

Synthesis, Characterization, Magnetic Susceptibility and Antibacterial Screening of Novel Transition Metal Ion Complexes of (E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one

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ABSTRACT

The novel transition metal ion complexes were synthesized by refluxing the ethanolic solutions of Schiff Base (E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one and Metal Acetates in 2:1 ratios respectively. The Structural confirmation and Characterization of synthesized complexes of Mn (II), Co (II), Ni (II), Cu (II) & Zn (II) were elucidated by using ¹H NMR, FT-IR, UV-Vis, & X-Ray spectroscopic techniques. The synthesized compounds were also been screened against gram +ve and gram -ve bacteria. The novel compounds were further carried out for the study of magnetic susceptibility.

Keywords: Schiff Base; transition Metal ion complexes; Antibacterial Screening; Magnetic Susceptibility.

I. INTRODUCTION

Schiff-base macroligands synthesized from reaction of dialdehydes and amino compounds [1-3] form stable complexes, perhaps selective to specific metallic ions with applications in electrochemistry, bioinorganic, antimicrobial activity, fluorescence properties, catalysis, metallic deactivators, separation processes, and environmental chemistry among others [3]. Preparation of new ligands is an important step in development of metal complexes, which exhibit unique properties and reactivity. For example, in asymmetric catalyst systems, small changes in donating ability of the ligand or the size of its substituents can have a dramatic effect on catalyst efficiency and enantioselectivities [3-4]. The nitro group is a strong electron-withdrawing group and due to its steric effects it has played an important role in affecting the reactivity and enantioselectivities in asymmetric cyclopropanation and allylic alkylation reactions [4]. In continuation of our research on preparation of Schiff bases [4-5] and their complexes [6-9], we decided to prepare new Schiff bases containing electron withdrawing and donating substituents. This article describes the synthesis and spectroscopic characterization of several Schiff bases and their complexes with transition metal ions. The corresponding materials were characterized by spectroscopic (IR, UV-Vis, ¹H-NMR) and physical (melting point, Magnetic Susceptibility) data.

II. MATERIALS AND METHODS

Preparation of Schiff Base (L₄) Derived From Guanine and Salicylaldehyde:

Synthesis of (E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one (GS-1) (L₄)

The Schiff base (ligand GS-1) was synthesized by taking Guanine (0.01 M) Salicylaldehyde (0.01 M) in ethanolic medium followed by the addition of 2-3 drops of conc. sulphuric acid in a catalytic amount and poured it in a round bottom flask connected with a reflux condenser. The above given reaction mixture was reflux for 7-8 hrs. Water formed during the reaction was collected through Deane Stark funnel. The solvent was removed under sunlight irradiation. The chemical reaction mentioned below in figure 2.1. The resulting pale yellowish solid was recrystallized from ethanol. Color - (Pale yellow), M.P. – 132.8 °C, Yield- 66%.

Reaction:

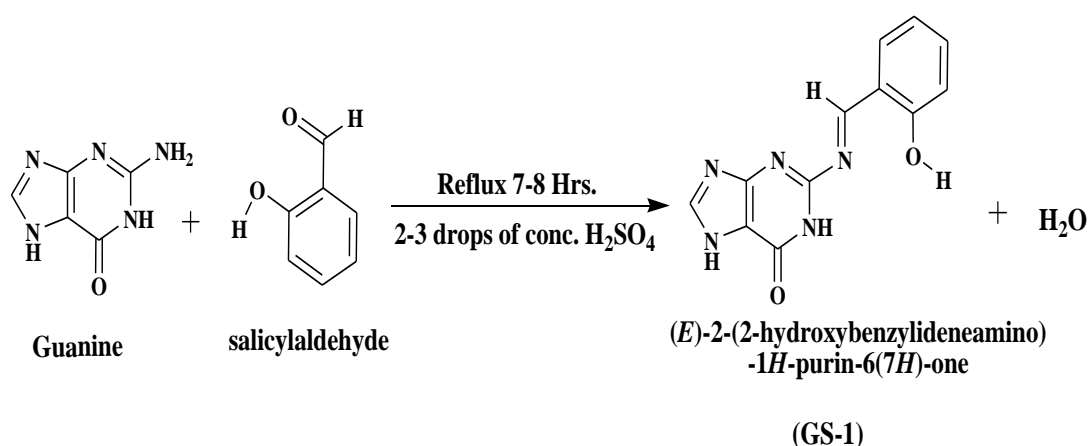


Figure 2.1: Preparation of (E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one (GS-1) from Guanine and Salicylaldehyde.

Synthesis of Transition Metal-Ligand Complexes of Schiff Base (L₄) Derived From Guanine and Salicylaldehyde.

