

Synthesis of Mono and Bi Dentate Schiff's Bases and their Complexes with $M(CO)_6$ [M= Cr, Mo, W]

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The development of bacterial resistance to available antibiotics and increasing incidence of multi resistant bacterial infections in hospitals and in the community has necessitated the search for new antibacterial agents to treat the bacterial infection. Thiazoles and their derivatives form a part of Vitamin B₁ and coenzyme carboxylase. They represent a very interesting class of compounds because of their wide applications as antimicrobial, anti-inflammatory, anti-degenerative and anti-HIV activities. In the light of the above we have synthesized some new noble Schiff's Bases and their G-6 metal carbonyl derivatives. Schiff's bases viz. N-[(E)-phenylmethylidene](naphtho[1,2-d][1,3]thiazol-2-amine) (SB¹), N-[(E)-(3-methoxyphenyl)methylidene](naphtho[1,2-d][1,3]thiazol-2-amine) (SB²) react with G-6 metal hexacarbonyls in benzene to give monosubstituted derivatives while N-[(E)-phenylmethylidene] (naphtho[1,2-d][1,3]thiazol-2-ylimino)methyl]phenol (SB³), 2-methoxy-6-[(E)-(naphtho[1,2-d][1,3]thiazol-2-ylimino)methyl]phenol (SB⁴) and N-[(E)-furan-2-ylmethylidene] (naphtho[1,2-d][1,3]thiazol-2-amine) (SB⁵) react with G-6 metal hexacarbonyls in benzene to give disubstituted derivatives.

Keywords: Schiff bases, Metal carbonyl, Naphtho[1,2-d][1,3]thiazol-2-amine.

1. INTRODUCTION

It has long been known that metal ions are involved in biological processes of life through bonding to the hetero atoms of heterocyclic residues of biological molecules i.e., proteins, enzymes and nucleic acids etc [1]. Schiff bases are characterized by the –N=CH– (imine) group which is important for elucidating the mechanism of transamination and racemization reaction in biological systems [2] and are also known to have biological activities such as antimicrobial [3,4,5], antifungal [6], antitumor [7] and herbicidal [8]. Schiff bases continue to occupy an important position as ligand in metal coordination chemistry [9,10], even almost a century since their discovery. Moreover, the incorporation of transition metal into Schiff bases enhances the biological activity of the ligand and decreases the cytotoxic effect of both the metal ion and ligand on the host [11]. We have synthesized new Schiff bases (SB¹⁻⁵) of naphtho[1,2-d]thiazol-2-amine purposely to combine the lipophilicity of naphthalene moiety to enhance membrane permeability with thiazole ring and azomethine linkage to study their effect on pathogenic strains of Gram positive and Gram negative bacteria. Typical $M(CO)_6$ (M=Cr, Mo, W) complexes of these Schiff's bases SB¹⁻⁵ were synthesized.

2. EXPERIMENTAL

Reactions were carried out under dry nitrogen or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs and CH_2Cl_2 solution. All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at 120°C , molecular weight of the complexes were determined cryoscopically in benzene, n-hexane, n-pentane, benzene were purchased from E. Merck, and $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), dichloromethane, naphtha[1,2-d]thiazol-2-amine were purchased from Sigma-Aldrich and were used as supplied.

Magnetic susceptibility measurements of the complexes were carried out by Gouy method. UV irradiation were performed with a medium pressure 400W mercury lamp through a quartz bulb.

2.1. General Method for Synthesis of Schiff Bases (SB^{1-5})

3.0g (15mmol) Naphtha[1,2-d] thiazole-2-amine was dissolved in 30ml of glacial acetic acid. Substituted aromatic aldehyde (15mmol) in 15ml glacial acetic acid was added dropwise with stirring and the reaction mixture was heated to reflux for over 12h. After completion of reaction, it was poured onto crushed ice, the solid thus obtained was filtered, washed with water and recrystallized from ethanol. This scheme is as shown in Figure 1.

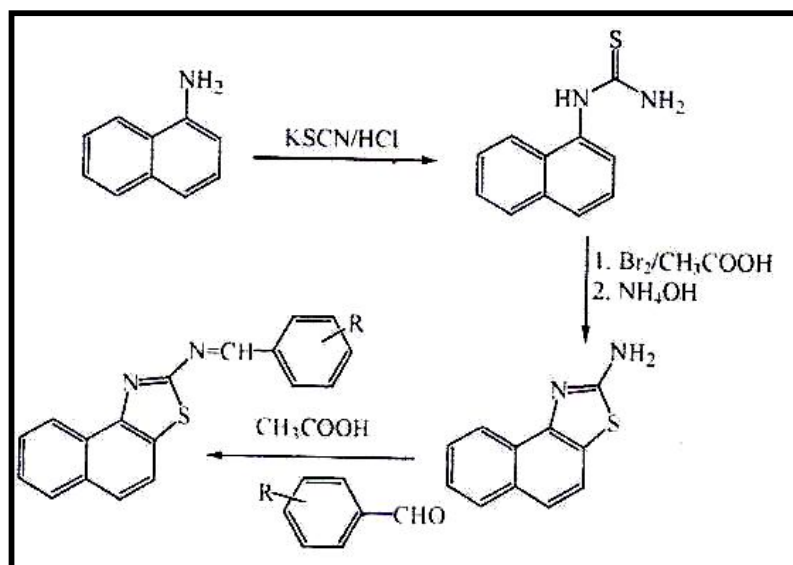


Fig. 1: General Synthesis of Schiff Bases.

