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Synthesis of Schiff base of 5-Bromosalicylaldehyde with 4,6-Dinitro-2-Aminobenzothiazole, their transition metal-ligand complexes and antibacterial study

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Abstract

A compound 4, 6-Dintro-2-aminobenzothiazole was reacted with 5-Bromosalicylaldehyde under acidic condition. The novel imine product has been synthesized by condensation method and their metal Ligand complexes have been synthesized by reflux. The synthesized compounds were elucidated by H^1 NMR, and IR spectroscopic methods. The prepared compound (Ligand) and metal ion complexes were screened against the Gram +Ve and Gram –Ve bacteria. Almost all complexes showed good activity against the bacteria.

Keywords: 4,6-Dintro-2-aminobenzothiazole, 5-Bromosalicylaldehyde, Schiff bases, Transition Metal- Ligand complexes, Antibacterial Activity.

Introduction

In recent years there has been considerable interest in the chemistry of transition metal complexes of Schiff bases [1–4], as these ligands offer opportunities for inducing substrate chirality, tuning the metal-centered electronic factor, and enhancing the solubility and stability of either homogeneous or heterogeneous catalysts [5–8]. Also, since the past few years the Schiff base complexes have become increasingly important as biochemical, analytical and antimicrobial reagents [9]. The Cobalt (II), Nickel (II) and Copper(II) complexes of Schiff bases derived from 4-hydroxysalicylaldehyde and amino acids have been shown to have stronger anticancer activity against Ehrlich ascites carcinoma (EAC) [10].

The promising class of bis (salicylaldiminato) metal Schiff base complexes [11] has been shown to exhibit quadratic non-linear optical (NLO) properties, which are currently attracting considerable interest. In addition, there is a continuing interest in investigating the relationship between the redox potentials and other electrochemical parameters and the spectral/ geometrical parameters of Schiff base metal complexes, which could be the result of steric and electronic effects. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configurations and structural liability and are sensitive to molecular environment. Four-coordinated copper (II) complexes usually form a square planar coordination geometry that may be distorted to pseudo-tetrahedral geometry depending on the ligand environment [12].

Methodology

Preparation of Schiff Base (L_1) Derived From 4,6-Dinitro-2-aminobenzothiazole and 5-Bromosalicylaldehyde: Synthesis of (E)-4-bromo-2-((5, 7-dinitrobenzo[d]thiazol-2-ylimino) methyl) phenol. **(Ligand L_1):** Schiff base ligand was prepared by taking 4,6-Dinitro-2-amino benzothiazole (0.01 M) and 5-Bromosalicylaldehyde (0.01 M) in ethanol and poured it in a round bottom flask equipped with a reflux condenser. The above reaction mixture was heated under reflux for 4- 5 hrs. Water formed during the reaction was collected through Deane Stark funnel. The solvent was removed under sunlight irradiation. The resulting pale yellowish solid was recrystallized from ethanol. Color - (Pale yellow), M.P.–154.5 ^{0}C, Yield- 72%

Reaction:

