



SYNTHESIS, CHARACTERIZATION OF BIOLOGICALLY ACTIVE N, N' - BIS(4-BENZENEAZOSALICYLIDENE)-O-PHENYLENEDIIMINATOCOBALT(II) COMPLEX

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ABSTRACT

A Schiff base was prepared as reported, its cobalt(II) complex was synthesized by refluxing ethanolic mixture of the prepared schiff base and cobalt(II) chloride. The cobalt(II) Schiff base complex synthesized is brown, of percentage yield 65% and has decomposition temperature of 258°C. The Schiff base and N, N' - bis(4-benzeneazo salicylidene)-o-phenylenediiminatocobalt(II) complex were characterized by solubility, melting point/decomposition temperature, molar conductivity, elemental analysis, IR spectra, bioassay and potentiometry. The Schiff base and its cobalt(II) complex are slightly soluble in methanol and ethanol but are readily soluble in DMSO and DMF. The molar conductance measurement of the complex determined is $4.6 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, revealing its non electrolytic nature. The infrared spectral data of the ligand showed a band at 1590cm^{-1} , which is attributed to $\nu(\text{C}=\text{N})$ stretching frequencies. The same band is observed in the synthesized cobalt(II) Schiff base complex, suggesting that the Schiff base is coordinated to the cobalt(II) Schiff base complex. The bands in the regions 585cm^{-1} and 511cm^{-1} in the complex are assigned to $\nu(\text{Co}-\text{N})$ and $\nu(\text{Co}-\text{O})$ stretching vibrations confirming the coordination of the Schiff base to the manganese(II) ion. The elemental analysis result of the complex is consistent with 1:1 metal to Schiff base ratio. The dissociation constant of the determined is 11.67, indicating a weak acid. The average number of Schiff base coordinated to cobalt ion is one, the stability constant and Gibbs free energy of the complex compound are 3.1×10^{11} and $-64.15 \text{ KJmol}^{-1}$, respectively, suggesting that the complex is very stable. The antifungal and antibacterial tests carried out on the Schiff base and its iron(II) complex showed good activity.

Keywords: 4-(Benzeneazo) Salicylaldehyde, Potentiometry, complex compound, schiff base, molar conductance and solubility.

INTRODUCTION

A Schiff base is a ligand, it contains of carbon – nitrogen double bond ($\text{C}=\text{N}$), in which the nitrogen atom is connected to an aryl or alkyl group but not hydrogen. The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketoimines. Schiff base transition metal complexes have been known, for example, Ettling (1840) isolated a dark green crystalline product from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia (Holm *et al.*, 1966). Ben Saber *et al.*, (2005), reported the synthesis of a Schiff base derived from salicylaldehyde, and histidine and its complex compounds with divalent transition metal ions. The complexes were investigated by elemental analysis and were found to be of 1:1 metal to ligand ratio. In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff base ligands due to their importance as catalyst in many reactions (Singh *et al.*, 2006).

Chohan *et al.* (2006) reported the synthesis, antibacterial and antifungal activities of schiff bases derived from acetylacetone and amino acids and their cobalt(II), copper(II), nickel(II), and zinc(II) complexes. The schiff bases and their complexes are intensively colored, air and moisture stable amorphous solids. They decompose without melting, are insoluble in common organic solvents and only soluble in water, DMF, and DMSO. The molar conductance values of the soluble complexes in DMF (10^{-3}M solution at 25°C) are

very low and fall in the range, 26-35 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating that they are all non-electrolytes. The complexes having molar ratios of metal: ligand as 1:1 showed higher values ($122\text{-}128 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) an indication that they are electrolytes. The elemental analysis data agreed well with the proposed formulae for the ligands and also confirmed the $[\text{M}(\text{L})_2(\text{OH})_2]$ and $[\text{M}(\text{L})(\text{OH})_4]\text{Cl}$ compositions of the metal(II) chelates. The synthesized amino acid-derived compounds showed antibacterial and antifungal properties. In comparison, the cobalt(II), copper(II), Nickel(II) and zinc(II) metal complexes of these compounds showed more activity against one or more bacterial and fungal stains.