The Metal-Ligand mole ratio was taken in 1:2 proportions. Metal Acetate salt (0.01M) and (E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one (GS-1) (0.02 M) was dissolved in 50 ml ethanolic solutions with vigorous stirring and warm it until the solution will not become clear. Then the solution was poured in round bottom flask equipped with refluxed condenser and refluxed it for 4-5 Hrs. The Solid complex with characteristic colored was formed within few minute after cooling at room temperature. The resultants filtered off by using whatman-41 filter paper and wash it with ethanol. The product was dried by irradiation with sunlight. The synthetic route of formation of complex is mentioned below in Figure.

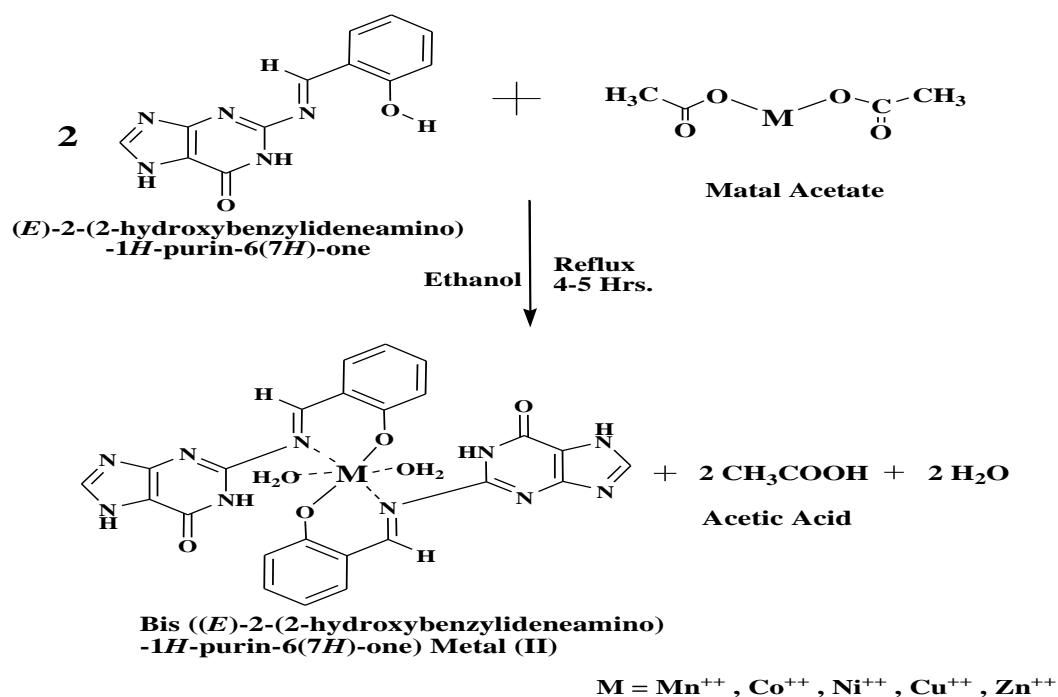
Reaction:

Figure 2.2: Preparation of Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Metal (II) complex.

III. RESULTS AND DISCUSSION

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 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.

(E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one (GS-1):

Solid, M.P.-132.8 °C, UV (λ max) in ethanol: 295 nm, (IR) ν max (KBr/cm^{-1}): 3460.33 (Ar-OH), 3314.50 (Ar-N-H), 3115.95 (Ar-C-H), 1668.34 (Amide), 1668.34 (Ar-C=C), 1547.22 (Ar-C=N), 1414.30 (C-C), 1200.24 (C-N), 1114.59 (C-O), 918.51 (Trans disubstituted C=N), 763.24 (Ortho disubstituted aromatic). 1H -NMR (δ -ppm): 4.90 (s, 1H, Ar-O-H), 6.80 - 7.50 (m, 4H Ar-H), 7.90 (s, 1H -N=C-H), 8.20 (d, 1H, Ar-N=C-H), 8.80 (s, 1H, Ar-N-H), 10.30 (d, 1H, Ar-N-H).

Bis((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one)Manganese(II) complex. (GSM-1):

Solid, M.P.-145.7 °C, UV (λ max) in ethanol: 288 nm, (IR) ν max (KBr/cm^{-1}): 3316.64 (Ar-N-H), 3107.62 (Ar-C-H), 1668.06 (Amide), 1622.12 (Ar-C=C), 1547.97 (Ar-C=N), 1415.70 (C-C), 1202.48 (C-N), 1115.10 (C-O),

921.58 (Trans disubstituted C=N), 774.22 (Ortho disubstituted aromatic), 686.23 (Mn-O). ¹H-NMR (δ -ppm): 6.70 - 7.60 (m, 4H Ar-H), 8.10 (s, 1H -N=C-H), 8.40 (d, 1H, Ar-N=C-H), 9.10 (s, 1H, Ar-N-H), 10.45 (d, 1H, Ar-N-H).

