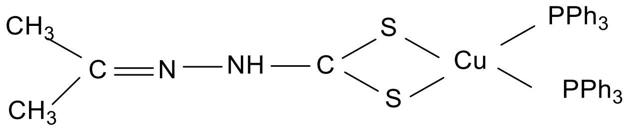


Figure 4.3 (c)

^{1}H NMR of Schiff base:



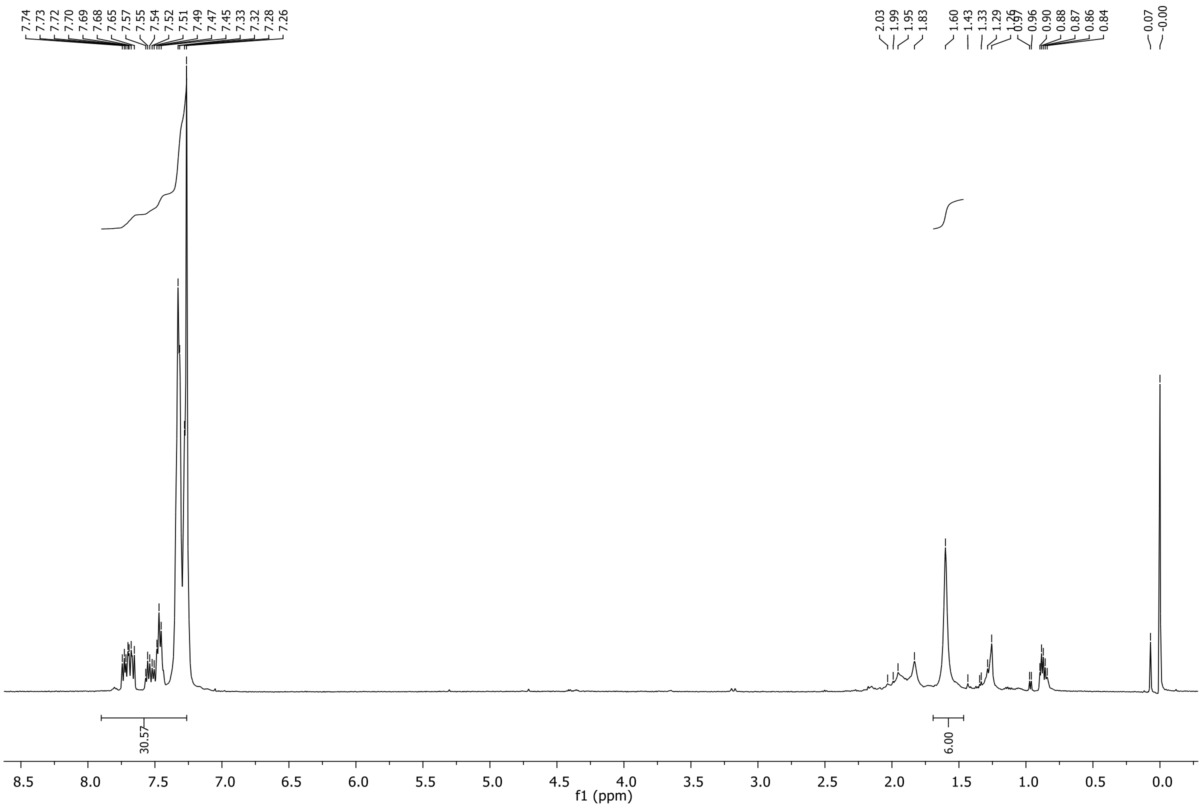


Figure 4.3(d) :^{1}H NMR

As shown in Figure 4.3 (d), Phosphine ligands having phenyl group is appeared from chemical shift range 7.26 to 7.74 ppm in the form of multiplate. Proton of –NH- group peak should appear in the range 7 ppm which is overlap in the range of phosphine group. In $-CH_3$ group, the proton shift show the range 1.6 ppm in the form of singlet. Other shifts show by the partial impurity in DCM solvent, as we were washed our complex using DCM to purify after synthesis.

