

**KERALA STATE COUNCIL FOR SCIENCE, TECHNOLOGY AND
ENVIRONMENT**

STUDENT PROJECT REPORT(FINAL) , 2016-17

- 1 Project Title : Synthesis, Characterization and Antimicrobial study of mixed ligand dithiocarbamate complexes of Cu (II)
- 2 File No : 5/SPS 59/2016/KSCSTE
- 3 Name & Address of the student : Julie George,II MSc Chemistry, Department of Chemistry, Baselius College, Kottayam
- 4 Name & Address of the Principal Investigator & Co-Investigator with mobile No. : Prof. Jinu Mathew, Assistant Professor,Department of Chemistry, Baselius College, Kottayam
Ph No. 9447701318
- 5 Broad area of Research : Inorganic Chemistry
- 6 Specific area : Synthesis of coordination complexes
- 7 Date of Start : 21/10/2016
- 8 Total cost of Project : Rs.8825/-
- 9 Approved Objectives of the proposal : Studies on mixed ligand complexes of transition metals.
To synthesize complexes having more pronounced antifungal and antibacterial properties

10. Methodology:

The work presented in this project is mainly concerned with the metal complexes isolated from the interactions of benzoic-dithiocarbamic anhydrides with metal halides. Dithiocarbamates are highly versatile mono-anionic chelating ligands which form stable complexes with all the transition elements and also the majority of main group, lanthanide and actinide elements. Cu(II) dithiocarbamates were first reported by Delpine as water insoluble precipitates obtained when aqueous Cu(II) ions were treated with aqueous solutions of the R₂dtc ligands. Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively. In azomethine derivatives, the C-

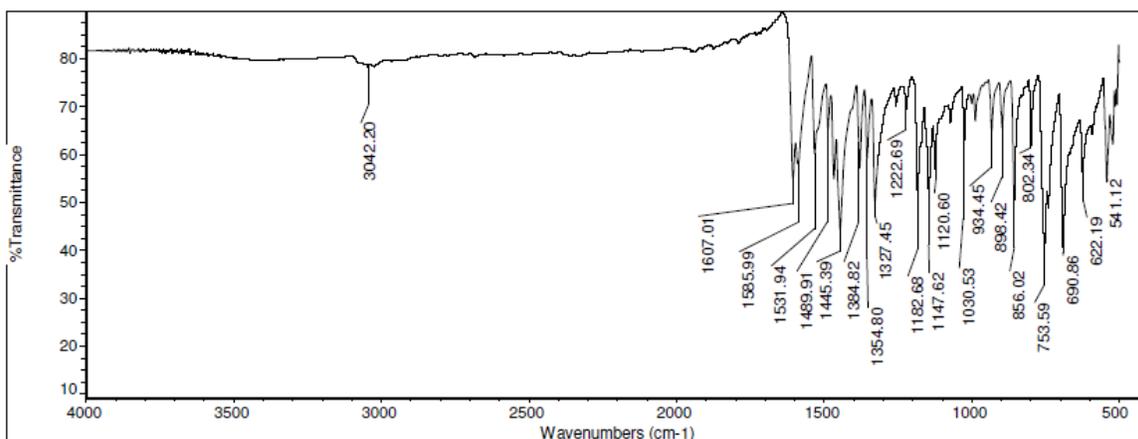
N linkage is essential for biological activity, several azomethine have been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial activities.

Three mixed ligand complexes of Copper (II) ion containing Schiff base and pyrrolidinedithiocarbamate bases were prepared. The complexes were characterized with electronic and infrared spectroscopy, conductance measurement, and elemental analysis. Resulting analytical data indicates that the Schiff base and dithiocarbamate groups are coordinated to the Copper ion in a bidentate fashion.