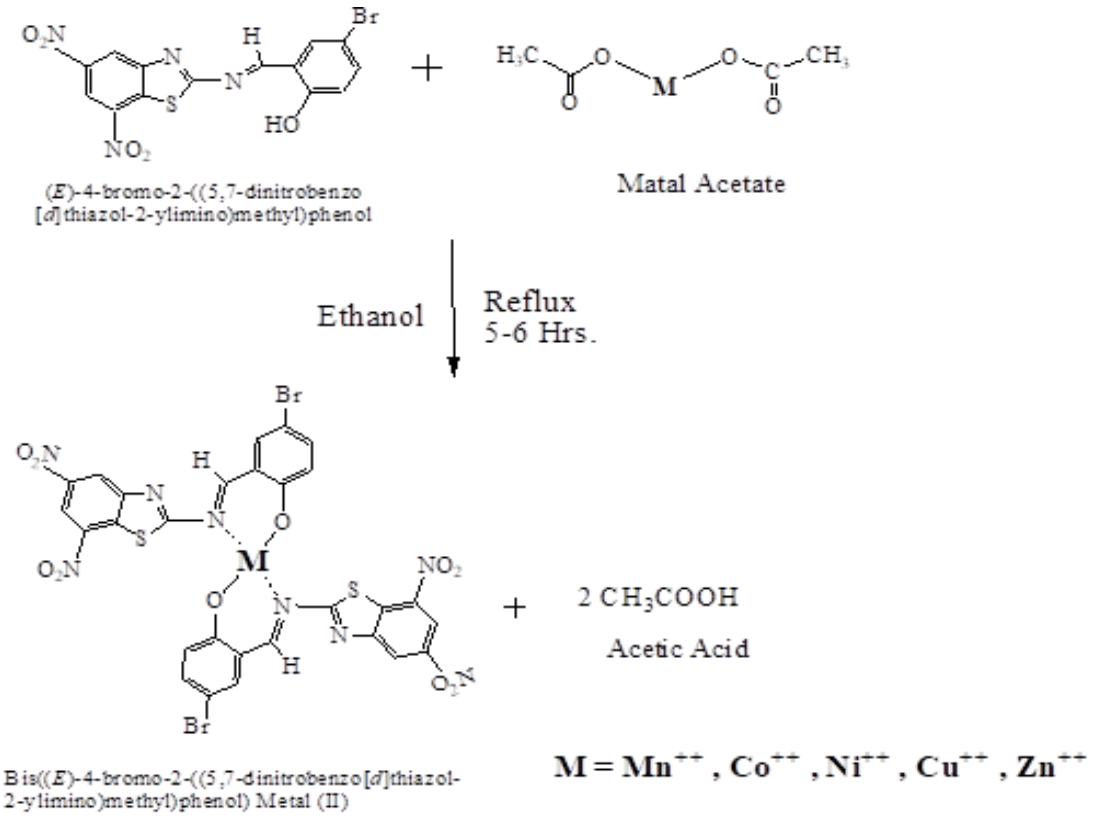
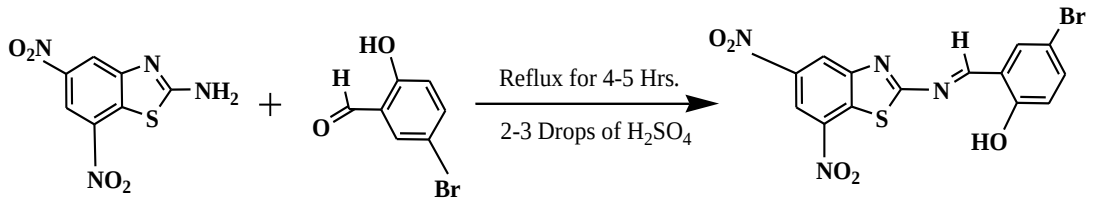


Figure 1: Preparation of Bis ((E)-4-bromo-2-((5, 7-dinitrobenzo[d]thiazol-2- ylimino)methyl)phenol) Metal (II) complex.

Reaction:



4, 6-Dintro-2-aminobenzothiazole **5-Bromosalicylaldehyde**

(*E*)-4-bromo-2-((5,7-dinitrobenzo [*d*]thiazol-2-ylimino)methyl)phenol

Figure 2: Preparation of (E)-4-bromo-2-((5, 7-dinitrobenzo[d]thiazol-2- ylimino)methyl) phenol. (L_1) from Adenine and 5-Bromosalicylaldehyde

Table: Antimicrobial Activity

Compound	Gram positive bacteria	Gram negative bacteria		
	Staphylococcus aureus	Salmonella enterica Serpara Typhi	Escherichia Coli	Klebsiella Pneumonia
(L_2)	**+**	**++**	**-**	**+**
LM-1	**+**	**+**	**+**	**-**
LC-2	**+**	**++**	**-**	**+**
LN-3	**+++**	**+**	**++**	**+++**
LC-4	**+**	**++**	**++**	**+**
LZ-5	**+++**	**++**	**+++**	**++**

+++ = Zone size 16-22 mm; ++ = Zone size 9-15 mm; + = Zone size 6-8 mm;— = No inhibition.

