

Synthesis, Characterization and Antibacterial Study of Schiff Base of 5-Nitrosalicylaldehyde with 4, 6-Dinitro-2-Aminobenzothiazole and Their Transition Metal Ion Complexes

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ABSTRACT

A compound 4,6-Dinitro-2-aminobenzothiazole was reacted with 5-Nitrosalicylaldehyde under acidic condition. The novel imine product was synthesized by condensation method and their metal Ligand complexes were prepared by reflux the metal ion salt with Schiff base. The synthesized compounds were elucidated by UV-Vis, H1 NMR, and IR spectroscopic techniques. The prepared compound (Ligand) and metal ion complexes were screened against the Gram +Ve and Gram -Ve bacteria.

Key-words: 4, 6-Dinitro-2-aminobenzothiazole, 5-Nitrosalicylaldehyde, Schiff bases, Transition Metal- Ligand complexes, Antibacterial Activity.

I. INTRODUCTION

Synthesis and antimicrobial activity of 2-aminobenzothiazole and its derivatives is reported [1]. Further, their other pharmacological activities such as anticancer, antiulcer, antihistaminic, anti-inflammatory activity and analgesic activities also reported [2-6]. It was envisaged that the compounds containing these moieties in their molecular frame work might show enhanced biological activity. Increasing physiological importance of oxygen donor organic compounds and active role played by coordination certain metal ions to them is of interest towards use in synthesizing and studying structural aspects of metal complexes with some oxygen, sulphur and nitrogen donor ligands. The aromatic benzothiazole nucleus is associated with a variety of antihistamine activity, pharmacological actions such as fungicidal and leishmanicidal activities. In the present study we have reported the synthesis of ligand (E)-2-((4,6-dinitrobenzo[d]thiazol-2-ylimino)methyl)-4-nitrophenol from 4, 6-dinitrobenzothiazole-2-amine and 5-Nitrosalicylaldehyde. The transition metal ions complexes prepared along with ligand. Ligands & metal ion complexes then proceeds for antibacterial screening.

II. MATERIALS AND METHODS

Synthesis of Schiff base (E)-2-((4,6-dinitrobenzo[d]thiazol-2-ylimino) methyl)-4-nitrophenol (Ligand):

A mixture of 4, 6-Dinitro-2-aminobenzothiazole (0.01 mol) & 5-Nitrosalicylaldehyde (0.01 mol) were refluxed for 3-4 hrs under acidic condition. The resultant crimson precipitate was filtered out and recrystallized with ethanol. The schematic route of synthesis of Ligand is shown below in figure 2.1.

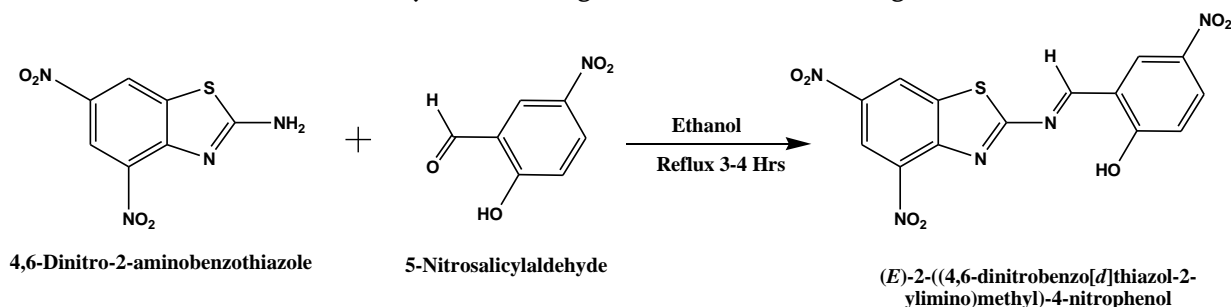


Figure 2.1: Synthesis of Schiff base from 4, 6-Dinitro-2-aminobenzothiazole & 5-Nitrosalicylaldehyde

Preparation of complexes:

All the metal complexes were prepared by refluxing the ethanolic solution of the transition metal ion salts (Stannous acetate, Cadmium acetate, Nickel acetate, Copper acetate, and Zinc acetate) and ligand for one hour. The 2:1 ratio of ligand to metal is maintained throughout all the experiments. The obtained crystalline colored precipitates upon cooling the solutions at room temperature were filtered off, washed with distilled water and recrystallized from ethanol.

