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Synthesis, Characterization and Anti-Microbial Assessment of N, N' - Bis(4-benzeneazo salicylidene)-o-Phenylenediiminatomanganese(II) Complex

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ABSTRACT

A Schiff base, N,N' –bis (4- Benzeneazo salicylidene)-o-phenylenediimine was prepared by 2:1 molar condensation of 4 – (Benzeneazo) salicylaldehyde with o-phenylenediamine. The manganese(II) complex of the schiff base was prepared and characterized by determination of its solubility, melting point and molar conductivity, as well as by elemental analysis, infrared spectroscopy, bioassay and potentiometry. The complex prepared is greenish yellow, decomposes at 263^{o}C, soluble in dimethylsulphoxide (DMSO) and dimethylformamide (DMF) but insoluble in most organic solvents. The molar conductivity of the complex determined is 5.50 ohm^{-1}cm^{2}mol^{-1}, revealing a non-electrolyte compound. The infrared spectral data of the Schiff base showed a band at 1590cm^{-1}, which is attributable to *v*(C=O) stretching frequency. The same band was observed in the manganese(II) complex but at a lower frequency of 1565cm^{-1}, suggesting coordination of the Schiff base ligand. The bands in the region 586cm^{-1} and 500cm^{-1} in the complex are assigned to *v*(Mn-N) and *v*(Mn-O) stretching vibrations, respectively, confirming coordination of the Schiff base to the manganese(II) ion. The dissociation constant of the Schiff base is 11.67, indicating a weak acid. The mean number of Schiff base coordinated to manganese (II) ion is one, and the stability constant and Gibb's free energy of the complex are 2.51x10^{12} and -69.16KJmol^{-1}, respectively. The antifungal and antibacterial tests carried out on the Schiff base and its manganese(II) complex showed moderate activity. The complex formed by the interaction of the prepared Schiff base and manganese (II) salt is stable and bioactive.

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

INTRODUCTION

Schiff base named after Hugo Schiff is a class of derivatives of the condensation of aldehyde or ketone with primary amine to produce a functional group that contains carbon nitrogen double bond (imine). A Schiff base can be synthesized from an aromatic or an aliphatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal followed by dehydration to generate an imine. Schiff bases are generally excellent chelating agents, especially when containing –OH or –SH present is close to the azomethine group (Patai, 1970). Tetradentate Schiff base ligands with nitrogen - oxygen donor atoms are well known to coordinate with metal ions and this has attracted the interest of many researchers as the complexes are reported to have antibacterial activity (Mohammad and Pearly, 2008: Raman *et al.*, 2001). For example, Raman *et al.*, (2001), reported the synthesis of neutral tetradentate N_2O_2 type complexes of copper(II), nickel(II), manganese(II), zinc (II)and vanadate (VO) using Schiff bases formed by condensation of o-phenylendiamine with acetoacetanilide in alcohol medium. The complexes were found to be square planar except Mn(II) and VO chelates that have octahedral and square pyramidal geometry, respectively. The analytical data of all the complexes corresponds to general formula ML while that of manganese complex was ML.2H_2O. The monomeric and neutral nature of the complex formed was confirmed by their magnetic susceptibility and low conductance values. They were also able to find that the coordinating possibility of o-phenylenediamine has been improved by condensing it with a variety of carbonyl compounds and the ligand system has both oxygen and nitrogen donor site with which it coordinates with the metal ion in a tetradentate manner through the enolisable carbonyl group of the acetoacetanilide moiety and the azomethine nitrogen of the Schiff base.

Xia *et al.*, (2006), synthesized Schiff base complexes by condensation of diaminocyclohexane with salicylaldehyde, 2 – pyridine carbonylaldehyde and 2,6 – hydroxyl – 1-napthaldehyde followed by metallation with manganese(II) cobalt(II), copper(II) and iron(II) salts. These Schiff bases and the metal complexes were characterized by IR, ^{1}H and ^{13}C NMR and UV – visible spectra. The results of their analysis showed that the complexes have metal to ligand ratio (M:L) of 1:1.

Schiff bases have been found to be active against bacteria and fungi, for example, Saxena and Shirivastava (1987), reported the synthesis of Schiff bases derived from furylglyoxal and p-toluidene and their antibacterial activity against *Eschericia coli, Staphylococcus aureus, Bacillus subtilis, and Proteus vulgaris*. Furthermore, Mishra *et al.,* (1991), reported some Schiff bases of quinazolinones and their antifungal activity against *Candida albicans, Trichophyton rubrum, T. mentagrophyytes, A. niger, and Micosporum gypseum*.