Analytical data of complexes

Complexes	Found (Calculated)					Colour
	C	H	N	S	Cu	
[Cu(SATO)pyrrdtc]	54.58 (55.21)	5.15 (5.33)	6.25 (6.44)	14.13 (14.74)	14.34 (14.61)	Dark green
[Cu(SAAN)pyrrdtc]	53.95 (54.2)	4.93 (5.03)	6.54 (6.65)	15.14 (15.23)	14.98 (15.09)	Light grey
[Cu(SANA)pyrrdtc]	48.89 (48.96)	4.24 (4.33)	8.99 (9.02)	13.47 (13.76)	13.52 (13.63)	Yellowish Brown

The bands originated by the $\nu(\text{C-N})$ mode are close to 1500cm^{-1} , which is in between the values expected for a single bond ($\nu=1350\text{-}1250\text{cm}^{-1}$) and double bond ($\nu=1680\text{-}1640\text{cm}^{-1}$). The appearance of a single band in the region indicates a bidentate coordination mode of the dithiocarbamate moiety through the two sulphur donor atom. The bands which appear in the regions $1588\text{-}1622\text{cm}^{-1}$ and $1196\text{-}1276\text{cm}^{-1}$ are assigned respectively to C=N and C-O stretching frequencies in the schiff base. In the complex $\bar{\nu}(\text{C=N})$ will shift to higher $\bar{\nu}$. The band at 1275cm^{-1} in ligands has been assigned to $\bar{\nu}(\text{C-O})$ phenolic stretching. The absence of band at 1275cm^{-1} indicates coordination through phenolic oxygen atom. The positions of the two bands indicates a bidentate coordination of schiff base moiety to Cu(II) ion through azomethine nitrogen and phenolic oxygen.



IR spectrum of [Cu(SAAN)pyrdtc]

SAAN- Schiff base from salicylaldehyde and aniline

Most of the dithiocarbamate complexes show bands at approximately 264, 268 & 432nm although precise assignments of these bands are yet to be determined. The bands near 264 and 268 nm are due to the intra ligand transitions mainly located on N-C=S and S-C=S group transition. The band at low wavelengths are due to transition in the ligand. Bands at 270 and 298 nm, appeared as a shoulder showing anisobidentate coordination of the dithiocarbamate group were assigned to the intraligand $\pi \rightarrow \pi^*$ transition mainly located on the N-C=S and S-C=S group respectively.

Electronic spectra of the mixed ligand complexes

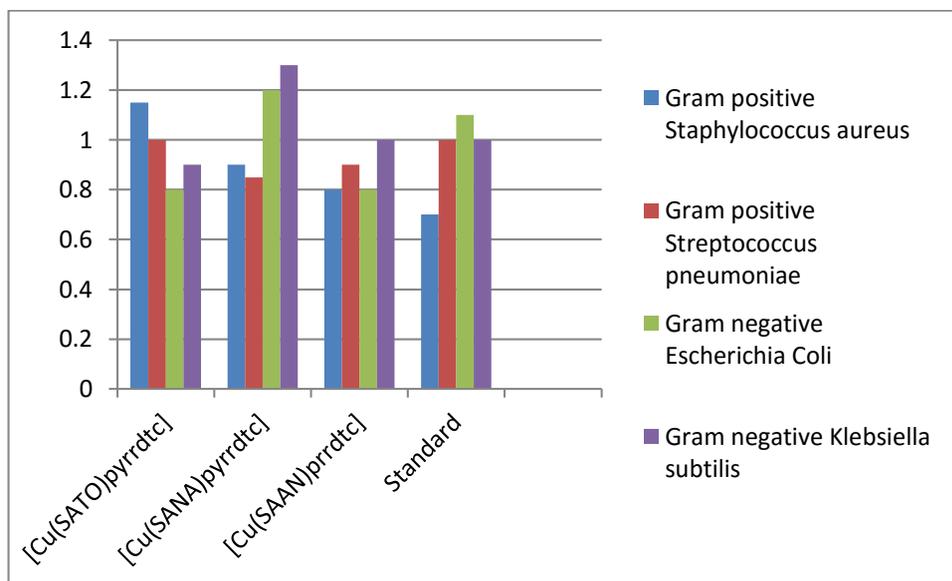
Complexes	Absorption maxima (nm)	Band assignments
[Cu(SATO)pyrrdtc]	297 350 420	Intraligand Transition Charge Transfer d-d Transition
[Cu(SAAN)pyrrdtc]	278 298 301	Intraligand Transition Intraligand Transition Intraligand Transition

	350	Charge Transfer
[Cu(SANA)pyrrdtc]	281	Intraligand Transition
	299	Intraligand Transition
	306	Intraligand Transition

A tentative square planar geometry may be assigned to all the complexes. The complexes were proposed to have a general formulae of [Cu(pyrrdtc)SB], where SB = Schiff base and pyrrdtc = pyrrolidine dithiocarbamate.