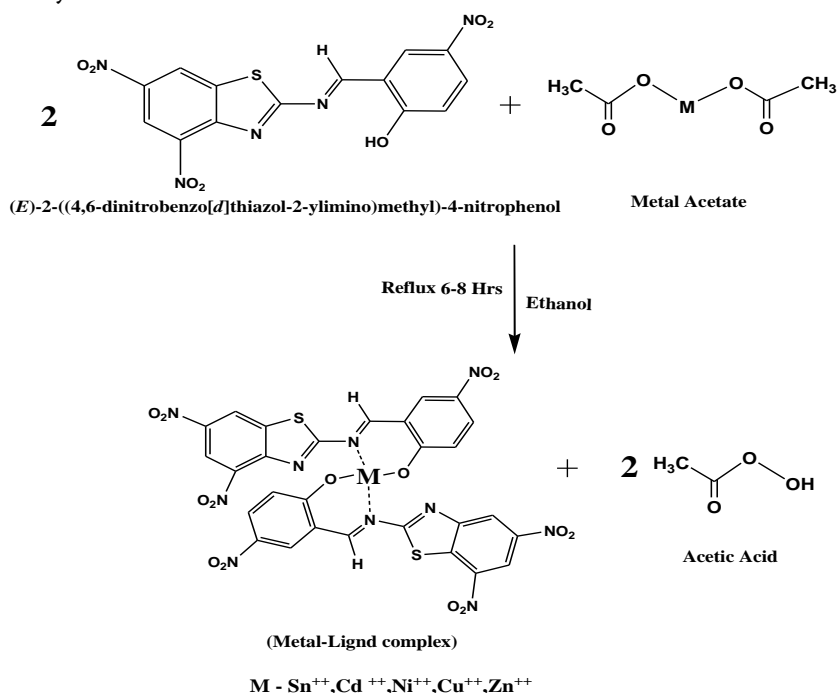


Figure 2.2: Synthesis of Transition metal ion complexes from (E)-2-((4, 6-dinitrobenzo[d]thiazol-2-ylimino)methyl)-4-nitrophenol and Transition metal acetates (II).

III. INSTRUMENTATION

FT-IR spectra in the range, 4000-200 cm^{-1} , were recorded on 8300 Shimadzu Spectrophotometer, UV-visible spectra were measured by using Shimadzu 160 spectrophotometer in the range 200-1000 nm. The magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility on Bruker Magnet B.M.6, The ^1H nuclear magnetic resonance spectra were recorded on a BRUKER ADVANCED II 400 MHz spectrometer in DMSO as a solvent, relative to the internal standard Tetramethylsilane (TMS). Melting points were recorded on a Tanco Laboratory melting point apparatus.

Schiff base (E)-2-((4, 6-dinitrobenzo[d]thiazol-2-ylimino) methyl)-4-nitrophenol (L):

Solid, mp 190°C, UV-Vis (λ_{max}) in ethanol: 310 nm, (IR) ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 3450 (Ar-O-H), 3141.56 (Ar-H), 1523 (C=N), 1244.85 (C-N), 1244.17 (C-S), 1529.12 and 1345.30 (NO_2). $^1\text{H-NMR}$ (δ -ppm): 5.00 (s, 1H, Ar-O-H), 7.10 (d, 1H, Ar-H), 8.22 (d, 1H, adjacent to NO_2), 8.74 (s, Ar-H, adjacent to NO_2), 8.10 (s, 1H, N=C-H), 9.10 (s, 1H, Ar-H), 9.50 (s, 1H, Ar-H, adjacent to NO_2).

Bis-(E)-2-((4,6-dinitrobenzo[d]thiazol-2-ylimino)methyl)-4-nitrophenol Stannous (II) Complex (ML1):

Solid, mp 175°C, UV-Vis (λ_{max}) in ethanol: 283 nm, (IR) ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 3150.63 (Ar-H), 1530 (C=N), 1248.66 (C-N), 1230.15 (C-S), 1530.78 and 1350.12 (NO_2), 720 (Sn-O) $^1\text{H-NMR}$ (δ -ppm): 7.00 (d, 1H, Ar-H), 8.15 (d, 1H, adjacent to NO_2), 8.66 (s, Ar-H, adjacent to NO_2), 8.00 (s, 1H, N=C-H), 9.00 (s, 1H, Ar-H), 9.40 (s, 1H, Ar-H, adjacent to NO_2).

Bis-(E)-2-((4,6-dinitrobenzo[d]thiazol-2-ylimino)methyl)-4-nitrophenol cadmium(II) Complex (ML2):

Solid, mp 190°C, UV-Vis (λ_{max}) in ethanol: 278 nm, (IR) ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 3132.12 (Ar-H), 1540 (C=N), 1242.74 (C-N), 1225.11 (C-S), 1535.55 and 1345.32 (NO_2), 710 (Cd-O) $^1\text{H-NMR}$ (δ -ppm): 7.15 (d, 1H, Ar-H), 8.20 (d, 1H, adjacent to NO_2), 8.46 (s, Ar-H, adjacent to NO_2), 8.15 (s, 1H, N=C-H), 9.20 (s, 1H, Ar-H), 9.55 (s, 1H, Ar-H, adjacent to NO_2).