This paper reports synthesis and characterization of N, N' - bis(4-benzeneazo salicylidene)-o-phenylenediiminatomanganese(II) complex.

MATERIALS AND METHODS

Materials

All the glassware 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 in Nujol, within 400 – 4000cm^{-1}. The pH measurements were carried out using Jenway pH meter model 3320. The molar conductivity measurements were carried out on a Cyber Scan 500 model and the melting/decomposition temperatures were determined using Gallenkamp melting point apparatus.

METHODS

Preparation of the Schiff Base Ligand

0.01mol (1.814g) of o-phenylenediamine was added slowly into a solution of 0.02mol (4.5245g) 4-(Benzeneazo) salicylaldehyde (an intermediate) in 20cm^3 ethanol. After refluxing the reaction mixture for 2 hours, the precipitate was separated, washed several times using ethanol, followed by recrystallisation in ethanol and drying at 50^{0}C in an oven overnight (Jiannings et al., 2005).

Preparation of Manganese(II) Schiff Base Complex

The complex was prepared by refluxing a mixture of aqueous solution of $MnCl_2.4H_2O$ (1.0mmol; 0.198g) and hot ethanolic solution of the prepared Schiff base (0.524g) 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^{0}C overnight (Jiannings et al., 2005).

Determination of Dissociation Constant (pKa) of the Tetradentate Schiff Base

The dissociation constant of the Schiff base ligand was determined by introducing a standardized pH meter electrode into a 400cm^3 beaker containing magnetic stirrering bar, 90cm^3 water, 100cm^3 of 0.2mol dm^{-3} KNO_3 and 10cm^3 of 0.4mol dm^{-3} Schiff base ligand solution. To this mixture, 10cm^3 of standardized 0.5mol dm^{-3} aqueous solution of NaOH was added gradually and the corresponding pH value recorded after each addition Geary, 1971).

Determination of Number of Coordinated Schiff Base in the Complex

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

RESULT AND DISCUSSION

The Schiff base has an orange colour, a melting point of 193^{o}C and percentage yield of 70%. The interaction of the prepared Schiff base and manganese (II) chloride gave N, N' - bis(4-benzeneazo salicylidene)-o-phenylenediiminatomanganese (II) complex. The complex is greenish yellow, has decomposition temperature of 263^{o}C and percentage yield of 67% as presented Table 1. The solubility tests of the Schiff base and its manganese(II) complex in common organic solvents and water showed that both the Schiff base and the complex are insoluble in water, slightly soluble in most organic solvents but readily soluble in dimethylsulphoxide (DMSO) and dimethylformamide (DMF) (Table 2). The molar conductance of the complex determined in 10^{-3}M DMSO solution (Table 3) is 5.5 ohm^{-1}cm^{2}mol^{-1}, which is low, suggesting that the complex is non-electrolyte (Geary, 1971). The infrared spectral band in the Schiff base at 1590cm^{-1} is assigned to *v*(C=N) stretching vibration. A similar band observed in the complex but in the lower frequency (1528cm^{-1}), suggests the coordination of the Schiff base to manganese(II) ion (Abdulsamath *et al.,* 1992). The bands at 586cm^{-1} and 500cm^{-1} are attributable to *v*(Mn-N) and *v*(Mn-O) stretching vibrations, respectively, confirming the coordination of the Schiff base to the metal ion (Abdulsamath *et al.*, 1992: Ahmed and Akhtar, 1983), as presented in Table 4. The antibacterial test carried out on the free Schiff base ligand revealed only low activity on *E. coli spp* with a diameter of inhibition zone of 13mm per 3000µg concentration. The metal complex on the other hand showed higher activity against the bacterial isolates particularly at 3000µg concentration and is also found to be more active on *E. coli spp*. But no activity was observed at 1000µg concentration (Table 5). The results of the antifungal activities of the Schiff base ligand and its 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 Schiff base ligand is 11.67, which revealed the basic nature of the compound as shown in Table 7. The average number of Schiff base ligand coordinated to the manganese(II) ion determined potentiometrically, is one and this is consistent with 1:1 metal – Schiff base ratio (Table 8). The stability constant of the complex is 2.51×10^{12} and the Gibb's free energy of the complex determined is $-69.16 KJmol^{-1}$, indicating that the complex is very stable (Table 9).

On the basis of the spectral data and other analytical results of the Schiff base and its manganese(II) complex, the following molecular structure of the complex is proposed.