Analysis of Bis(dithiocarbazate) with $[Cu(PPh_3)_2]^+$:

SEM (Scanning Electron Microscopy):

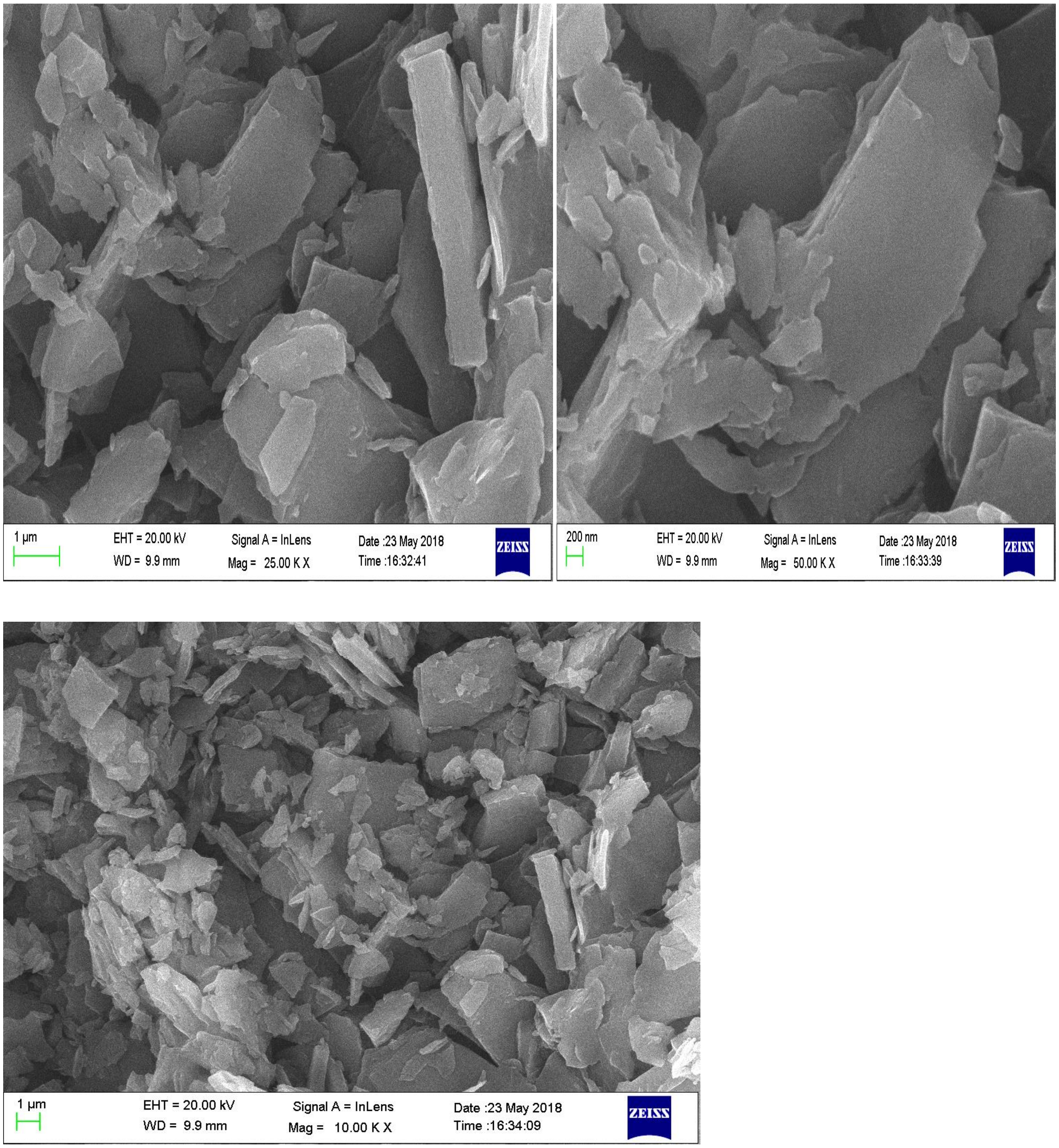
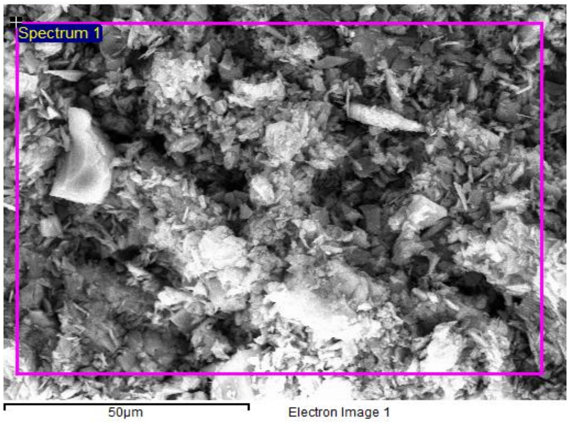