The metal complexes were screened against gram positive bacteria (Streptococcus pneumonia and Staphylococcus aureus) and gram negative bacteria (Klebsiella subtilis and Escherichia coli) using Agar diffusion test. The complexes recorded a moderate activity against the screened pathogens.

Histogram representation of the antibacterial screening of the mixed ligand complexes



In an earlier investigation, bis(dithiocarbamato)- μ -dichlorodicopper (II) complexes were synthesized by the reaction of mixed benzoic –dithiocarbamic anhydrides with copper(II) chloride. It was felt that these type of complexes could serve as the starting material for the synthesis of mixed ligand complexes consist of four main stages

a) Synthesis of sodium pyrrolidine dithiocarbamate:

The synthesis involved reaction between an aqueous solution of NaOH and pyrrolidine at 0°C.

CS₂ was added drop wise and the mixture was stirred for about 2 hours.

Mixed benzoic –dithiocarbamic anhydrides:

Benzoyl chloride was added to an ice cold solution of pyrrolidine dithiocarbamate when yellow crystals of mixed benzoic dithiocarbamate anhydride separated out. The crude product was washed a few times with distilled water and finally with methanol.

b) Synthesis of copper (II) complexes:

Bis(pyrrolidine-N-carbodithioato)- μ -dichlorocopper(II) was prepared by mixing CuCl₂.2H₂O and the freshly recrystallized benzoic pyrrolidine-N-carbodithioic anhydride dissolved in minimum quantity of methanol. The chloro complex separated out as a black crystalline powder.

c) Synthesis of Schiff base :

The Schiff base was prepared by mixing Salicylaldehyde and corresponding amine (p-toluidine, aniline, m-nitro aniline) which was dissolved in methanol. The mixture was then refluxed for 3 hours. The precipitate obtained was washed with ether and dried over anhy. CaCl₂.

d) Synthesis of mixed ligand complex

Sodium salt of schiff base was prepared by stirring a mixture of corresponding Schiff base and sodium hydroxide in methanol for half an hour. To this bis(pyrrolidine-N-carbodithioato)- μ -dichlorodicopper (II) in DMF was added and refluxed for 2 hours. The residue obtained was filtered and washed with methanol.

All the complexes obtained are characterized using elemental analysis, IR, electronic spectroscopy and NMR spectroscopy. The mixed ligand complex obtained is screened for antimicrobial activity.

11. Salient Research Achievements:

a. New observations: Metal complexes of S-, N-, and O-chelating ligands have attracted considerable attention because of their interesting physico-chemical properties, pronounced biological activities and their use as models for metalloenzyme active sites. These results motivated making the present study that deals with the preparation and characterization of complexes of dithiocarbamate and Schiff base containing an SNO donor system. The newly synthesized mixed ligand complex containing pyrrolidine dithiocarbamate and Schiff base were found to have antibacterial activity.

b. Innovations/ Technologies generated: It is noticed that many of the tridentate ligands are found to show striking biochemical characters where the azomethine linkage are blended into stable structured inorganic metal chelates.

c. Application Potential : Both dithiocarbamate and Schiff base have appreciable antibacterial activity. When the metal centre is coordinated to both these ligands the resulting complexes may have more pronounced antibacterial activity. By the detailed antibacterial studies, we can check whether it can be used as drug or not.

d. Any other: We tried the nano synthesis of the complex by sonication and to compare whether nano particle have better antibacterial activity. But it was a failure; maybe we could not provide enough frequency for the synthesis. Also it would be a green alternative for the synthesis. One Paper

based on the work entitled Synthesis, Characterisation and Antibacterial Studies of Copper (II) Mixed Ligand Complexes of Pyrrolidine Dithiocarbamate and Schiff Base has been published, International Journal of Pharmaceutical Biological and Chemical Sciences ISSN 2278-5191 (Online), Volume 6, Issue 3, July-Sept, 2017, pp 10-17.

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