Bis((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Cobalt (II) complex. (GSC-2):

Solid, M.P.- 155.6 °C, UV (λ max) in ethanol: 290 nm, (IR) ν max (KBr/cm⁻¹): 3316.82 (Ar-N-H), 3109.50 (Ar-C-H), 1664.97 (Amide), 1617.41 (Ar-C=C), 1557.08 (Ar-C=N), 1415.54 (C-C), 1254.43 (C-N), 1114.98 (C-O), 947.40 (Trans disubstituted C=N), 772.25 (Ortho disubstituted aromatic), 688.21 (Co-O). ¹H-NMR (δ -ppm): 6.30 - 7.20 (m, 4H Ar-H), 7.70 (s, 1H -N=C-H), 7.90 (d, 1H, Ar-N=C-H), 8.60 (s, 1H, Ar-N-H), 10.50 (d, 1H, Ar-N-H).

Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Nickel (II) complex. (GSN-3):

Solid, M.P.- 160.2 °C, UV (λ max) in ethanol: 295 nm, (IR) ν max (KBr/cm⁻¹): 3314.94 (Ar-N-H), 3111.11 (Ar-C-H), 1668.44 (Amide), 1615.26 (Ar-C=C), 1556.31 (Ar-C=N), 1416.80 (C-C), 1250.47 (C-N), 1115.98 (C-O), 947.31 (Trans disubstituted C=N), 774.52 (Ortho disubstituted aromatic), 685.22 (Ni-O). ¹H-NMR (δ -ppm): 6.50 - 7.50 (m, 4H Ar-H), 8.00 (s, 1H -N=C-H), 8.60 (d, 1H, Ar-N=C-H), 9.20 (s, 1H, Ar-N-H), 10.40 (d, 1H, Ar-N-H).

Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Copper (II) complex. (GSC-4):

Solid, M.P.- 168.6 °C, UV (λ max) in ethanol: 285 nm, (IR) ν max (KBr/cm⁻¹): 3316.86 (Ar-N-H), 3111.64 (Ar-C-H), 1668.42 (Amide), 1615.26 (Ar-C=C), 1557.38 (Ar-C=N), 1415.73 (C-C), 1256.48 (C-N), 1116.45 (C-O), 947.94 (Trans disubstituted C=N), 775.01 (Ortho disubstituted aromatic), 697.13 (Cu-O). ¹H-NMR (δ -ppm): 6.70 - 7.70 (m, 4H Ar-H), 8.00 (s, 1H -N=C-H), 8.55 (d, 1H, Ar-N=C-H), 9.30 (s, 1H, Ar-N-H), 10.70 (d, 1H, Ar-N-H).

Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Zinc (II) complex. (GSZ-5):

Solid, M.P.- 157.8 °C, UV (λ max) in ethanol: 290 nm, (IR) ν max (KBr/cm⁻¹): 3315.37 (Ar-N-H), 3110.43 (Ar-C-H), 1666.40 (Amide), 1619.57 (Ar-C=C), 1556.48 (Ar-C=N), 1410.05 (C-C), 1252.25 (C-N), 1114.85 (C-O), 946.97 (Trans disubstituted C=N), 751.96 (Ortho disubstituted aromatic), 689.84 (Zn-O). ¹H-NMR (δ -ppm): 6.80 - 7.60 (m, 4H Ar-H), 7.90 (s, 1H -N=C-H), 8.20 (d, 1H, Ar-N=C-H), 8.90 (s, 1H, Ar-N-H), 10.30 (d, 1H, Ar-N-H).

Table: Magnetic Moment, Conductivity measurements in DMF solvent

Symbol	Name	Conductivity ohm ⁻¹ cm ² mol ⁻¹	Magnetic moment (B.M)	Suggested structure
(GS-1) (L4)	(E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one.	-	-	-
(GSM-1)	Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one)Manganese(II) Complex.	17	4.30	Tetrahedral
(GSC-2)	Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-	14	3.46	Tetrahedral

	6(7H)-one) Cobalt(II)complex.			
(GSN-3)	Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Nickel(II)complex.	18	4.88	Tetrahedral
(GSC-4)	Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Copper(II)complex	28	1.90	Square planner
(GSZ-5)	Bis ((E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one) Zinc(II)complex.	16	3.85	Tetrahedral

IV. 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, Klebsiella Pneumonia and Pseudomons aeruginosa.

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.