Figure 4.4 (a): SEM

EDS (Energy-dispersive X-ray spectroscopy):

Elemental ratio is -

Element	Weight%	Atomic%
P K	60.50	70.59
S K	12.44	14.02
Cu K	27.06	15.39
Totals	100.00	



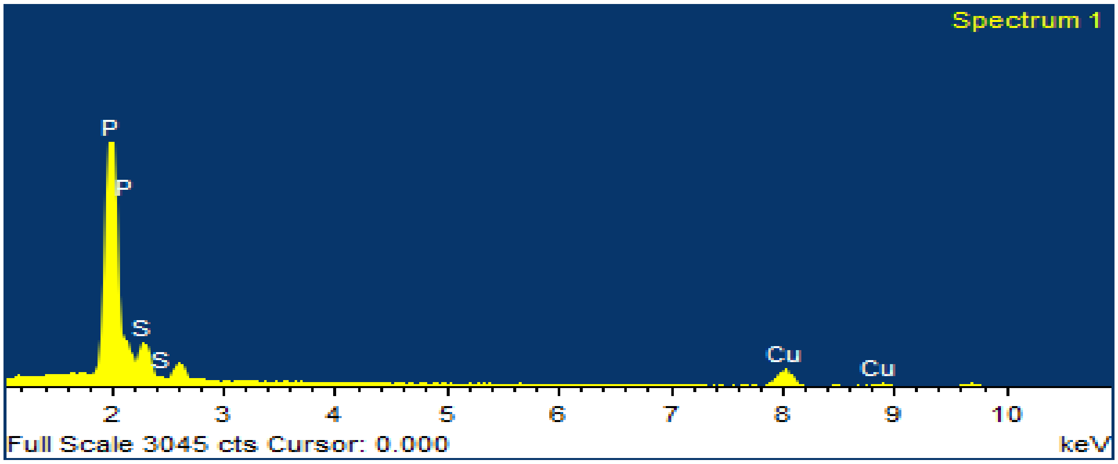


Figure 4.4(b): EDS

Mapping:

