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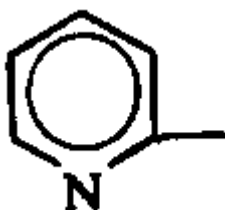
Ligands Based on Nitrogen-Sulphur and Their Metal Complexes

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ABSTRACT: Tris- and bis-ligand complexes of nickel(II) with S-benzylthiocarbamate (SBDTC) having the general formulae $Ni(SBDTC)_3X_2 \cdot H_2O$ ($X = Cl, Br$ and NO_3) and $Ni(SBDTC)_2X_2$ ($X = Cl$ and NCS), respectively, were synthesized and characterized by electronic and IR spectroscopy and magnetic measurements. The ligand acts as a bidentate sulphur-nitrogen chelating agent. Both the tris- and bis-ligand cationic nickel(II) complexes are high-spin with magnetic moments of ca. 3.10 B.M. On the basis of magnetic and spectral evidence octahedral structures are assigned to these complexes.

Under alkaline conditions complexes of the deprotonated ligand having the formulae $M(SBDTCA)_2$ [$M = Ni(II)$ and $Zn(II)$; SBDTCA = anion of SBDTC] were isolated. The nickel(II) complex is square-planar.



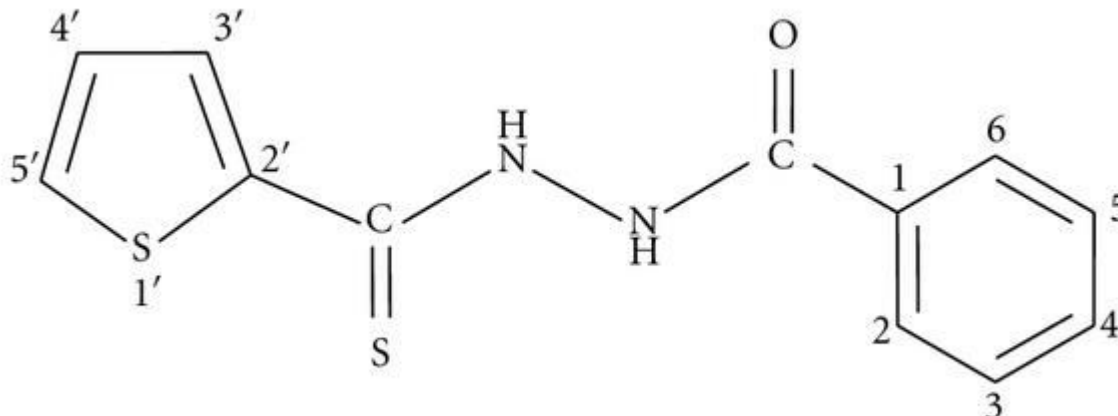
The Schiff base $CH=N-NHCSS_2C_6H_5(NNSH)$ forms intensely coloured crystalline complexes with nickel(II) and copper(II) having the general formula $M(NNS)X$ [$M = Ni(II)$ and $Cu(II)$; $X = Cl, Br$ or NO_3 and NNS is the anion of $NNSH$]. The nickel(II) complexes are diamagnetic. The magnetic behaviour of the $Cu(NNS)X$ ($X = Cl$ and Br) complexes over the temperature range 320-93°K obeys the Curie-Weiss law. The variable-temperature magnetic data coupled with IR and electronic spectral evidence support square-planar stereochemistries for the copper(II) complexes.

KEYWORDS-Ligands,Nitrogen,Sulphur,Metal,Complexes

I. INTRODUCTION

Sulphur and nitrogen containing ligands and their transition metal complexes were also used as corrosion inhibitors [9, 10] and extreme pressure lubricant additives [11]. Keeping in view the above biological activity of the sulfur and nitrogen containing ligands, we planned to undertake the synthesis, characterization, antibacterial, and antifungal activity of N-benzoyl-N'-2-thiophenethiocarbohydrazide (H_2 BTTH) (Figure 1) and its Mn(II), Fe(II), Ni(II), and Cu(II) complexes. This ligand is expected to form addition complexes without loss of protons, and deprotonated complexes by loss of one or both the hydrazinic protons.[19-20]

