

Spectral and Potentiometric Studies On Manganese (II) and Cobalt (II) Complexes with Schiff Base Derived From 2-Thiophenecarboxylaldehyde and 2-Aminobenzoic Acid

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ABSTRACT

Reaction of ethanolic solutions of 2-aminobenzoic acid and 2-thiophenecarboxylaldehyde gave a Schiff base. The reaction of the ethanolic solutions of the Schiff base with metal (II) chlorides formed complex compounds. Their solubility, melting point/decomposition temperature, molar conductance, and IR were carried out. The melting point of the Schiff base and the decomposition temperature of the complexes determined are high. The Schiff base and its metal complexes are soluble in common organic solvent but insoluble in water. The molar conductance of the complexes determined suggested that the complex compounds are non-electrolytes. The empirical formula calculation of the complex compounds indicated the formula $[ML_2].H_2O$. The infrared spectral data of the Schiff base and its metal complexes showed bands at 1600 cm^{-1} and 1610 cm^{-1} , which are assigned to $\nu(C=N)$ stretching frequencies. The bands at 500 – 515 cm^{-1} and 490 – 495 cm^{-1} are attributable to $\nu(M-O)$ and $\nu(M-N)$ stretching vibrations. The spectral bands in the range 3092 – 3298 cm^{-1} are assigned to $\nu(O-H)$ stretching frequencies. The dissociation constant of the Schiff base is 6.8, indicating a weak acid. The stability constants of the complexes are high.

Keywords: 2-aminobenzoic acid, 2-thiophenecarboxylaldehyde, Schiff base, complex compound, stability constant and dissociation constant.

1. INTRODUCTION

The condensation of either an aldehyde or a ketone with primary amine yields Schiff base (Pierre, 1987). The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketoimines. It has been known that different metal ions on interaction with Schiff bases yield chelates, for example; Tsumaki, (1983) reported $[Co(sal_2-en)]$ Complex which received a great attention owing to its ability to undergo reversible adduct formation with molecular oxygen. The oxygenation ability of the complex was first recognized by Hassan *et al.*, (1998), however, the mechanism for the oxygenation process was not well understood until recently with the advent of modern physical techniques. Xishi *et al.*, (2003) reported the synthesis and characterization of a novel Schiff base ligand formed from the condensation of 2,2-bis (p-methoxyphenylamine) and Salicylaldehyde and its Mn(II), Co(II) and Cu(II) complexes. The Ben Saber *et al.*, (2005) reported the synthesis and characterization of Cr(III), Fe(III), Co(II) and Ni(II) complexes with a Schiff base derived from 4-dimethylamino benzaldehyde and primary amines. The chemical analysis data showed the formation of (1:1) metal - ligand ration and a square planar geometry was suggested for Co(II) and Ni(II) complex while an octahedral structure for Cr(III) and Fe(III) complexes. In another report, Cu(II), Co(II), Ni(II) and Zn(II) complexes of new heterocyclic Schiff base derived from

1-amino – 5- benzoyl – 4- phenyl – 1H – pyrimidine – 2-on with salicylaldehyde have been synthesized and investigated by elemental analysis (Sonmez and Sekerel, 2002). An octahedral geometry was suggested for all the complexes. 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.

Transition metal Schiff base complexes are used in various fields, such as medicine, agriculture, industries etc. For example, $[Co(acac_2-en)]$ in dimethylformamide, pyridine and substituted pyridines proved to be involved in oxygen metabolism (Hanna and Mona, 2001). Transition metal complexes with 1, 10 – phenanthroline and 2, 2 – bipyridine are heavily used in petroleum refining (John *et al.*, 1976). Schiff base formed by the condensation of 1-formyl-2-hydroxy-3- naphtholic arylamide with O-hydroxyl or O-methoxy aniline complexes of Co(II), Ni(II), Cu(II) and Zn(II) are useful as pigments (Gupta *et al.*, 2002). Oxovanadium Complexes have been found strongly active, against some type of Leukemia (Dong *et al.*, 2002). Transition metal complexes derived from a number of amino acids have been reported to have biological activity (Zahid *et al.*, 2007). Morad *et al.*, (2007), reported the antibacterial activity of Ni(II) with salicylaldehyde and 2-amino-

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benzoic acid complex. Popova and Berova, (1981) reported that copper is good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis hepatitis, leprosy, anemia and Leukemia in children. This paper reports the studies on manganese (II) and cobalt (II) complexes of the Schiff base derived from 2-aminobenzoic acid and 2-thiophenecarboxylaldehyde due to paucity of information.