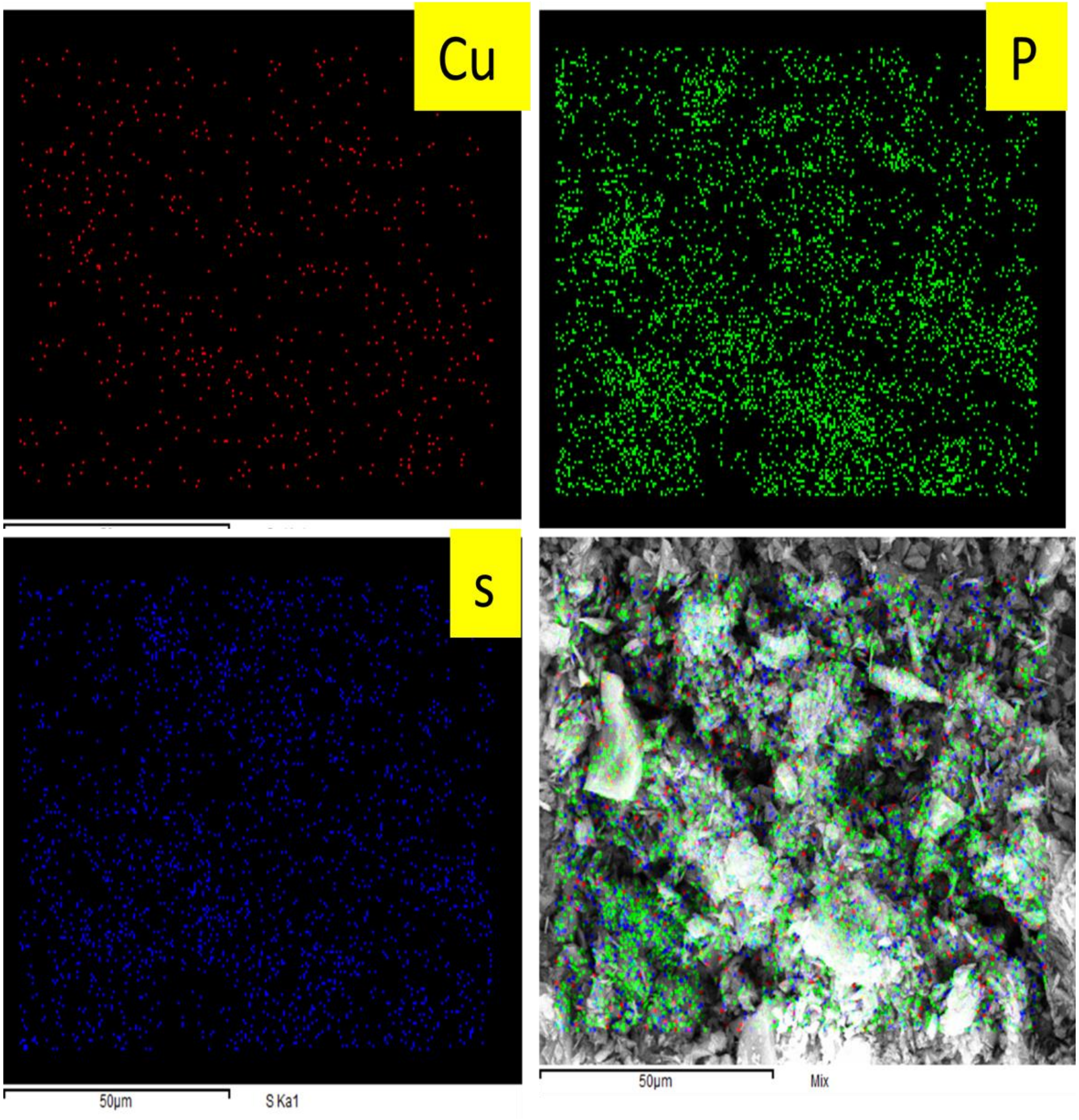


Figure 4.4(c): MAP

Analysis of Bis(dithiocarbazate) with $[Ag(PPh_3)_2]^+$:

SEM (Scanning Electron Microscopy):