Bis-(E)-2-((4,6-dinitrobenzo[d]thiazol-2-ylimino)methyl)-4-nitrophenol Nickel (II) Complex (ML3):

Solid, mp 185°C UV-Vis (λ_{max}) in ethanol: 266 nm, (IR) ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 3163.14 (Ar-H), 1560 (C=N), 1260.10 (C-N), 1230.45 (C-S), 1529.53 and 1348.63 (NO_2), 700 (Ni-O) $^1\text{H-NMR}$ (δ -ppm): 7.18 (d, 1H, Ar-H), 8.25 (d, 1H, adjacent to NO_2), 8.60 (s, Ar-H, adjacent to NO_2), 8.10 (s, 1H, N=C-H), 9.10 (s, 1H, Ar-H), 9.45 (s, 1H, Ar-H, adjacent to NO_2).

Bis-(E)-2-((4,6-dinitrobenzo[d]thiazol-2-ylimino)methyl)-4-nitrophenol Copper(II) Complex (ML4):

Solid, mp 195°C UV-Vis (λ_{max}) in ethanol: 288 nm, (IR) ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 3170.26 (Ar-H), 1548 (C=N), 1258.56 (C-N), 1238.89 (C-S), 1524.86 and 1353.27 (NO_2), 730 (Cu-O) $^1\text{H-NMR}$ (δ -ppm): 7.20 (d, 1H, Ar-H), 8.30 (d, 1H, adjacent to NO_2), 8.45 (s, Ar-H, adjacent to NO_2), 8.00 (s, 1H, N=C-H), 9.25 (s, 1H, Ar-H), 9.80 (s, 1H, Ar-H, adjacent to NO_2).

Bis-(E)-2-((4,6-dinitrobenzo[d]thiazol-2-ylimino)methyl)-4-nitrophenol Zinc(II) Complex (ML5):

Solid, mp 182°C UV-Vis (λ_{max}) in ethanol: 290 nm, (IR) ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 3150.41 (Ar-H), 1535 (C=N), 1262.52 (C-N), 1240.90 (C-S), 1530.69 and 1350.78 (NO_2), 715 (Zn-O) $^1\text{H-NMR}$ (δ -ppm): 7.30 (d, 1H, Ar-H), 8.40

(d, 1H, adjacent to NO₂), 8.50 (s, Ar-H, adjacent to NO₂), 8.10 (s, 1H, N=C-H), 9.30 (s, 1H, Ar-H), 9.70 (s, 1H, Ar-H, adjacent to NO₂).

IV. PHARMACOLOGY

Antibacterial activity

The compounds were screened for their antibacterial activity using disc diffusion method. The bacterial organisms used included both gram positive and gram negative strains like Staphylococcus aureus, Escherichia coli, Streptococcus pyogens, Salmonella enteric Serparatyphi, S.entricasertyphi and Micrococcus luteus.

For antibacterial susceptibility testing, the sterile disc of 6 mm diameter (SD067, HiMedia, and Mumbai) was loaded with 20µl of title compound solution (1000 µg/ml) in DMF. The discs were then placed at centre on the Mueller-Hinton agar seeded with bacterial inoculums approximately 10⁶ CFU/ ml, incubated at 37° C for 24 hrs and growth inhibition zone formed around disc was measured. Test was done in triplicate and mean value was considered as inhibition zone. Solvents were used as controls and showed no inhibitions in preliminary studies. All the synthesized complexes exhibited moderate to good activity against the test organisms. The activity of complexes of Nickel and Zinc showed excellent activity against all organisms.

Table: Antibacterial Activity

Compound	Gram negative bacteria			Gram positive bacteria		
	S.typhi	Salmonella typhi	E.Coli	Streptococcus pyrogens	Micrococcus luteus	S.aureus
L	-	-	+	-	++	-
ML 1	+	+	+	-	-	+
ML 2	-	+	+	++	-	-
ML 3	++	++	+	+++	++	+
ML 4	+	+	-	+	+++	+

Ligand (L), Cd complex (ML1), Cu complex (ML2), Ni complex (ML3), Zn complex (ML4); +++ = Zone size 16-22 mm; ++ = Zone size 9-15 mm; + = Zone size 6-8 mm; — = No inhibition.

V. CONCLUSION

The ligand 4, 6-Dinitrobenzothiazole-2-amine was successfully synthesized by condensation method. The ligand was treated to different metal salts to afford the corresponding transition metal ion (II) complexes. Among ligands and metal ligand complexes Nickel and Zinc complexes shows best activity against the all bacteria where as other complexes and ligand shows moderate activity.

VI. REFERENCES

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