Gavali and Henkarep, 2007 reported the preparation of Co(II), Ni(II) Cu(II), Zn(II) and Cd(II) complexes of tridentate ligand derived from 5-(2'-thiazolylazo) salicylaldehyde and p-chloroaniline and characterization by various physico-chemical methods. The ligand was prepared by refluxing equimolar concentration of 5-(2'-thiazolylazo) salicylaldehyde (0.2334g, 1mole) in 50cm^3 ethanol with p-chloroaniline (0.1412g, 1mole) in 15cm^3 ethanol for 4 hours. The result of the characterization revealed that the complexes were brightly coloured and thermally stable at least up to 200°C . They are soluble in water and common organic solvent but show maximum solubility in DMF and DMSO at room temperature.

They show very low molar conductance of about $20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicates their non-electrolytic nature. The analytical data of the complexes indicated 1:1 metal : Schiff base stoichiometry. The IR spectra of the ligand shows a medium broad band centered at 3000 cm^{-1} due to intra-molecular hydrogen bond $\nu(\text{O-H})$. In the spectra of metal complexes the broad band disappears indicating deprotonation and involvement of the phenolic oxygen in bonding with metal ions. The strong band at 1625 cm^{-1} is assigned to the $\nu(\text{C=N})$ stretching vibration observed in the ligand and this band undergoes a negative shift (-10 cm^{-1}) in the complexes indicating the participation of the azomethine nitrogen in coordination. The spectral region at $1600\text{-}1400 \text{ cm}^{-1}$ is complicated because of the stretching modes of $\nu(\text{C=C})$ and $\nu(\text{N-N})$ which are superimposed in the same region. The bands observed in region 470 cm^{-1} and 320 cm^{-1} can be attributed to M-O and M-N atom. The ligand and its metal complexes were screened against *Escherichia coli*, *Bacillus subtilis*, *Klebsiella pneumonia*, *Pseudomonas aerogens*, *salmonella paratyphi B*, *staphylococcus aurens* and *proteus vulgaris* by disc diffusion technique. The test solutions were prepared in DMF and DMSO at different concentrations. Nutrient agar was used as culture medium. The zones of inhibition formed were measured in millimeter. Cu(II) complex was found to be highly active against *staphylococcus aureus* and Cd(II) complex exhibited moderate activity against *Bacillus subtilis*. The Co(II) and Cd(II) complexes were found to be highly active inhibitor for *Rhizopus* fungus. This paper reports synthesis, characterization of biologically active N, N' - bis(4-benzeneazo salicylidene)-o-phenylenediiminatocobalt(II) complex

MATERIALS AND METHODS

All the glass-wares used were washed with detergent, rinsed with distilled water and dried in an oven. All the reagents and solvents used were of analytical grade (AnalaR or BDH) and were used without further purification. Molar conductance measurements were carried out using Cyber Scan 500 model. Electric metler balance model AB 54 was used for weighing. Infrared spectral analysis data were recorded using Fourier Transform IR Genesis series model Nujol, within $400 - 4000 \text{ cm}^{-1}$. The pH measurements were carried out using Jenway pH meter model 3320. The melting/decomposition temperatures were carried out using Gallenkamp melting point apparatus.

Preparation of the Schiff base ligand

A 0.01 mol (1.814 g) of o-phenylenediamine was added slowly into a solution of 0.02 mol (4.5245 g) 4-(Benzeneazo) salicylaldehyde (an intermediate) in 20 cm^3 ethanol. After refluxing the reaction mixture for 2 hours, the precipitate that formed was separated, washed several times using ethanol, followed by recrystallisation in ethanol and drying at 50°C in an oven overnight (Jianning *et al.*, 2005).

Preparation of cobalt(II) Schiff base complex

The complex was prepared by refluxing a mixture of aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol ; 0.238 g) and hot ethanolic solution of the prepared Schiff

base (0.524 g) for 2 hours. The reaction mixture was allowed to cool in an ice bath and the greenish yellow precipitate obtained was separated, washed with ethanol and diethyl ether, followed by drying at 50°C overnight (Jianning *et al.*, 2005).

Determination of dissociation constant (pKa) of the Schiff base

The dissociation constant of the Schiff base ligand was determined by introducing a standardized pH meter electrode into a 400 cm^3 beaker containing magnetic stirrer bar, 90 cm^3 water, 100 cm^3 of 0.2 mol dm^{-3} KNO_3 and 10 cm^3 of 0.4 mol dm^{-3} Schiff base ligand solution. To this mixture, 10 cm^3 of standardized 0.5 mol dm^{-3} aqueous solution of NaOH was added gradually and the corresponding pH value recorded after each addition (Gregory *et al.*, 1978).