All the complexes are insoluble in water, methanol, and ethanol but are soluble in polar organic solvents such as DMSO and DMF. It was determined by Job's method that the complexes having 1 : 1 metal-ligand stoichiometry are formed by loss of two protons from the ligand, generating a conjugated system. Because of steric considerations, all the four potential sites cannot be attached to a single metal and, therefore, the ligand binds in a polymeric fashion.[1-7] The following equations represent the formation of the ligand and the complexes:



II. DISCUSSION

The coordinated imine groups of the Schiff's base – zinc complexes derived from various 2-substituted benzothiazolines are easily reduced with sodium borohydride to the corresponding amines. Removal of the metal ion from these reduced complexes yields the free ligands, providing a simple route to novel aminomercaptan chelating agents. Compounds of bi-, tri-, and tetradentate types were prepared in this manner. Evidence is given for a disproportionation of 2,2'-dimethyl-2,2'-bibenzothiazolyl into 2-methylbenzothiazoline and 2-methylbenzothiazole in chloroform solution.

The complexes $[Pd(HL)X_2]$ [$X = Cl$ or Br], $[(PdLX)_2]$ [$X = Cl$, Br , or I], and $[Pd_3L_4]Cl_2 \cdot 2H_2O$, where HL and L denote respectively 3-(mercaptomethyl)piperidine in its zwitterionic and anionic forms, have been prepared and characterized. Complex has been shown crystallographically to contain centrosymmetrical trinuclear cations where terminal PdL_2 units, containing $cis-S_2PdN_2$ square-planar metal environments, are bound also in a square-planar fashion to a central palladium atom through bridging mercapto groups. The three planar metal environments exhibit equivalent dihedral angles. Complexes exhibit trans mercapto-bridged dimeric structures containing S_2PdNX square-planar metal centres. Similar sulphur-bridged dimeric structures, with planar S_2PdX_2 metal environments, are proposed for complexes. Complexes and are among the first known chelates of γ -mercaptopyperidines.

In continuation to our work for the preparation of Schiff base complexes of transition metal and their antimicrobial screening, we in the present communication have synthesized some new Co(II), Ni(II) and Cu(II) complexes with tridentate Schiff base ligand, 3-amino 2-ethyl quinazoline 4(3H) thiosemicarbazone (AEQT). The obtained complexes were characterized on the basis of their molar mass, elemental analyses, electronic spectra, IR, magnetic susceptibility, molar conductance as well as thermal analysis. Spectral studies show that the Schiff base behaves as tridentate and coordination takes place through primary amino group, azomethine nitrogen and thione sulphur atom. The Schiff base and their complexes have been screened for their antibacterial effect by disc diffusion method.

Schiff bases¹⁻⁹ are useful chelators because of their ease of preparation, structural varieties, varied denticities and subtle steric and electronic control on their framework. Recently a great deal of interest have developed in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their applications as catalysts for many reactions and relation to synthetic and natural oxygen carriers. The biocidal effect of Schiff bases as well as its metal complexes is of interest due to their pharmacological activities. Keeping the above facts in mind and in continuation of our recent work¹⁰⁻¹⁵ on Schiff bases and their metal complexes, in our present endeavour, we have chosen to synthesis of a Schiff base 3-amino 2-ethyl quinazoline 4(3H) thiosemicarbazone (AEQT) and its Co(II), Ni(II) and Cu(II) metal complexes. The ligand and its metal complexes were also screened for in vitro antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. [11-18]

