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Research Article

Synthesis the meal complexes containing the metal ions Cu (II), Co (II) and Ni (II) of Schiff bases derived from substituted thiophenes as" NO " and "ONO"donors

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ABSTRACT

Thienothiophene derivatives developed for various purposes in the field of medicinal chemistry have been reported as potential antiviral, antibiotic, and anti-glaucoma drugs or as inhibitors of platelet aggregation. There is a resurgence of interest in metal complexes of Schiff bases due to their inbuilt structural frame work containing both hard nitrogen/ oxygen and soft sulphur donor atoms. As a result they can readily coordinate with many transition metals giving stable complexes. In this paper we discuss about synthesis of bivalent colored metal complexes from NO and ONO donors of substituted thiophene schiff bases. And products are further confirmed by analytical, spectroscopic method by physico-chemical process.

Keywords: Thiophene, Schiff bases, analytical, spectroscopic method.

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CHEMISTRY RESEARCH ARTICLE

Synthesis the meal complexes containing the metal ions Cu (II), Co (II) and Ni (II) of Schiff bases derived from substituted thiophenes as" NO " and "ONO"donors

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ABSTRACT

Thienothiophene derivatives developed for various purposes in the field of medicinal chemistry have been reported as potential antiviral, antibiotic, and anti-glaucoma drugs or as inhibitors of platelet aggregation. There is a resurgence of interest in metal complexes of Schiff bases due to their inbuilt structural frame work containing both hard nitrogen/ oxygen and soft sulphur donor atoms. As a result they can readily coordinate with many transition metals giving stable complexes. In this paper we discuss about synthesis of bivalent colored metal complexes from NO and ONO donors of substituted thiophene schiff bases. And products are further confirmed by analytical, spectroscopic method by physico-chemical process.

Keywords: Thiophene, Schiff bases, analytical, spectroscopic method.

1. INTRODUCTION

The coordination chemists are interested mainly in stereo chemical, thermodynamic, kinetic, spectral & magnetic properties of coordination compounds. Apart from these, there has been a growing interest in the role of the metal ions and their complexes in biological systems. It is well known fact that zinc is essential for human life. Alkali and alkaline earth metal complexes of crown ethers and cyclic ligands play an important role in the biological systems. The complexes of copper and iron are involved in biological systems as oxygen carriers. As a result there is a growing interest in understanding the mechanism of oxygen carriers [1-3].

Nitrogen, oxygen and sulphur are the most documented donor atoms. Nitrogen and oxygen are found to be the key donor atoms in most of the metallobiomolecules [4-5].The extent and mode of coordination of these donor atoms is unique, different from each other and is a function of atomic properties. It should also be noted that the structure of organic core which bears the donor atoms also plays very important role in deciding the coordination behavior. Thus, it will be very interesting to study the structure and functional activities of the complexes having these three donor atoms constituting coordination cavity suitably fitted with transition metal ions.

Copper compounds are known in several oxidation states, usually 2+, where they often impart blue or green colors to natural minerals such as turquoise and have been used widely as pigments. Copper (II) ion is soluble in water and at low concentration it exhibits bacteriostatic and fungicidal activity. At lower concentration Cu (II) is an essential trace nutrient to all higher plant and animal life. In animals, including humans, it is found widely in tissues, with concentration in liver, muscle and bone. It functions as a co-factor in various enzymes and copper-based pigments.

The human body normally requires copper at a level of about 1.4 to 2.1 mg for each kg of body weight. Copper is found in a variety of super oxide dismutase. Because of its role in facilitating iron uptake, copper deficiency can often produce anemia-like symptoms. In humans, the symptoms of

Wilson's disease are caused by an accumulation of copper in body tissues.

Cobalt in small amount is essential to many living organisms, including humans. Although cobalt proteins are less common than proteins containing metals like manganese, iron, or zinc etc. are known. Most cobalt proteins use a cofactor based on the corrin cobalt, derived from vitamin B12, but there are also a few proteins known in which cobalt is directly coordinated by the protein structure; Methionine aminopeptidase-2 and Nitrile hydrates are two examples[6].

Nickel is used in many industrial and consumer product. It plays numerous roles in the biology of microorganisms and plants [7]. A nickel-tetrapyrrole coenzyme, F430, is present in the methyl coenzyme M reductase which powers methanogenic archea. One of the carbon monoxide dehydrogenase enzymes consists of a Fe-Ni-S cluster [8]. Other nickel containing enzymes include a class of superoxide dismutase [9] and a glyoxalase [10]. Coordination compounds based on nickel ions are also of great interest in the field of catalysis as they are electrochemically active and can exist even in the 4+oxidationstate.