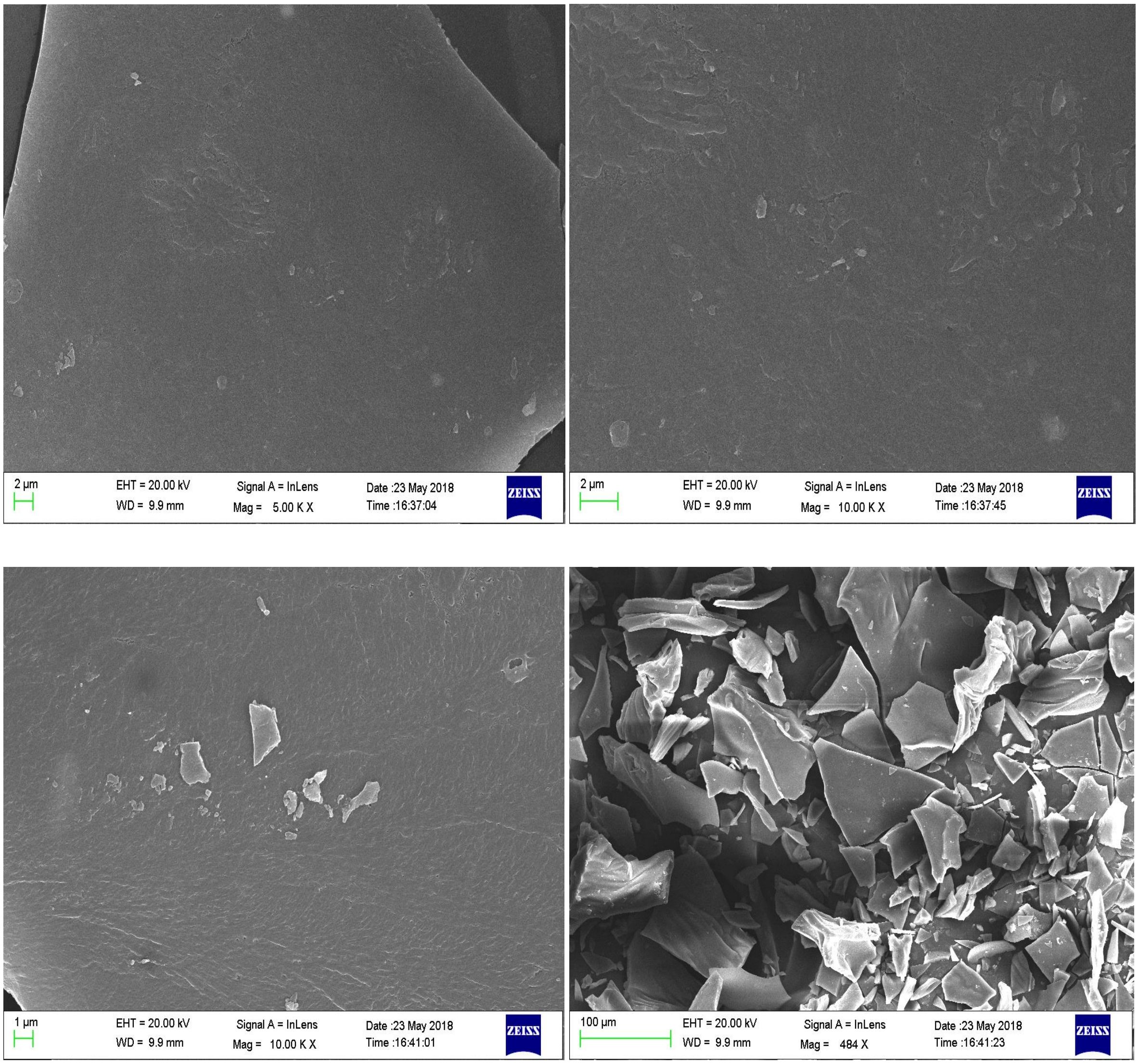
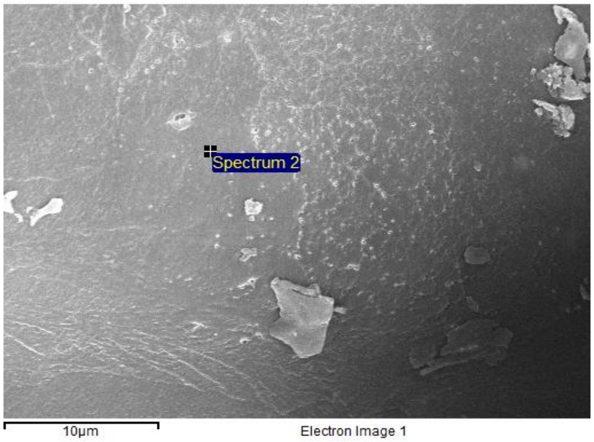