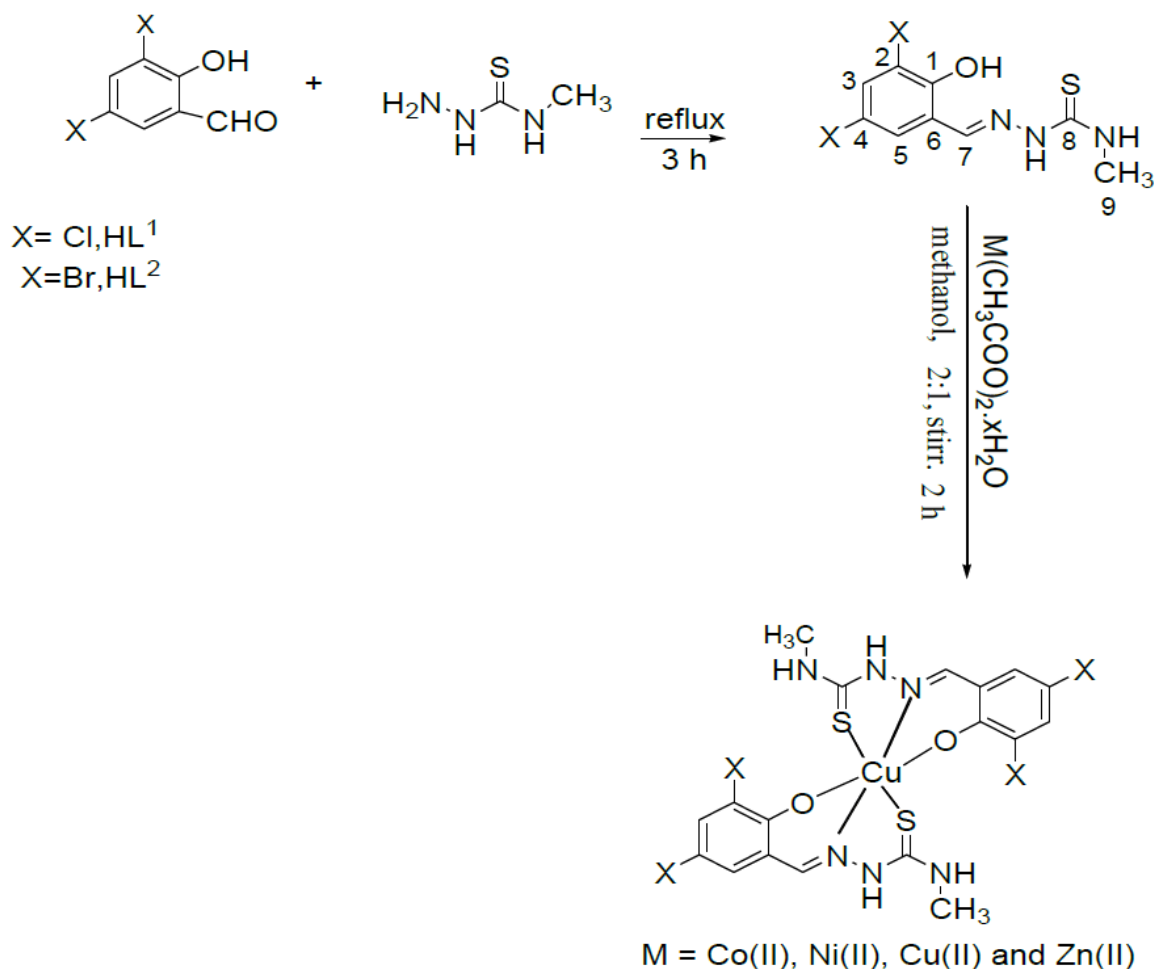
Molar conductivity:

Conductivity of the complexes were measured in the solvent dimethyl formamide at the concentration 10^{-3} M and all the complexes were found to be electrolytic in nature of 1:2 type. The molar conductivity value of the complexes are found in the range $136.7-149.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. [7-10]

Antimicrobial discussion :

All the Co(II), Ni(II) and Cu(II) complexes as well as ligand AEQT were tested against Gram positive and Gram negative bacteria. The results indicates that all the complexes were active against Gram positive bacteria while less active against E. coli which is Gram negative. The complexes were more active than the Schiff²⁷ base which indicates that metallation increases the activity.

In vitro antibacterial activity of the ligand and the metal complexes were tested using paper disc diffusion method²⁸. On the basis of analytical and spectral data the tentative structure of Co(II) and Ni(II) complexes are proposed to be octahedral in geometry whereas distorted octahedral geometry is proposed for Cu(II) complexes.