Most of the major classes of pharmaceutical agents which are in current clinical use contain number of coordination compounds [11-13]. The utility of metal complexes as pharmaceutics has a special emphasis because of their ability to undergo biotransformation.

Hydrazones are compounds obtained by the condensation of hydrazides with aldehydes or ketones. Substituted hydrazones can be obtained by introducing substituted hydrazides and carbonyl compounds. General formula for a substituted acylhydrazone **(1)**.

Amide oxygen and azomethine nitrogen are the available donor sites in hydrazone compounds. Further, the number of coordination sites can be increased by suitable substitution on the hydrazone framework. If a hetero ring is attached to the hydrazone framework, the hetero atom can also coordinate to the metal center thus increasing the denticity. A tridentate acylhydrazone **(2)**.

In hydrazones, it is well known that a proton transfer can occur between thehydrazine-N and keto group of hydrazide part. Therefore tautomerization equilibrium exists between amido form and iminol form through intramolecular proton transfer. In solid state, hydrazones predominantly exist in amido form, whereas in solution iminol form predominates **(3)**.

Due to tautomerism in hydrazones the amide oxygen can be in neutral *keto* form **(5)** or enolic form **(6).** The actual ionization state is dependent upon the condition and the metal salts employed. In basic solution amide oxygen get deprotonated and coordinates to the metal center in the enolic form whereas strongly acidic condition favor compounds formulated with a neutral ligand [14-18].

In certain cases there is a possibility in which two deprotonated ligand moieties coordinate to the same metal centre giving rise to six coordinate distorted octahedral complexes [19-24] **(7).** These types of complexes have increased stability which arises due to chelation.

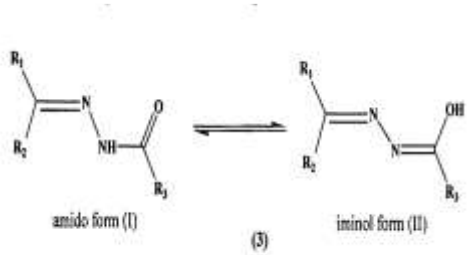
There are cases in which hydrazones form bridged complexes. In some cases, an atom or group of atom may act as bridging ligand which results in a dimericstructure **(8).** Halogens, azide and thiocyanate ligands can act as these types of bridges. In ONO donor hydrazones containing phenolic group, phenolate oxygen atom can form a bridge between the metal centres thus forming a dimer **(9).**

Presence of additional donor sites in the kenotic part offers much more coordination possibilities which may result in multinuclear complexes. If -OMe like groups are present in the carbonyl compound, it can utilize both the chelating and bridging capability leading to formation of multinuclear complexes **(10).**

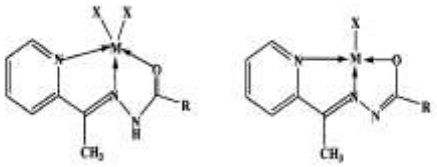
The biological activity of o-phenylenediamine and 2-amino thiophenol metal complexes are less than that of Tavinic, but higher than that of Traivid. For Schiff base like OPD complexes, the biological activity of

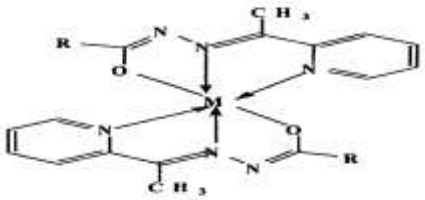
Fe (III), Co (II), Cu (II), and U02 (II) complexes is higher than that of the ligand and Traivid, while their activity is comparable with that of standard Tavinic. For Ni (II) and Zn (II) complexes, their biological activity is nearly the same as that of o-phenylenediamine. The biological activity of the complexes follow the order Fe (III) = Co (II) = Cu (II) = U02 (II) > Zn (II) > Ni (II).