2.2. General Method for Synthesis of $\text{M}(\text{CO})_5(\text{SB}^{1-2})$

A quantity of 0.33 g (1.5 mmol) of $\text{Cr}(\text{CO})_6$ was dissolved in 50ml of n-Heptane. Then, 0.47g (1.5mmol) of N-[(E)-phenylmethylidene](naphtho[1,2-d][1,3]thiazol-2-amine) (SB^1)

was added to the above solution with constant stirring. The mixture was irradiated for 14 hrs. During the irradiation, the color of the reaction mixture changed from red to brown colour. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a deep brown solid. The solid residue was then washed with n-hexane so as to remove any $\text{Cr}(\text{CO})_6$, ligand itself, and other n-hexane soluble impurities. The deep brown residue or remnant was dissolved in 1:1 $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ solution for recrystallization. This scheme is as shown in Figure 2 and 3.

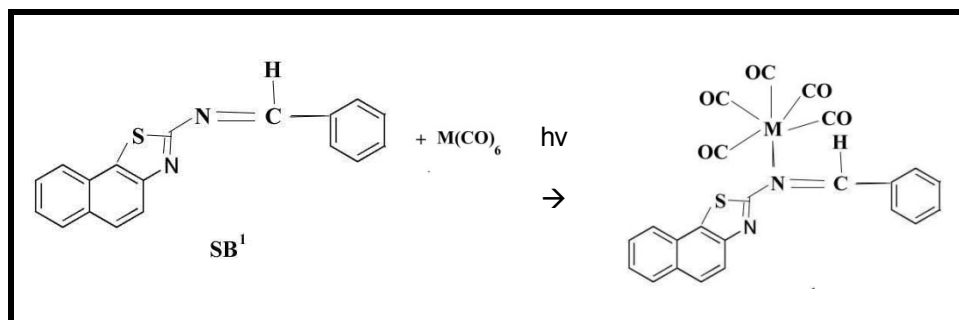


Fig. 2: General synthesis of complexes $M(\text{CO})_5(\text{SB}^1)$.

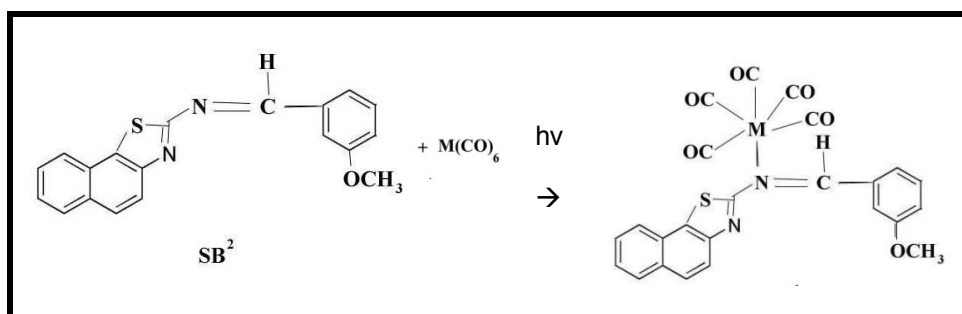
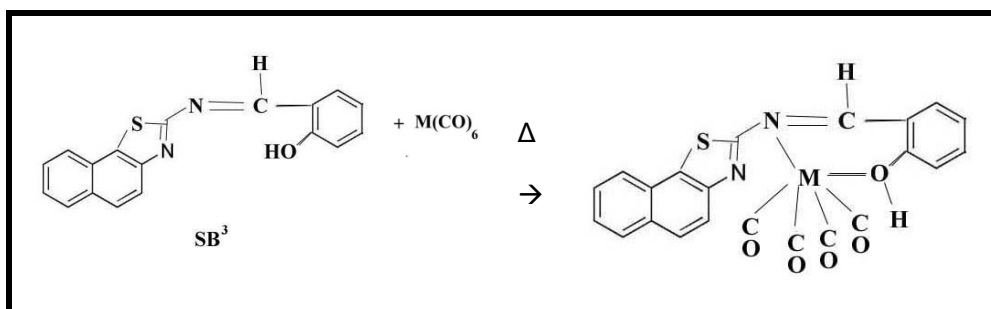
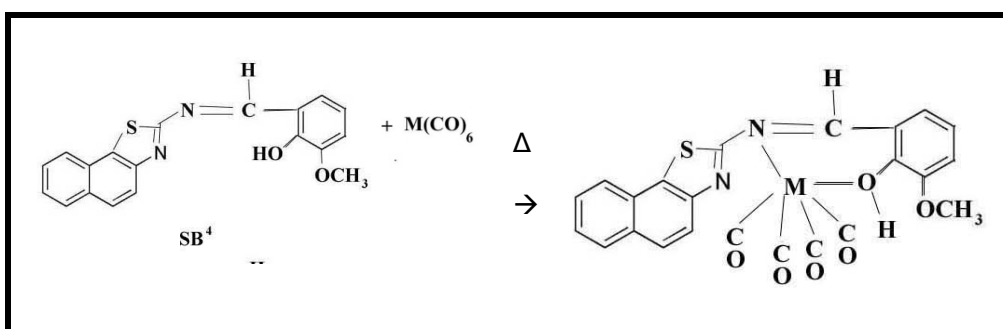
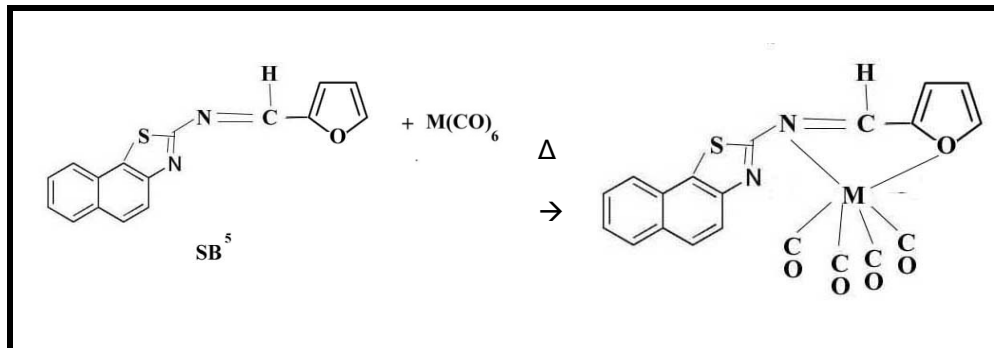