Scheme 1: Synthesis of ligands and their metal complexes

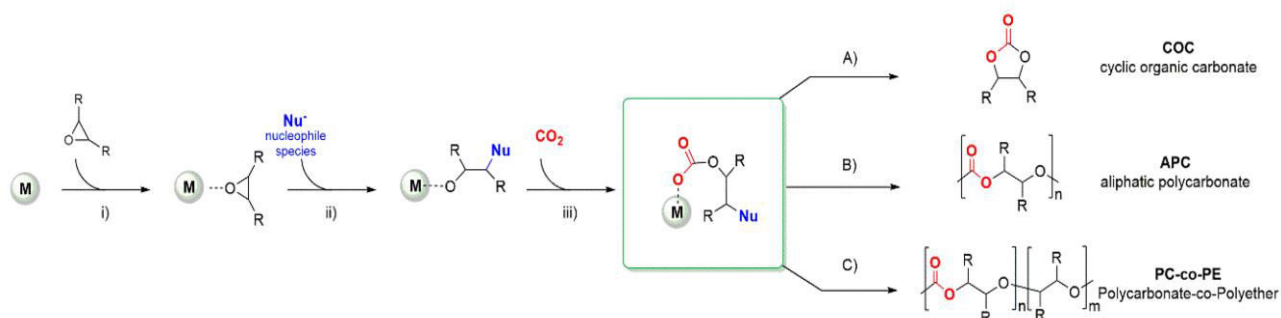
III. RESULTS

Homogeneous catalysis is one of the most fast-developing areas of chemistry because of the possibility to finely tune the course of a given reaction by rational design of the catalyst architecture. Indeed, compared to heterogeneous catalysis, mechanisms governing the activity and selectivity are easier to be understood and therefore the overall performances can be consequentially greatly improved.[22-28] In particular, the use of soluble transition-metal complexes in catalysis opened unprecedented possibilities to control the product features by a judicious modification of the electronic and steric properties of the ancillary ligand. Inspired by this simple concept, chemists have unfolded countless stereoselective reactions encompassing all families of chemical transformations (oxidations, cross-coupling reactions, polymerizations, etc.) [1,2,3].

Parallel to this trend, in the last two decades, the use of renewable feedstocks has gained momentum because of the growing demand for more sustainable chemical processes. In particular, carbon dioxide utilization (CDU) has

emerged as an important tool for the transition to a carbon-neutral society because of the possibility to close, through the use of renewable energies, an anthropogenic carbon cycle avoiding net emission of greenhouse gases. Besides, CO₂ displays evident advantages in terms of toxicity, flammability, and the possibility of storage with respect to other C₁ feedstocks (such as phosgene and carbon monoxide) that render the implementation of industrial processes based on this molecule quite promising [4,5,6,7,8,9].

Among the possible products obtainable from CO₂, cyclic organic carbonates (COCs) and aliphatic polycarbonates (APCs) have received considerable attention because of their wide range of application and straightforward synthetic pathway starting from the corresponding epoxides [10,11,12,13,14,15,16,17,18,19]. The coupling between CO₂ and an epoxide can result in the formation of the cyclic product or of the polymeric one depending on many factors such as the nature of the substrate, the reaction conditions, and the catalytic system. Notwithstanding the efforts to develop efficient metal-free catalysts, most of the active systems are based on the combination of a metal complex activated by a suitable nucleophile, often added as ammonium or phosphonium salt. The basic reaction mechanism can be exemplified following the steps depicted in Scheme 1: (i) The coordination of the epoxide to the metal center; (ii) the ring-opening of the activated epoxide by the nucleophilic attack and the formation of the metal-alkoxo bond; (iii) the insertion of CO₂. At this stage, the intermediate can give an intramolecular ring-closing with the formation of the COC (path A) or the alternating insertion of epoxide and CO₂ with the formation of the APC (path B). Since two consecutive insertions of the epoxide are possible as well (path C), often the resulting polymer also contains some polyether linkages [20]



IV. CONCLUSIONS

Schiff-base ligands are versatile compounds synthesized by condensation between carbonyl compounds and primary amines. Schiff-base ligands can coordinate with different transition metal ions [1-3] and stabilize in various oxidation states. Schiff-base complexes show excellent catalytic activity [4] and exhibit broad range of biological activity [5,6]. Schiff-base complexes containing Co(II), Ni(II), Cu(II), and Zn(II) have been studied for enzymatic reactions [7], structure-redox relationships [8], magnetic properties [9,10], and used in coordination chemistry of transition metal ions [11].