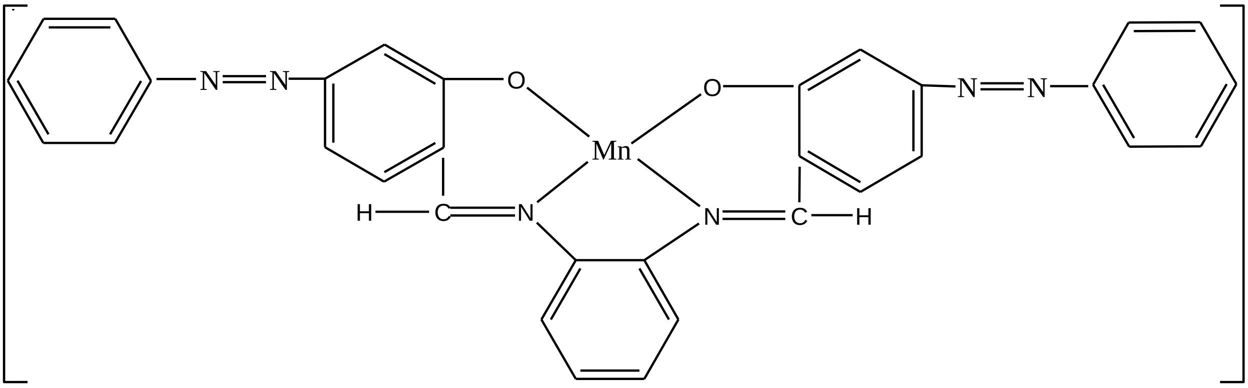

Fig. 1: The Proposed Molecular Structure of the Manganese(II) Schiff Base Complex

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

Compound	Colour	Melting point (^oC)	Decomp. temp (^oC)	Percentage Yield (%)
Schiff base	Orange yellow	193	-	70
[MnL]	Greenish yellow	-	263	67

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

Compound	H_2O	Ethanol	Benzene	Acetone	Methanol	DMSO	DMF
Schiff base	IS	S	SS	SS	S	S	S
[MnL]	IS	SS	SS	IS	IS	S	S

Key
S – Soluble
SS – Slightly Soluble
IS – Insoluble

Table 3: Conductivity Measurement of the Manganese(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}
Mn $C_{32}H_{22}N_6O_2$	1x10^{-3}	5.5	5.5

Table 4: Infrared Spectral Data of the Schiff Base and its Manganese(II) Complex

Compound	*v* (C = N)	*v* (phenolic C - O)	*v*(M - N)	*v* (M - O)
Schiff base	1590	1340	-	-
[Mn L]	1565	1304	586	500

Table 5: Antibacterial Activity of Schiff Base and its Manganese(II) Complex

Compound	Clinical isolate		Diameter /Concentration							
	E. coli *spp*	Staph *spp*	3000µg		2000µg		1000µg		Control	
Schiff base	√	√	11mm	00	00	00	00	00	00	00
Mn complex	√	√	12mm	00	9mm	00	00	00	00	00

Table 6: Antifungal Activity of Schiff Base and its Manganese(II) Complex

Compound	Clinical isolate		Diameter /Concentration							
	A niger	C. albican	3000µg		2000µg		1000µg		**Control**	
Ligand	√	√	13mm	15mm	00	10mm	00	00	00	00
Mn complex	√	√	18mm	25mm	00	14mm	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	0.50	9.56	1.80E-10	8.80E-05	1.20E-03	0.019950	10.9645
2	1.00	9.91	8.20E-11	2.00E-04	2.39E-03	0.019900	10.9919
3	1.50	10.22	4.00E-11	4.00E-04	3.57E-03	0.019851	11.1152
4	2.00	10.51	2.10E-11	7.80E-04	4.75E-03	0.019802	11.2851
5	2.50	10.74	1.20E-11	1.33E-03	5.93E-03	0.019753	11.4323
6	3.00	10.93	7.90E-12	2.05E-03	7.09E-03	0.019704	11.5684
7	3.50	11.07	5.70E-12	2.84E-03	8.26E-03	0.019656	11.6639
8	4.00	11.18	4.40E-12	3.65E-03	9.41E-03	0.019608	11.7356
9	4.50	11.27	3.60E-12	4.49E-03	1.06E-02	0.019560	11.7916
10	5.00	11.34	3.10E-12	5.28E-03	1.17E-02	0.019512	11.8233
11	5.50	11.41	2.60E-12	6.20E-03	1.28E-02	0.019465	11.8702
12	6.00	11.46	2.30E-12	6.96E-03	1.40E-02	0.019417	11.8816
13	6.50	11.51	2.10E-12	7.81E-03	1.51E-02	0.019370	11.9031
14	7.00	11.55	1.90E-12	8.56E-03	1.62E-02	0.019324	11.9064
15	7.50	11.58	1.80E-12	9.18E-03	1.73E-02	0.019277	11.8877
16	8.00	11.63	1.60E-12	1.03E-02	1.85E-02	0.019231	11.9365
17	8.50	11.66	1.50E-12	1.10E-02	1.96E-02	0.019185	11.9306
18	9.00	11.69	1.40E-12	1.18E-02	2.07E-02	0.019139	11.9301
19	9.50	11.72	1.30E-12	1.27E-02	2.18E-02	0.019093	11.9353
20	10.00	11.74	1.20E-12	1.33E-02	2.29E-02	0.019048	11.9082