Determination of number of coordinated Schiff base in the complex

To a 400 cm^3 beaker containing 100 cm^3 of 0.2 mol dm^{-3} KNO_3 , 10 cm^3 of 0.1 mol dm^{-3} HNO_3 , 90 cm^3 of water and 1 mmol of cobalt(II) chloride were added. Now 10 cm^3 of 0.4 mol dm^{-3} sodium salt of the Schiff base ligand which was prepared by neutralizing a weighed solid ligand with calculated amount of standardized 0.5 mol dm^{-3} NaOH solution. After each 0.2 cm^3 aliquote addition the corresponding pH was recorded. From the knowledge of the pH recorded, the average number of coordinated Schiff base permanganese(II) ion was calculated as reported by Robert and Angelici (1977).

RESULTS AND DISCUSSION

The ligand, N, N' - bis(4-benzeneazo salicylidene)-o-phenylenediime was prepared and recrystallized as reported by Jianning *et al.* (2006). It has an orange colour, a melting point of 193°C and percentage yield of 70%. The reaction of prepared ligand and cobalt(II) chloride gave N, N' - bis(4-benzeneazo salicylidene)-o-phenylenediiminatocobalt(II) complex. The complex is brown in colour, has decomposition temperature of 257°C and percentage yield of 65% (Table 1). The solubility tests of the ligand and its cobalt(II) complex in water and common organic solvents carried out showed that both the ligand and the cobalt(II) complex are insoluble in water, slightly soluble in most organic solvents but readily soluble in dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF). The result can be seen in Table 2.

The molar conductance measurements (Table 3) on the complex determined in 10^{-3} M DMSO solution is $4.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, which is low, suggesting that the complex is non electrolyte (Geary, 1971). The infrared spectral band of the Schiff base ligand at 1590 cm^{-1} is assigned to $\nu(\text{C=N})$ stretching vibration. The same spectral band was observed in the complex but in the lower frequency, 1530 cm^{-1} , suggests the coordination of the Schiff base to cobalt(II) ion.

The bands at 585 cm^{-1} and 511 cm^{-1} are attributable to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ stretching vibrations, respectively, confirming the coordination of the ligand to the cobalt ion (Ahmed and Akhtar, 1983; Abdulsamath *et al.*, 1992).

The result is presented in Table 4. The antibacterial test carried out on the ligand showed only minimal activity on *E. coli spp* with a diameter of inhibition zone of 13mm per 3000µg concentration. The cobalt(II) complex on the other hand showed higher activity against the bacterial isolates particularly at 3000µg concentration with a diameter of inhibition zone of 25mm (Table 5). The results of the antifungal activities of the ligand and its cobalt(II) complex also showed that the metal complex exhibits higher activity against the fungal isolate than the ligand. The result also showed that the activity is higher in 3000µg concentration and the complex is more active against

C. Albican spp as indicated by larger diameter of inhibition (Table 6). The dissociation constant of the ligand determined is 11.67, which revealed that it is highly basic (Table 7). The ratio of cobalt(II) ion – ligand determined potentiometrically is 1:1 (Table 8). The stability constant and the Gibb's energy of cobalt(II) complex are 3.16×10^{11} and $-64.15 \text{ KJmol}^{-1}$ (Table 9).

On the basis of the spectral data, other analytical results and literature, the following molecular structure of the complex is proposed.

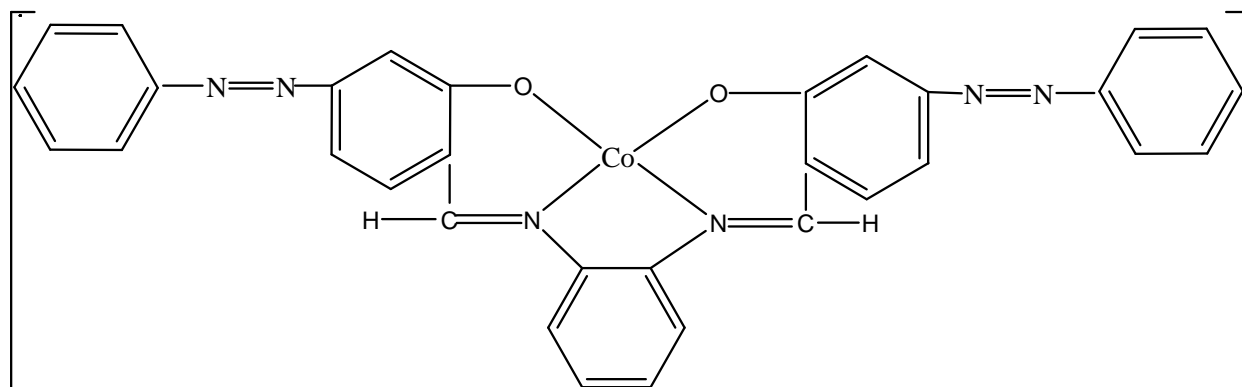


Figure 1: Proposed molecular structure of the cobalt(II) Schiff base complex.