Thiosemicarbazide based Schiff bases have been widely studied since 1950 due to their tendency to bind with metal centers [12] and also due to the fact that these molecules and their complexes have been used as therapeutics and imaging agents [13]. Also, literature shows that transition metal complexes of sulfur-nitrogen chelating agents, mainly those formed from thiosemicarbazide show variety of medicinal properties such as anticancer, antibacterial, antiviral, antitumour, antifungal, antimalarial etc. [14-19]. Thiosemicarbazides has also been used due to their variable applications in industry and analytical chemistry [20]. The molecules containing a chromophore based on the thiosemicarbazide moiety has imported in increasing the light fastness [21]. Impressed by the applications of thiosemicarbazides, here in this paper we have reported the synthesis and characterization of Co(II), Ni(II), Cu(II), and Zn(II) complexes of Schiff base derived from 4-methyl-3-thiosemicarbazide and dihalosalicylaldehydes.[25-28]

REFERENCES

- Alexander A., Chem. Rev., 95, 273 (1995).
- Vigato P. A., Tamburini and Bertolo L., Coord. Chem. Rev., 251, 1311 (2007).
- Padhye S. B. and Kalfman G. B., Coord. Chem. Rev., 03, 127 (1985).
- Dilwarth J. R., Arnold P, Morales D., Wong Y. L. and Cheng Y., Modern Coord. Chem., 217 (2002).



5. Quiruga A. G. and Raninger C. N., *Coord. Chem., Rev.*, 248, 119 (2004).
6. West D. X., Liberta A. E., Padhye S. B., Chikate, R. C., Sonawane P. B., Kumbhar A. S. and Yerande R. G., *Coord. Chem. Rev.* 123 (1993).
7. Wang T. and Guoz, *Curr. Med. Chem.*, 13, 525 (2006).
8. Coires A. C. F., *Antixancer Agents in Med. Chem.*, 7, 484 (7).
9. Lobana T. S., Shama R., Bawa G., Khanna S., *Coord. Chem. Rev.*, 253, 977 (2009).
10. Rai B.K. and Anand Rahul, *Asian J. Chem.*, 25, 583 (2013); Rai B. K. and Kumari Rachana, *Asian J. Chem.*, 23, 4625 (2011); Rai B. K., Kumari Rachana and Thakur Amrita, *Orient J. Chem.*, 28, 943 (2012).
11. Rai B.K., Thakur Amrita and Divya, *Asian J. Chem.*; 25, 583(2013).
12. Rai B.K. and Vidyarthi S.N., kumara Punam, Kumari Suman, Kumari Lakshmi and Singh Rajkishore, *Asian J. Chem.*, 25, 941(2013).
13. Rai B.K. and Kumar Arun, *Asian J. Chem.*, 25, 1160(2013).
14. Rai B.K., *J. Indian Chem., Soc*; 90, 105(2013).
15. Rai B. K., Vidyarthi S. N., Sinha Puja, Singh Vineeta and Kumar Sanjiv, *Orient J. Chem.*, 29, 271 (2013),
16. Vogel A.I., *A textbook of quantitative Chemical Analysis*, Revised by Menaham J., Denny R.C., Barnes J.D. and Thomas M, Pearson Education, 7th Edn, London (2008).
17. Cook D., *Can J. Chem.*, 39, 2009 (1961).
18. Percu G. C. and Thornton D. A., *Inorg. Nucl. Chem., Lett.*, 7, 599 (1971).
19. Kolinski R. A. and Korybut Daszkiewicz, *Inorg. Chim. Acta*, 14, 237 (1975).
20. Meglynn S. P. and Smith J. K., *J. Mol. Spectros*, 6, 164 (1961).
21. Babukutty P. V., Prabhakaran C. P., Anantaraman R. and C. G. R. Nair, *J. Inorg. Nucl. Chem.*, 36, 3685 (1974).
22. Banerjee P., Singh I. P., *Indian J. Chem.*, 6, 34 (1968).
23. Ferraro J. R., *Low Frequency Vibration of Inorganic and Coordination Compound*, Plenum Press, New York.
24. Lever A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 395 (1968).
25. Figgis B.N., *Introduction to LIgand Field*, Wiely Eastern Ltd., New Delhi, 279(1976).
26. Carlin R.L. and Van Deynevetedt A.J., *Magnetic properties of transition metal compounds* springer-ver lag, New York, (1997).
27. Singh H. Z., Khungar B., Tripathi U. D., Varshney A. K., *Main Group Met. Chem.*, 24, 5 (2003).
28. Mukherjee P. K., Saha K., Giri S. N., Pal M. and Saha B.P., *Indian J.I Microbiology*, 35 (1995).



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