2. MATERIALS AND METHODS

All glass wares used were well washed with detergent, rinsed with distilled water and dried in an oven. All chemicals and solvents used were of analytical grade (AnalaR or BDH) while 2-aminobenzoic acid, 2-thiophenecarboxylaldehyde were obtained from Sigma-Aldrich and were used without further purification. All weighing were carried out on electric balance model AB 54. Infrared spectral analysis were recorded using a Fourier transformed IR Genesis series model in Nujol in the range 400-4000 cm^{-1} . pH measurements were also carried out using Jenway pH meter model 3320 and electrical conductivity meter model 5003. Absorbance measurements were carried out using Unicam UV spectrophotometer. Melting point measurement was carried out using Bibby Stuart Scientific Melting Point SMP 1.

Preparation of the Schiff base.

The Schiff base was prepared by mixing hot ethanolic solutions of 2-thiophenecarboxaldehyde (2.24g, 10mmol) and 2-aminobenzoic acid (2.74g, 10mmol), and the resulting mixture refluxed for 2hrs. The reaction mixture was concentrated and allowed to cool in an ice bath to precipitate the product, which was separated, recrystallized from ethanol, washed with diethyl ether and dried in a vacuum over anhydrous calcium chloride (Mohammed *et al.*, 2005).

Preparation of the metal (II) Schiff base complexes

The metal (II) Schiff base complexes, were prepared by mixing hot ethanol-water mixture (1:1) of the respective metal (II) chloride (1mmol) and hot ethanolic solution of the Schiff base (0.231g, 2mmol). The resulting mixture was refluxed for 1 hour and allowed to cool in an ice bath to precipitate the product, which was separated, washed with a 1:1 ethanol-water mixture and then diethyl ether (Mohammed *et al.*, 2005).

Determination of dissociation constant (pKa) of the Schiff base

To a 500 cm^3 beaker containing a magnetic stirrer was added 90 cm^3 of distilled water, 100 cm^3 of 0.2M KNO_3 and 10 cm^3 of 0.4M Schiff base solution. A 0.5M standardized aqueous NaOH was added to a total volume of 10 cm^3 . After each 0.5 cm^3 aliquot addition, the corresponding, pH value was recorded (Gregory *et al.*, 1978).

Determination of stability constant of the metal (II) Schiff base complex.

To a 500 cm^3 beaker containing a magnetic stirrer was added 90 cm^3 of distilled water, 100 cm^3 of 0.2M KNO_3 , 10 cm^3 of 0.1M HNO_3 and 0.001mol of a metal (II) chloride. A 0.4M solution of sodium salt of a Schiff base prepared by neutralizing a known quantity of the ligand with a calculated amount of the standardized aqueous NaOH was gradually added into the beaker to a total volume of 10 cm^3 . After each 0.2 cm^3 aliquot addition with constant stirring, the pH of the reaction mixture was recorded (Gregory *et al.*, 1978).

3. RESULTS AND DISCUSSION

The prepared Schiff base is yellow, has melting point of 143°C and percentage yield of 60%. The manganese (II) and cobalt (II) Schiff base complexes are light yellow, have decomposition temperature of 300 and 320°C and percentage yield of 55 and 78%, respectively. These high values of decomposition temperature, revealed that the complex compounds are quite stable (Table 1). The Schiff base is soluble in most organic solvents but insoluble in water, however, the manganese (II) and cobalt(II) Schiff base complexes are slightly soluble in most organic solvents except DMSO (Table 2). The molar conductance measurements of the complexes in 10⁻³M DMSO determined are 16.73 and 16.95 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, for manganese (II) and cobalt (II) complexes, respectively, indicating their non electrolytic nature (Table 3). The IR spectral data of the Schiff base showed a band at 1600 cm^{-1} , which is assigned to $\nu(\text{C}=\text{N})$ stretching vibration, a feature found in Schiff bases. This band is also observable in the complex compounds, suggesting that the Schiff base has coordinated to the respective metal (II) ions (Prabhu and Dodwad, 1986). The strong band observed in the free Schiff base at 3460 cm^{-1} , is absent in the complex compounds, which suggests deprotonation of the Schiff base on coordination to the respective metal ion (Jezowska *et al.*, 1988). The bands in the regions 515 – 516 cm^{-1} and 490 – 495 cm^{-1} are attributed to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretching vibrations respectively, confirming the coordination of the Schiff base to the respective metal ions (Byeong-Goo *et al.*, 1996). The broad band in the region 3390-3550 cm^{-1} is accorded to $\nu(\text{O}-\text{H})$ stretching vibrations, a feature indicating the presence of water (Table 4). The empirical formula of the complexes