Average pKa = 11.67308

Table 8: Result of Determination of Average Number of Coordinated Schiff Base to Manganese(II) ion

S/NO	Vol(cm^3)	pH	$[H^+]$	$[OH^-]$	M_{total}	Log$[A^{2-}]$	$\bar{n}$
1.	0.00	2.28	0.003512	4.59939E-12	-	-	-
2.	0.20	2.33	0.00313	5.1606E-12	0.004995	-11.84	0.51
3.	0.40	2.38	0.002789	5.79029E-12	0.00499	-11.87	0.52
4.	0.60	2.44	0.002429	6.64814E-12	0.004985	-11.89	0.53
5.	0.80	2.53	0.001975	8.179E-12	0.0049801	-11.98	0.52
6.	1.00	2.64	0.001533	1.05366E-11	0.0049751	-12.13	0.51
7.	1.20	2.75	0.00119	1.35738E-11	0.0049702	-12.47	0.52
8.	1.40	2.91	0.000823	1.962E-11	0.0049652	-12.34	0.53
9.	1.60	3.18	0.000442	3.65342E-11	0.0049603	-11.57	0.53
10.	1.80	3.62	0.000161	1.00624E-10	0.0049554	-10.96	0.56
11.	2.00	5.08	5.57E-06	2.90202E-09	0.0049505	-9.42	0.59
12.	2.20	7.17	4.52E-08	3.57026E-07	0.0049456	-7.33	0.68
13.	2.40	8.39	2.73E-09	5.92515E-06	0.0049407	-6.11	0.76
14.	2.60	8.26	3.68E-09	4.39238E-06	0.0049358	-6.24	0.84
15.	2.80	8.23	3.94E-09	4.09921E-06	0.004931	-6.27	0.92
16.	3.00	8.4	2.66E-09	6.06317E-06	0.0049261	-6.09	0.99
17.	3.20	8.6	1.68E-09	9.60948E-06	0.0049213	-5.89	1.08
18.	3.40	8.71	1.3E-09	1.23794E-05	0.0049164	-5.78	1.16
19.	3.60	8.68	1.4E-09	1.15531E-05	0.0049116	-5.82	1.24
20.	3.80	8.65	1.5E-09	1.0782E-05	0.0049068	-5.85	1.32
21.	4.00	8.65	1.5E-09	1.0782E-05	0.004902	-5.85	1.39
22.	4.20	8.62	1.61E-09	1,00624E-05	0.0048972	-5.88	1.48
23.	4.40	8.56	1.84E-09	8.76395E-06	0.0048924	-5.94	1.56
24.	4.60	8.7	1.34E-09	1.20976E-05	0.0048876	-5.79	1.64
25.	4.80	8.66	1.46E-09	1.10332E-05	0.0048828	-5.84	1.72
26.	5.00	8.75	1.19E-09	1.35738E-05	0.004878	-5.74	1.79
27.	5.20	8.7	1.34E-09	1.20976E-05	0.0048733	-5.79	1.88
28.	5.40	8.68	1.4E-09	1.15531E-05	0.0048685	-5.82	1.96
29.	5.60	8.6	1.68E-09	9.60948E-06	0.0048638	-5.89	2.04
30.	5.80	8.6	1.68E-09	9.60948E-06	0.0048591	-5.89	2.12
31.	6.00	8.52	2.02E-09	7.99282E-06	0.0048544	-5.98	2.19

Average n $\bar{}$value = 1.132

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

Compound	Stability constant (K)	Gibb's Free Energy ($kJmol^{-1}$)
[MnL]	$2.51X10^{12}$	-69.16

CONCLUSION

The preparation of the schiff base and its manganese(II) complex was achieved. The melting point of the schiff base and the decomposition temperature determined are high, revealing stable compounds. The result of elemental analyses of the schiff base and its manganese(II) complex is consistent with !:1 manganese - schiff base ratio. The schiff base and its complex have been found to be biologically active.

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