Table 1: Physical properties of the Schiff base ligand and its cobalt(II) complex

Compound	Colour	Melting point(°C)	Decomp. temp(°C)	Percentage(%)
Schiff base	Orange yellow	193	-	70
[CoL]	Brown	-	257	65

Table 2: Solubility of the Schiff base and its cobalt(II) complex

Compound	H ₂ O	Ethanol	Benzene	Acetone	Methanol	DMSO	DMF
Schiff base	IS	S	SS	SS	S	S	S
[CoL]	IS	SS	IS	IS	SS	S	S

Key: S – Soluble, SS – Slightly Soluble, IS – Insoluble

Table 3: Conductivity measurement of the cobalt(II) Schiff base complex

Schiff base complex	Concentration (moldm ⁻³)	Electrical Conductivity (Ohm ⁻¹ cm ⁻¹ x 10 ⁻⁶)	Molar Conductivity (Ohm ⁻¹ cm ² mol ⁻¹)
[CoL]	1x10 ⁻³	4.6	4.6

Table 4: Infrared spectral data of the Schiff base and its cobalt(II) complex

Compound	$\nu(\text{C} = \text{N}) \text{ cm}^{-1}$	$\nu(\text{phenolic C} - \text{O}) \text{ cm}^{-1}$	$\nu(\text{M} - \text{N}) \text{ cm}^{-1}$	$\nu(\text{M} - \text{O}) \text{ cm}^{-1}$
Schiff base	1590	1340	-	-
[CoL]	1530	1336	585	511

Table 5: Antibacterial activity of Schiff base and its cobalt(II) complex

Compound	Clinical isolate		Diameter /Concentration							
	<i>E. coli spp</i>	<i>Staph spp</i>	3000µg	2000µg	1000µg	Control	3000µg	2000µg	1000µg	Control
Schiff base	√	√	11mm	00	00	00	00	00	00	00
[CoL]	√	√	25mm	16mm	18mm	00	00	00	00	00

Table 6: Antifungal activity of Schiff base and its cobalt(II) complex

Compound	Clinical isolate		Diameter /Concentration							
	<i>A niger</i>	<i>C. albican</i>	3000µg	2000µg	1000µg	Control	3000µg	2000µg	1000µg	Control
Schiff base	√	√	13mm	15mm	00	00	00	10mm	00	00
[CoL]	√	√	15mm	22mm	14mm	19mm	00	00	00	00

Table 7: Dissociation constant(pKa) of the tetradentate Schiff base

S/No	Vol. of NaOH(cm ³)	pH	[H ⁺]	[OH ⁻]	[Na ⁺]	A _{total}	pKa	
1	200.5	0.5	9.56	1.80E-10	8.80E-05	1.20E-03	0.01995	10.9645
2	201.0	1.0	9.91	8.20E-11	2.00E-04	2.39E-03	0.0199	10.9919
3	201.5	1.5	10.22	4.00E-11	4.00E-04	3.57E-03	0.019851	11.1152
4	202.0	2.0	10.51	2.10E-11	7.80E-04	4.75E-03	0.019802	11.2851
5	202.5	2.5	10.74	1.20E-11	1.33E-03	5.93E-03	0.019753	11.4323
6	203.0	3.0	10.93	7.90E-12	2.05E-03	7.09E-03	0.019704	11.5684
7	203.5	3.5	11.07	5.70E-12	2.84E-03	8.26E-03	0.019656	11.6639
8	204.0	4.0	11.18	4.40E-12	3.65E-03	9.41E-03	0.019608	11.7356
9	204.5	4.5	11.27	3.60E-12	4.49E-03	1.06E-02	0.01956	11.7916
10	205.0	5.0	11.34	3.10E-12	5.28E-03	1.17E-02	0.019512	11.8233
11	205.5	5.5	11.41	2.60E-12	6.20E-03	1.28E-02	0.019465	11.8702
12	206.0	6.0	11.46	2.30E-12	6.96E-03	1.40E-02	0.019417	11.8816
13	206.5	6.5	11.51	2.10E-12	7.81E-03	1.51E-02	0.01937	11.9031
14	207.0	7.0	11.55	1.90E-12	8.56E-03	1.62E-02	0.019324	11.9064
15	207.5	7.5	11.58	1.80E-12	9.18E-03	1.73E-02	0.019277	11.8877
16	208.0	8.0	11.63	1.60E-12	1.03E-02	1.85E-02	0.019231	11.9365
17	208.5	8.5	11.66	1.50E-12	1.10E-02	1.96E-02	0.019185	11.9306
18	209.0	9.0	11.69	1.40E-12	1.18E-02	2.07E-02	0.019139	11.9301
19	209.5	9.5	11.72	1.30E-12	1.27E-02	2.18E-02	0.019093	11.9353
20	210.0	10.0	11.74	1.20E-12	1.33E-02	2.29E-02	0.019048	11.9082