In the light of these reports, we thought it is worthwhile to synthesize the complexes of Schiff bases derived from thieno[2,3-b]thiophenes containing the metal ions like Cu(II), Co(II) and Ni(II). The hydrazones have been investigated and proved to be promising chelating agents for a number of transition and inner-transition metals. They are known for their varied behaviour in the complexes. With the help of IR studies they are shown to exhibit keto-enol tautomerism. Many of the physiological activities of hydrazone compounds find applications in the treatment of several diseases such as tuberculosis, leprosy and mental disorder. On the other hand, aryl hydrazones are reported to possess tuberculostatic activity. This is attributed to the formation of stable chelates with transition metals present in the cell. Hydrazones act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators. Metal complexes are currently being utilized in the diagnosis of wide variety of disease states ranging from heart disease, brain disorders, cancer and diabetics.



(3)
Tautomerism in acylhydrazones


(5) (6)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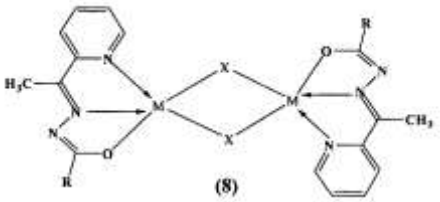
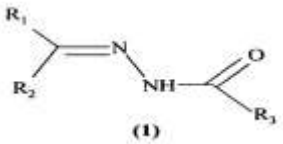
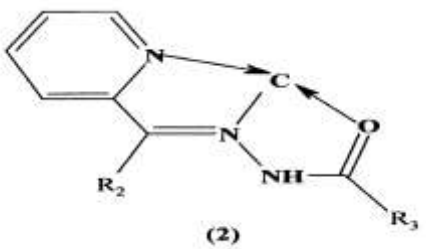
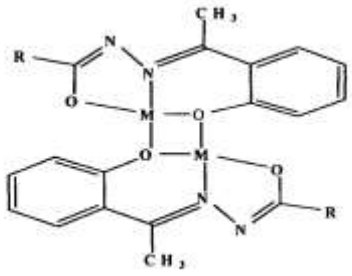
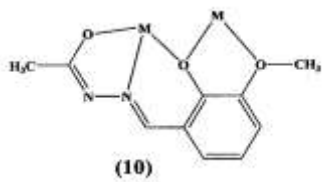

(8)

Figures 1 (1-3; 5-10)


(1)


(2)
An example for a tridentate acylhydrazone


(9)


(10)

2. MATERIALS AND METHOD

In this method of synthesis of ligands, elemental analysis and physico-chemical techniques employed in characterizing the ligands have been discussed. Solvents such as ethyl alcohol, methyl alcohol, and ether are purified before use. Spectroscopic grade dimethyl formamide was used without further purification. Chemicals used directly for the synthesis of hydrazone ligands are of SD-Fine, BDH and Aldrich grade.

3. PREPARATION OF LIGANDS

Preparation of N'2, N's-bis (2-hydroxybenzylidene)-3, 4-dimethyIthieno [2, 3- b] thiophene-2,5dicarbohydrazide (L1H)

Preparation of 3, 4-Dimethyltbieno [2, 3-b] thiophene-2, 5-diester (I)

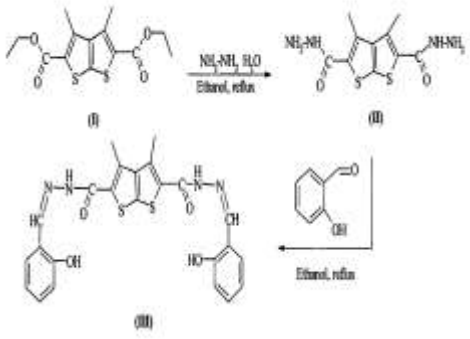
A mixture of acetyl acetone (10.26 mL, 10 mmol) and anhydrous potassium fluoride (3g) dissolved in dimethylformamide 20 mL was added to a solution of carbon disulfide (9.06 mL, 10.5 mmol) in DMF (20 mL) and stirred at 40 °C for half an hour. Ethylchloroacetate (24.5 mL, 20 mmol) was then added dropwise and refluxed at 60 °C for three hours. Then the reaction mixture was cooled down to 40 °C and poured into cold water including a few drops of concentrated HC1. The solid material was filtered off, washed well with water, dried and recrystallized twice from ethanol.

Preparation of 3, 4 - Dimethylthieno [2, 3-bJ thiophene-2, 5-diearbo Hydrazide (ll)

A mixture of 3, 4-dimethylthieno [2,3-b] thiophene-2,5- diester (I) (3.12 g, 10 mmol) and hydrazine hydrate (50 mmol) was stirred for two hours and then refluxed in ethanol (50 mL) for another two hours. The reaction mixture was cooled down and the resulting precipitate was collected by filtration and washed with alcohol to get yellow amorphous powder.