Synthesis of Metal-Ligand Complexes of Transition Metal Ions and Schiff Base (L_1)

Metal Acetate salt (0.01 M) and the (E)-2-((7H-purin-6-ylimino) methyl)-4-bromophenol (ligand) (0.02 M) were dissolved in 20 ml of hot ethanol separately. These two solutions were slowly mixed at very hot condition with vigorous stirring and refluxed it for 5-6 Hrs. Solid products with characteristic color formed by cooling at room temperature then it was filter off by washing with ethanol and dried under sunlight. The yield, color and physical nature were noted.

Results & Discussions

Instrumentation: FTIR spectra in the range, 4000-400 cm^{-1}, were recorded on Agilent Technology Spectrophotometer; Uv-visible spectra were measured by using Shimadzu 160 spectrophotometer in the range 200-800 nm. 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.

(E)-4-bromo-2-((5, 7-dinitrobenzo[d]thiazol-2-ylimino) methyl) phenol (L1): Solid, M.P.-117.5^oC, **UV (λ max) in ethanol:** 270 nm, **(IR) υ max (KBr/cm^{-1}):** 3450.12 (Ar-OH), 3100.13 (Ar-C-H), 1645.63 (Ar-C=C), 1620.14 (Ar-C=N), 1530.87 -1345.25 (-NO_2), 1278.23 (C-C), 1220.46

(C-N), 1075.12 (C-O), 944.36 (Trans disubstituted C=N), 814.47 (Para disubstituted aromatic), 760.14 (Ortho disubstituted aromatic), 678.56 (C-Br) . **^{1}H-NMR (δ-ppm):** 5.20 (s, 1H, Ar-O-H), 6.60 (d, 1 H Ar-H), 7.30 (d, 1 H Ar-H), 7.60 (s, 1H, Ar-H), 8.10 (s, 1H, Ar-N=C-H), 8.90 (s, 1H, Ar-H), 9.40 (s, 1H, Ar-N-H).

Bis((E)-4-bromo-2-((5,7-dinitrobenzo[d]thiazol-2-ylimino)methyl) phenol)Manganese(II)complex. (LM-1): Solid, M.P.-177.5°C, **UV (λ max) in ethanol:** 280 nm, **(IR) υ max (KBr/cm^{-1}):** 3120.25 (Ar-C-H), 1655.30 (Ar-C=C), 1625.22 (Ar-C=N), 1535.60 -1340.36 (-NO_2), 1256.33 (C-C), 1245.77 (C-N), 1062.32 (C-O), 936.78 (Trans disubstituted C=N), 816.92 (Para disubstituted aromatic), 740.42 (Ortho disubstituted aromatic), 698.45 (C-Br) . **^{1}H-NMR (δ-ppm):** 6.80 (d, 1 H Ar-H), 7.50 (d, 1 H Ar-H), 7.40 (s, 1H, Ar-H), 8.00 (s, 1H, Ar-N=C-H), 8.80 (s, 1H, Ar-H), 9.20 (s, 1H, Ar-N-H).

Bis((E)-4-bromo-2-((5,7-dinitrobenzo[d]thiazol-2-ylimino)methyl) phenol)Cobalt(II)complex. (LC-2): Solid, M.P.-175.2°C, **UV (λ max) in ethanol:** 275 nm, **(IR) υ max (KBr/cm^{-1}):** 3090.35 (Ar-C-H), 1660.15 (Ar-C=C), 1635.40 (Ar-C=N), 1530.20 -1325.40 (-NO_2), 1242.30 (C-C), 1235.28 (C-N), 1076.13 (C-O), 925.70 (Trans disubstituted C=N), 815.60 (Para disubstituted aromatic), 738.41 (Ortho disubstituted aromatic), 691.36 (C-Br) . **^{1}H-NMR (δ-ppm):** 6.90 (d, 1 H Ar-H), 7.60 (d, 1 H Ar-H), 7.20 (s, 1H, Ar-H), 8.20 (s, 1H, Ar-N=C-H), 8.70 (s, 1H, Ar-H), 9.40 (s, 1H, Ar-N-H).