Figure 4.5 (a): SEM

EDS(Energy-dispersive X-ray spectroscopy):

The elemental ratio of Bis(dithiocarbazate) with $[Ag(PPh_3)_2]^+$ is:

Element	Weight%	Atomic%
P K	40.13	65.36
S K	6.00	9.44
Ag L	53.87	25.20
Totals	100.00	



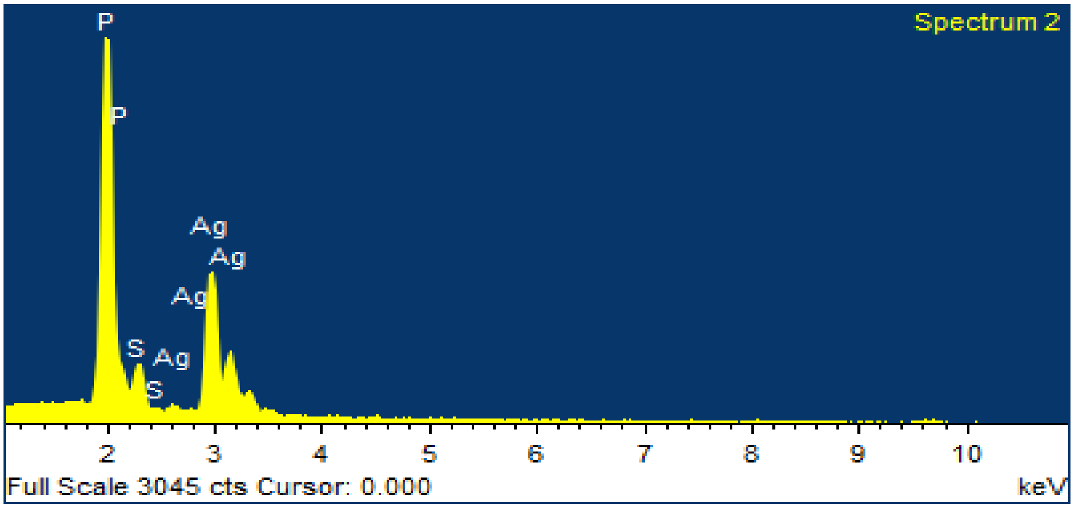


Figure 4.5(b): EDS

Mapping:

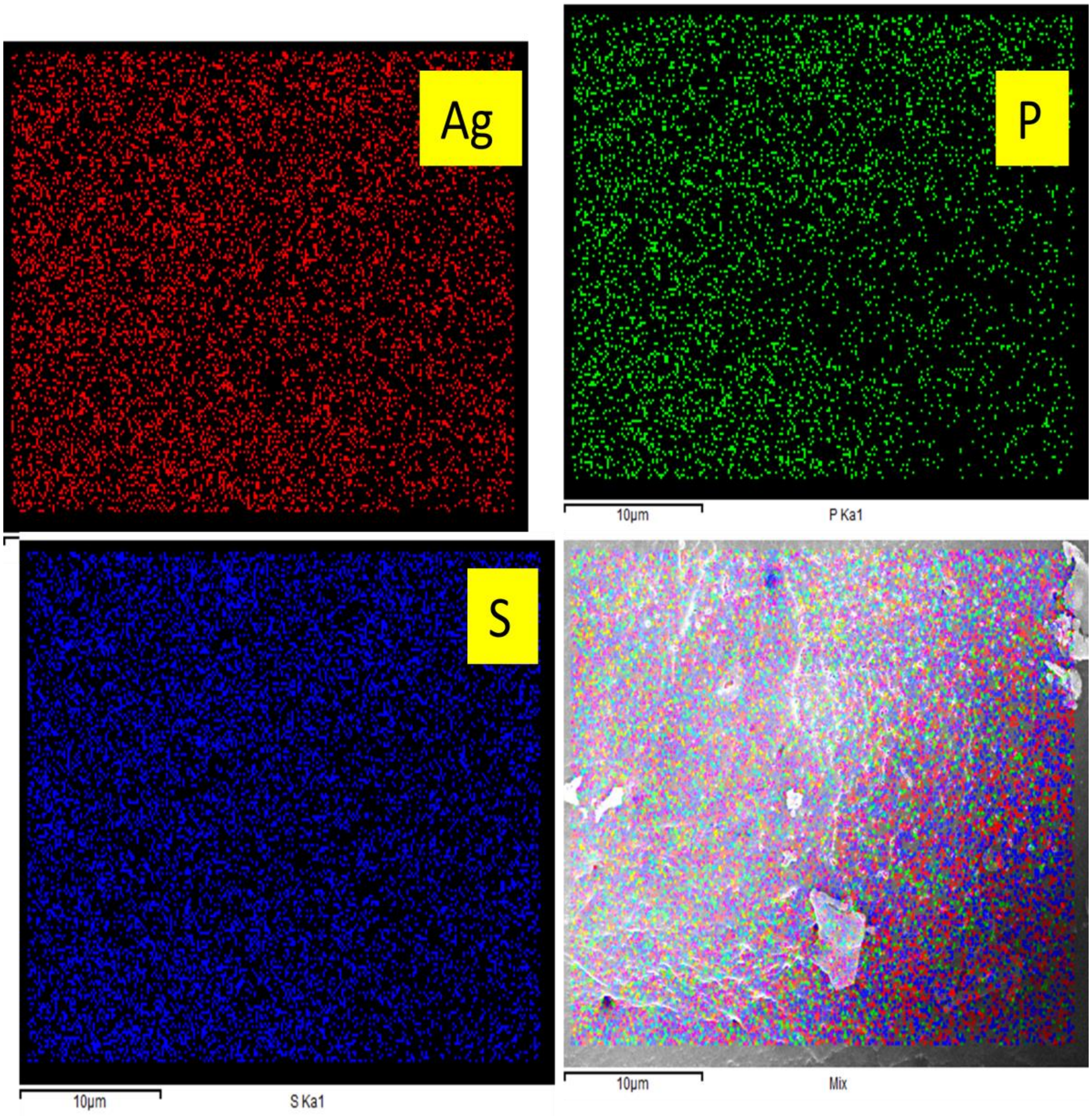


Figure 4.5(c)

CHAPTER 5

CONCLUSION

I have synthesized Dithiocarbazate ligand and utilized it for the complexations with copper and silver metals (I) salts. I have also synthesized Schiff base of dithiocarbazate copper(I) metal salts. All the metal salts, $[Cu(PPh_3)_2]^+$ and $[Ag(PPh_3)_2]^+$ are monovalent. The synthesis of Ag/Cu(I) complexes using aformetioned ligand has been done first time as previously all the synthesis have been done with divalent metal (Cu/Ag) salt. Moreover, we have characterized the ligand and all the complexes with ligand properly by using different spectroscopical methods such as ^{1}H NMR, ^{13}C NMR, SEM, EDS, MAP etc. from all the characterization we have confirmed that the ligand and all complexes has been formed. The presence of phosphine ligands intitates, higher nuclearity polymers convert into lower nuclearity complexes. Such complexes can be used as mono-precursors to isolate nanomaterials in near future.

CHAPTER 6

REFERENCES

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