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were determined from known values of percent compositions of the metal ions, the Schiff base and water of crystallization, the result suggested the formula $[ML_2] \cdot H_2O$ (Morad *et al.*, 2007). The dissociation constant (pKa) of the Schiff base is 6.8283, indicating weak acid (Table 5). The stability constants of manganese (II) and cobalt (II) Schiff base complexes determined are 1.40×10^{11} and 2.01×10^{11} , respectively

(Table 6 and 7), and the corresponding Gibb's free energy are -63.56 and -64.45 KJmol^{-1} , respectively (Table 8). The ratio of metal ion to Schiff base for each complex compound determined as reported potentiometrically is 1:2 (Gregory *et al.*, 1978).

Table 1: Physical properties of the Schiff base and the complexes

Compound	% Yield	Colour	M. P. ($^{\circ}\text{C}$)	Decomposition Temp ($^{\circ}\text{C}$)
Schiff base (L)	60	Yellow	143	-
$[MnL_2] \cdot H_2O$	55	Yellow	-	300
$[CuL_2] \cdot H_2O$	78	Grey	-	320

Table 2: Solubility of the Schiff base and the complexes

Compound	Water	Ethanol	Metanol	Acetone	DMF	DMSO	Nitro benzene
L	IS	S S	S S	S S	S	S	S
$[CuL_2] \cdot H_2O$	SS	SS SS	SS SS	SS SS	S	SS	SS
$[MnL_2] \cdot H_2O$	SS	SS SS	SS SS	SS SS	S	SS	SS

Key

S = Soluble

IS = Insoluble

SS = Slightly soluble

Table 3: Measurement of molar conductance of the complexes in 10^{-3}M DMSO solution

Complex	Electrical conductivity ($\text{ohm}^{-1}\text{cm}^{-1}$)	Molar conductivity ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
$[CuL_2] \cdot H_2O$	1.673×10^{-5}	16.73
$[MnL_2] \cdot H_2O$	1.695×10^{-5}	16.95

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Table 4: The infrared spectral data of the Schiff base and the complexes

Name	$\nu(\text{O-H})$		$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
	cm^{-1}	cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}
L	3460	1600	1429	-	-	
[CuL ₂].H ₂ O	3550	1592	1410	515		490
[MnL ₂].H ₂ O	3390	1596	1464	516		495

Table 5: Determination of dissociation constant of the Schiff base

Vol. of NaOH added (cm ³)	pH	[H ⁺]	[OH ⁻]	[Na ⁺]	A _{tot}	pKa
0.5	3.81	0.0001	7.002E-11	1.25E-03	0.01995	4.742
1.0	4.31	3.275E-05	2.214E-10	2.49E-03	0.0199	4.786
1.5	4.39	2.724E-05	2.662E-10	3.72E-03	0.0199	4.843
2.0	4.60	1.680E-05	4.317E-10	4.95E-03	0.0198	4.898
2.5	4.8	1.060E-05	6.842E-10	6.17E-03	0.0198	4.965
3.0	4.98	7.002E-06	1.036E-09	7.39E-03	0.0197	5.025
3.5	5.18	4.418E-06	1.641E-09	8.60E-03	0.0197	5.114
4.0	5.4	2.661E-06	2.724E-09	9.80E-03	0.0196	5.225
4.5	5.68	1.397E-06	5.190E-09	1.10E-02	0.0196	5.396
5.0	6.1	5.311E-07	1.365E-08	1.22E-02	0.0195	5.703
5.5	6.24	3.848E-07	1.885E-08	1.34E-02	0.0195	5.723
6.0	6.82	1.012E-07	7.165E-08	1.46E-02	0.0194	6.168
6.5	7.07	5.691E-08	1.274E-07	1.57E-02	0.0194	6.258
7.0	7.85	9.445E-09	7.677E-07	1.69E-02	0.0193	6.829
7.5	7.98	7.002E-09	1.036E-06	1.81E-02	0.0193	9.329
8.0	8.18	4.418E-09	1.641E-06	1.92E-02	0.0192	12.338