Average pKa = 11.67308

Table 8: Determination of average number of coordinated Schiff base to cobalt(II) ion

S/NO	Vol(cm ³)	pH	[H ⁺]	[OH ⁻]	M _{total}	Log[A ²⁻]	n̄
1.	0.00	2.3	0.0033535	4.81615E-12			
2.	0.20	2.33	0.0031297	5.1606E-12	5.00E-03	-11.84	0.51
3.	0.40	2.39	0.0027258	5.92516E-12	4.99E-03	-11.87	0.51
4.	0.60	2.48	0.0022156	7.28954E-12	4.99E-03	-11.94	0.49
5.	0.80	2.55	0.0018858	8.56446E-12	4.98E-03	-11.99	0.49
6.	1.00	2.65	0.001498	1.0782E-11	4.98E-03	-12.15	0.51
7.	1.20	2.76	0.0011628	1.38899E-11	4.97E-03	-12.53	0.52
8.	1.40	2.94	0.0007682	2.10233E-11	4.97E-03	-12.19	0.52
9.	1.60	3.18	0.0004421	3.65342E-11	4.96E-03	-11.57	0.53
10.	1.80	3.77	0.0001136	1.42135E-10	4.96E-03	-10.78	0.55
11.	2.00	4.52	2.021E-05	7.99282E-10	4.95E-03	-9.99	0.61
12.	2.20	5.31	3.277E-06	4.92833E-09	4.95E-03	-9.19	0.68
13.	2.40	6.81	1.036E-06	1.55848E-08	4.94E-03	-8.69	0.76
14.	2.60	6.18	4.421E-07	3.65342E-08	4.94E-03	-8.32	0.84
15.	2.80	6.54	1.93E-07	8.36951E-08	4.93E-03	-7.96	0.92
16.	3.00	7.01	6.539E-08	2.47002E-07	4.93E-03	-7.49	0.99
17.	3.20	7.58	1.76E-08	9.17698E-07	4.92E-03	-6.92	1.08
18.	3.40	7.93	7.861E-09	2.05447E-06	4.92E-03	-6.57	1.16
19.	3.60	8.05	5.963E-09	2.70832E-06	4.91E-03	-6.45	1.24
20.	3.80	8.1	5.315E-09	3.03879E-06	4.91E-03	-6.39	1.32
21.	4.00	8	6.691E-09	2.41379E-06	4.90E-03	-6.49	1.39
22.	4.20	8.04	6.102E-09	2.64667E-06	4.90E-03	-6.46	1.48
23.	4.40	7.89	8.62E-09	1.8737E-06	4.89E-03	-6.61	1.56
24.	4.60	7.95	7.508E-09	2.1513E-06	4.89E-03	-6.55	1.64
25.	4.80	8	6.691E-09	2.41379E-06	4.88E-03	-6.49	1.72
26.	5.00	8.07	5.695E-09	2.83596E-06	4.88E-03	-6.43	1.79
27.	5.20	7.99	6.847E-09	2.35885E-06	4.87E-03	-6.51	1.88
28.	5.40	7.92	8.045E-09	2.00771E-06	4.87E-03	-6.58	1.96
29.	5.60	8.01	6.539E-09	2.47002E-06	4.86E-03	-6.49	2.04
30.	5.80	8.06	5.828E-09	2.77141E-06	4.86E-03	-6.44	2.12

Average n value = 1.130

Table 9: Stability constant and the Gibb's free energy of the complex

Compound	Stability constant(K)	Gibb's Free Energy (kJmol ⁻¹)
[MnL]	3.16x10 ¹¹	-64.15

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