Bis((E)-4-bromo-2-((5,7-dinitrobenzo[d]thiazol-2-ylimino)methyl) phenol)Nickel(II)complex. (LN-3): Solid, M.P.-169.5°C, **UV (λ max) in ethanol:** 281 nm, **(IR) υ max (KBr/cm^{-1}):** 3100.13 (Ar-C-H), 1665.23 (Ar-C=C), 1652.00 (Ar-C=N), 1532.14 -1350.00 (-NO_2), 1250.11 (C-C), 1230.42 (C-N), 1077.23 (C-O), 930.26 (Trans disubstituted C=N), 820.00 (Para disubstituted aromatic), 735.77 (Ortho disubstituted aromatic), 685.33 (C-Br) . **^{1}H-NMR (δ-ppm):** 6.80 (d, 1 H Ar-H), 7.50 (d, 1 H Ar-H), 7.10 (s, 1H, Ar-H), 8.10 (s, 1H, Ar-N=C-H), 8.60 (s, 1H, Ar-H), 9.30 (s, 1H, Ar-N-H).

Bis(E)-4-bromo-2-((5,7-dinitrobenzo[d]thiazol-2-ylimino)methyl) phenol)Copper(II)complex.(LC-4): Solid, M.P.-170.3°C, **UV (λ max) in ethanol:** 285 nm, **(IR) υ max (KBr/cm^{-1}):** 3130.13 (Ar-C-H), 1662.41 (Ar-C=C), 1630.10 (Ar-C=N), 1530.45 -1345.77 (-NO_2), 1250.41 (C-C), 1235.68 (C-N), 1069.45 (C-O), 935.00 (Trans disubstituted C=N), 825.10 (Para disubstituted aromatic), 740.55 (Ortho disubstituted aromatic), 680.62 (C-Br) . **^{1}H-NMR (δ-ppm):** 6.70 (d, 1 H Ar-H), 7.60 (d, 1 H Ar-H), 7.40 (s, 1H, Ar-H), 8.15 (s, 1H, Ar-N=C-H), 8.70 (s, 1H, Ar-H), 9.40 (s, 1H, Ar-N-H).

Bis(E)-4-bromo-2-((5,7-dinitrobenzo[d]thiazol-2-ylimino)methyl) phenol)Zinc(II)complex. (LZ-5): Solid, M.P.-173.6°C, **UV (λ max) in ethanol:** 292 nm, **(IR) υ max (KBr/cm^{-1}):** 3120.41 (Ar-C-H), 1666.23 (Ar-C=C), 1625.90 (Ar-C=N), 1535.00 -1347.23 (-NO_2), 1260.55 (C-C), 1230.88 (C-N), 1070.36 (C-O), 939.70 (Trans disubstituted C=N), 830.59 (Para disubstituted aromatic), 745.60 (Ortho disubstituted aromatic), 685.33 (C-Br) . **^{1}H-NMR (δ-ppm):** 6.90 (d, 1 H Ar-H), 7.80 (d, 1 H Ar-H), 7.50 (s, 1H, Ar-H), 8.20 (s, 1H, Ar-N=C-H), 8.80 (s, 1H, Ar-H), 9.30 (s, 1H, Ar-N-H).

Pharmacology

Antibacterial activity:

The titled 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, Salmonella enteric Ser para typhi and Klebsiella Pneumonia.

For antibacterial susceptibility testing of title compounds, the sterile disc of 6 mm diameter (SD067, Hi-Media, 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. [1]

Conclusion

The Schiff Base (L1) was prepared by condensation method. The ligand (L1) was reacted with Mn(II),Co(II),Ni(II),Cu(II),Zn(II) metal acetate salts to synthesized the respective Metal-Ligand complexes. The Analysis data of ^{1}H NMR, IR & U.Vis proved the successful formation of Schiff Base and their complexes. The Antibacterial screening shows that Ni(II) & Zn(II) metal ion complexes gave best results towards all the strains of bacteria where as other complexes showed good activity against the gram positive and gram negative bacteria.

Conflicts of interest: The authors stated that no conflicts of interest.

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