Preparation of N'2, N'5 - bis (2 - hydroxybenzylidene) - 3, 4-dimethylthieno [2, 3-b] Thiophene-2,5dicarbohydrazide (L1H) (III)(Schem-1)

By refluxing a mixture of hot ethanolic solution (30 mL) of salicylaldehyde (0.01 mol) and ethanolic solution (30 mL) of compound 3,4-imethylthieno[2,3-b]thiophene-2,5-icarbohydrazide (0.01 mol) containing few drops of hydrochloric acid was refluxed for 4-5 hours. The precipitate formed was filtered, washed with cold ethanol and recrystallized from hot ethanol.



Scheme-1

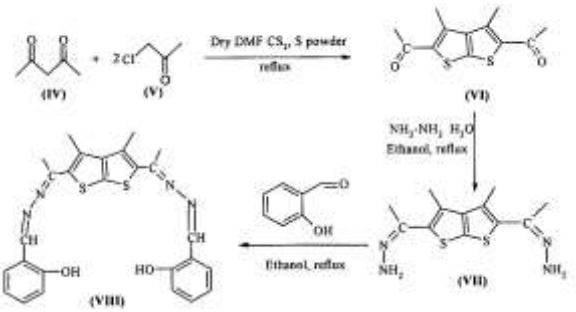
Preparation of 2,2'((((3,4dimethylthieno[2,3-b]thiophene-2,5-diyI) bis(ethanl-ylidene))bis(hydrazine-2,l-diyIidene))bis(methanylylidene))diphenoI (L2H) (Scheme-2)

Preparation of l-(3,4-dimethylthieno[2,3-b]thiophen-2,5-diyI)diethanone (VI)

A mixture of acetyl acetone **(IV)(** 10.26 mL, 10 mmol) and anhydrous potassium fluoride (3g) dissolved in dimethylformamide 20 mL was added to asolution of carbon disulfide (9.06 mL, 10.5 mmol) in DMF (20 mL) and stirred at 40 °C for half an hour. Chloroacetone (V) (24.5 mL, 20 mmol) was then added drop wise and refluxed at 60°C for three hours. Then the reaction mixture was cooled down to 40°C and poured into cold water including a few drops of concentrated HC1. The solid material was filtered off, washed well with water, dried and recrystallized twice from ethanol; colorless needles were obtained; yield: 80%.

Preparation of 2,2'((((3,4dimethylthieno[2,3-b]thiophene-2,5-diyl) bis (ethan-l-yl-1-ylidene)) bis(hydrazine-2,l-diylidene)) bis(methanylylidene))diphenol(L2H) (VIII)(Schem-2)

By refluxing, a mixture of hot ethanolic solution (30 mL) of salicylialdehyde (O.Olmol) and ethanolic solution (30 mL) of compound, ((3, 4-dimethyl-thieno [2, 3-b] thiophen-2, 5-diyl) bis(ethan-l-yl-l-ylidene))bis(hydrazine)(VII) (O.Olmol) containing few drops of hydrochloric acid was refluxed for 4-5 hr. The precipitate formed was filtered, washed with cold ethanol and recrystallized from hot ethanol.



Scheme-2

Preparation of (E)-ethyl 2-(5-bromo-2-hydroxybenzylideneamino)-4, 5, 6, 7-tetrahydrobenzo[b]thiophene-3-carboxylate (L3H)

Preparation of ethyl 2-amino-4, 5, 6, 7-tetrahydrobenzo [A]thiophene-3-carboxylate (XI)

The starting material ethyl 2-amino-4, 5, 6, 7-tetrahydrobenzo [6] thiophene-3- carboxylate, was prepared by Gewald synthesis2. A mixture of cyclohexanone **(IX)** (1.06 mL, 10 mmol), ethyl cyanoacetate **(X)** (1.15 mL, 10 mmol), morpholine (0.90 mL, 10 mmol), sulphur (0.32 g, 10 mmol) in ethanol (10 mL) was stirred and refluxed for overnight. After completion of the reaction, the reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The crude solid was washed with cold ethanol and filtered through sintered funnel, dried under vacuum. The crude product was dissolved in dichloromethane and washed with brine. The organic layer was collected and concentrated under low vacuum to give the compound **3;** yield: 73%.