Fig. 3: General synthesis of complexes $M(\text{CO})_5(\text{SB}^2)$.

2.3. General Method for Synthesis of $M(\text{CO})_4(\text{SB}^{3-5})$

A quantity of 0.610g (2mmol) of ligand N-[(E)-phenylmethylidene](naphtho[1,2-d][1,3]thiazol-2-ylimino)methylphenol (SB^3) was dissolved in 30ml of THF and a solution of 0.44 g (2mmol) $\text{Cr}(\text{CO})_6$ in THF was added dropwise to the ligand solution with continuous stirring and the mixture was refluxed overnight. The complexes were precipitated with dry diethyl ether (15ml). The precipitates were filtered, washed with water and cold ethanol, after that it dried at room temperature. This scheme is as shown in Figure 4, 5 and 6.

Fig. 4: General synthesis of complexes $M(CO)_4(SB^3)$.Fig. 5: General synthesis of complexes $M(CO)_4(SB^4)$.Fig. 6: General synthesis of complexes $M(CO)_4(SB^5)$.

3. CONCLUSION

The five new Schiff's base ligands viz. N-[(E)-phenylmethylidene]naphtho[1,2-d][1,3]thiazol-2-amine (SB^1), N-[(E)-(3-methoxyphenyl)methylidene]naphtho[1,2-d][1,3]thiazol-2-amine (SB^2), N-[(E)-phenylmethylidene]naphtho[1,2-d][1,3]thiazol-2-ylidene)methylphenol (SB^3), 2-methoxy-6-[(E)-(naphtho[1,2-d][1,3]thiazol-2-ylidene)methyl]phenol (SB^4) and N-[(E)-furan-2-ylmethylidene]naphtho[1,2-d][1,3]thiazol-2-amine (SB^5) were prepared by coupling of diazotized naphtho[1,2-d]thiazole-2-amine with substituted aromatic

aldehyde. The SB¹⁻² behave as monodentate ligands coordinating via azo nitrogen and SB³⁻⁵ behaves as bidentate ligands coordinating via azo nitrogen and the enolic oxygen.

4. ACKNOWLEDGEMENT

Sincere thanks are due to Head, Dept. of Chemistry, A.I.M.T., Greater Noida, Head, Dept. of Chemical Sciences, JJTU, Rajasthan and Gaurav Pharma Limited, Pitampura, New Delhi for providing research facilities. Authors are also thankful to Dr. Vivek Kumar, Professor, IIT Roorkee, (Saharanpur Campus) for his constant encouragement to carry out such research work. Special thanks are also due to CDRI, Lucknow, Intertek, Mumbai, I.I.T., Roorkee, Research Lab, Delhi University and TIFR, Mumbai for allocation of time for various analyses.

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