Table: Antimicrobial Activity

Compound	Gram positive bacteria	Gram negative bacteria			
		Salmonella enterica Serpara Typhi	Escherichia Coli	Klebsiella Pneumonia	Pseudomons aeruginosa
(GS-1) (L4)	-	+	++	-	+
(GSM-1)	++	+	-	++	-
(GSC-2)	+	-	++	+	-
(GSN-3)	++	++	++	++	+
(GSC-4)	+	+++	+	++	+++
(GSZ-5)	++	++	++	+++	+

+++ = Zone size 16-22 mm; ++ = Zone size 9-15 mm; + = Zone size 6-8 mm;

— = No inhibition.

Infra-red spectroscopy:

The above given data of FT-IR spectrum of the ligand ABS-3, shows the characteristic bands at 3630.05 cm^{-1} , 3290.30 cm^{-1} & 1590.63 cm^{-1} which are assigned to Ar-O-H, Ar-N-H & C=N stretching respectively. These bands reveal the formation of Schiff Base. The formation of complexes of Schiff Base with Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) acetates was confirmed by the disappearance of -O-H band in the region of $3200\text{--}3600\text{ cm}^{-1}$ and occurrence of Metal-Oxide bands at 717.45 cm^{-1} , 722.86 cm^{-1} , 725.78 cm^{-1} , 732.59 cm^{-1} and 729.58 cm^{-1} for Mn-O, Co-O, Ni-O, Cu-O, Zn-O stretching respectively. In the free ligand, the band at 1590.63 cm^{-1} was assigned to the stretching of C=N bond. On complexation this band was shifted to a lower frequency region. This shift is due to the metal-ligand electron sharing effect. The IR data of the compounds are shown in the table lists the stretching frequency (ν) for some of the characteristics groups exhibited by the ligand and complexes.

Ultraviolet-visible spectroscopy:

The ultraviolet visible electronic spectrums of the compounds were recorded in DMSO solvent. The bands at wavelengths (290, 288, 285, 280, 295 and 282 nm) these transitions are attributed to $\pi \rightarrow \pi^*$ electronic transition [11]. The electronic spectra of complexes showed, as expected, different absorptions from that of the free ligand. In the complexes these bands were shifted to different wavelength than the corresponding bands in the ligand as shown above, which appears in the wavelength range between 280-300 nm. The ligand field electronic transitions between the metal d orbital's appear in Ni (II) and Cu (II) bands located in the visible region at 460 nm for Ni (L)₂ assigned to the transition $3A_2 \rightarrow 3T_1$ (p) and 610 nm for Cu (L)₂ assigned to the transitions $2B_{1g} \rightarrow 2A_{1g}$. The other complexes were diamagnetic as expected for d10 ions so that no (d-d) transition can be expected in the visible region.

NMR spectroscopy:

The data of proton NMR of the ligand (ABS-3) and its complexes displayed good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the complexes. The observed changes are the evidences of complexation had happened because the chemical shift of a compound is heavily depended on its electronic environment. The ¹H NMR spectrum of the complexes confirmed the disappearance of O-H signal at 4.90 ppm in the free ligand. The δ 6.80 - δ 7.50 ppm resonance signal protons of the aromatic ring shifted to the higher field upon complexation. It is most likely that shift is due to the decrease of electron density at ¹H protons when oxygen is bonded to metal ion.

Magnetic susceptibility and conductivity measurements:

The experimental magnetic moments for metal complexes are listed in Table. Magnetic measurements are widely used in studying transition metal complexes. The magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbital in the outer shell of these elements. This magnetic measurement gives an idea about the electronic state of the metal ion in the complexes. The magnetic moment for Mn(II), Co(II), Ni(II) & Zn(II) in any complex is approximately 3.46 to 4.88 B.M., this value refers to a high spin tetrahedral structure, while the value of Cu (II) is approximately 1.90 led to suggest the square planar

structure which can become in a good agreement with the data of electronic transitions. Other complexes have no magnetic moment because it's diamagnetic. Molar conductivity measurement in DMF solvent at 25°C showed that the complexes were non-electrolyte.

V. CONCLUSION

The ligand **(E)-2-(2-hydroxybenzylideneamino)-1H-purin-6(7H)-one** (GS-1) was successfully synthesized by condensation method. The ligand (GS-1) was treated with Mn(II),Co(II),Ni(II),Cu(II),Zn(II) metal acetate salts to afford the corresponding complexes. The Characterization data of ¹H NMR, IR & UV-Vis reveals the successful formation of ligand and their complexes. The Magnetic susceptibility data was attributed to the square planar geometry for Cu (II) complex and tetrahedral geometry of other complexes. The Antibacterial Study reveals that Ni(II), Cu(II) & Zn(II) metal ion complex showed best inhibition activity towards all the strains of bacteria where as other complexes showed good activity against the gram positive and gram negative bacteria.

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