Preparation of (E)-ethyl 2-(5-bromo-2-hydroxybenzylideneamino)-4, 5, 6, 7-tetra hydrobenzo[b]thiophene-3-carboxyIate2 (L3H) (XII)

A mixture of 3 (2.0g, 8.80 mml), and 5-bromosalicylaldehyde (1.8g, 8.80mmol), in EtOH (20.0 mL) was stirred at refluxing temperature for 8 h. After completion of the reaction (indicated by TLC), the reaction mixture was cooled to room temperature and the separated solid product is filtered, washed with ethanol and dried to get the ligand as dark yellow solid; 88%.

Preparation of Cu (II), Co (II) and Ni (II) complexes

4. RESULTS AND DISCUSSION

Preparation of Cu (II), Co (II) and Ni (II) complexes by the known procedure with Schiff bases. All the Cu (II), Co (II) and Ni (II) complexes are colored, stable and no hygroscopic in nature. These complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The elemental analysis showed that the Cu (II), Co (II) and Ni (II) complexes have 1:2 stoichiometry of the type ML and M2L, where 'L' stands for a deprotonated ligand. The Schiff bases like L1H, L2H ,L3H form octahedral complex with CoCl2- 6H20/NiCl2-6H20/CuCl2-2H20 in ethanol. The complex separated was filtered, dried and further purified by recrystallization from hot ethanol. (Fig., 2- Figure 4)

5. CONCLUSION

The newly synthesized Cu(II), Co(II) and Ni(II) complexes by using L1H ,L2H ,L3H ligands have been concluded on the basis of analytical and spectral studies. The proposed structures of formed products are shown below. And which are further confirmed by spectral and analytical analysis.

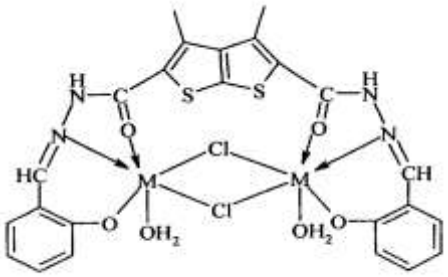


Figure 2 M-L1H complexes

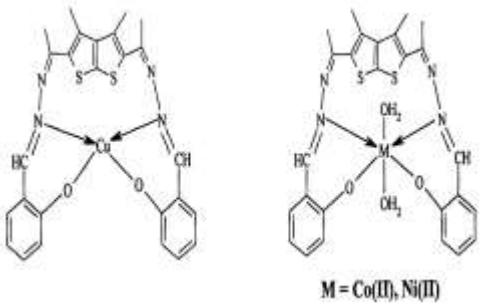


Figure 3 M-L2H complexes

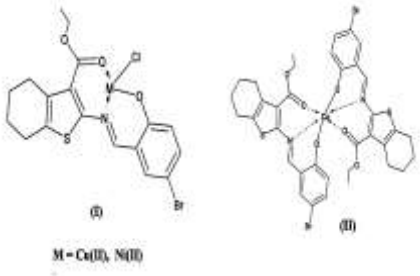


Figure 4 M-L3H complexes

^{1}H NMR Spectral data

The NMR spectrum of the Schiff base (L1H), NH protons exhibited signals at δ 10.03 ppm (s, 2H). A characteristic proton signal at δ 8.57 ppm (s, 2H) and δ 7.59 ppm (s, 2H) is assigned to the -CH and -OH proton respectively. In addition to this, the multiplet signals in the region δ 6.52-6.94 ppm (m, 8H) and a sharp singlet signal at δ 2.5 ppm (s, 6H) are due to aromatic protons and CH3 protons respectively.

The NMR spectrum of the Schiff base (L2H), the signals observed at δ 9.18 ppm (s, 2H) are attributed to the CH proton. A signal at δ 8.42 ppm (s, 2H) is ascribed to the -OH proton. The signals observed as a multiplet in the region 7.01-7.87 (m, 8H) and as a singlet at δ 2.59 and 2.66 (s, 6H) ppm are due to aromatic and CH3 protons respectively.

The proton NMR spectrum of the Schiff base (L3H), recorded in DMSO-d6 exhibited a signal at δ 12.81. The downward shift of the proton is presumably due to strong internal hydrogen bonding23. Signal for the hydrogen of the azomethine group has been observed at δ 8.895. Signals appearing at δ 1.705 and 2.705 can be attributed to methylene protons of cyclohexane ring and Signals appearing at δ 1.305 and 4.305 respectively of the ethyl ester group. On the basis of the spectral values, an internally hydrogen bonded phenolimine structure has been proposed for the ligand.

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