Ave pKa = 6.8283

Table 6: Determination of mean number of Schiff base per metal ion in Mn (II) complex

Vol. of Na. Liganate added (cm ³)	pH	[H ⁺]	[OH ⁻]	A _{TOT}	M _{TOT}	Log [A ⁻]	\bar{n}
3.8	5.50	2.11E-06	3.43E-09	0.005911	0.004926	-3.4352	0.7607
4.0	5.51	2.07E-06	3.51E-09	0.006299	0.004921	-3.4252	0.7589
4.2	5.51	2.07E-06	3.51E-09	0.006686	0.004916	-3.4252	0.9645
4.4	5.52	2.02E-06	3.59E-09	0.007073	0.004912	-3.4152	0.9628
4.6	5.52	2.02E-06	3.59E-09	0.007458	0.004907	-3.4152	0.96474
4.8	5.53	1.93E-06	3.68E-09	0.007843	0.004902	-3.4052	1.0651
5.0	5.53	1.97E-06	3.68E-09	0.008227	0.004897	-3.4052	1.1492
5.2	5.54	1.93E-06	3.76E-09	0.008611	0.004892	-3.3952	1.2294
5.4	5.54	1.93E-06	3.76E-09	0.008993	0.004888	-3.3952	1.3140
5.6	5.55	1.89E-06	3.85E-09	0.009375	0.004883	-3.3852	1.3737
5.8	5.55	1.89E-06	3.85E-09	0.009756	0.004878	-3.3851	1.4588
6.0	5.56	1.84E-06	3.94E-09	0.010136	0.004873	-3.3851	1.5391
6.2	5.56	1.84E-06	3.94E-09	0.010516	0.004869	-3.3851	1.6382
6.4	5.56	1.84E-06	3.94E-09	0.010895	0.004864	-3.3751	1.7001
6.6	5.57	1.80E-06	4.03E-09	0.011273	0.004859	-3.3805	1.7829
6.8	5.57	1.80E-06	4.03E-09	0.01165	0.004854	-3.3805	1.8691
7.0	5.58	1.76E-06	4.12E-09	0.012027	0.00485	-3.3714	1.9313
7.2	5.58	1.76E-06	4.12E-09	0.012403	0.004845	-3.3714	2.0181
7.4	5.59	1.76E-06	4.21E-09	0.012778	0.00484	-3.3622	2.1011
7.6	5.59	1.72E-06	4.21E-09	0.013153	0.004836	-3.3622	2.1884
7.8	5.59	1.72E-06	4.21E-09	0.013527	0.004831	-3.3532	2.2529
8.0	5.59	1.72E-06	4.21E-09	0.013900	0.004826	-3.3532	2.3430
8.2	5.60	1.72E-06	4.21E-09	0.014272	0.004822	-3.3541	2.4240
8.4	5.60	1.68E-06	4.31E-09	0.014644	0.004817	-3.3550	2.4916
8.6	5.60	1.68E-06	4.31E-09	0.015014	0.004812	-3.3550	2.5727
8.8	5.61	1.64E-06	4.42E-09	0.015385	0.004808	-3.3445	2.6639
9.0	5.61	1.64E-06	4.42E-09	0.015754	0.004803	-3.3350	2.7266

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9.2	5.61	1.64E-06	4.42E-09	0.016123	0.004798	-3.33450	2.8101
9.4	5.62	1.60E-06	4.52E-09	0.016491	0.004794	-3.3359	2.9387
9.6	5.62	1.60E-06	4.52E-09	0.016858	0.004789	-3.3359	2.9736
Ave \bar{n} = 1.8324							

Table 7: Determination of mean number of Schiff base per metal ion in Co (II) complex

Vol. of Na. Liganate added (cm ³)	pH	[H ⁺]	[OH ⁻]	A _{TOT}	M _{TOT}	Log [A ⁻]	\bar{n}
3.8	5.13	4.96E-06	1.46E-09	0.007843	0.004902	-3.8942	0.600115
4.0	5.14	4.84E-06	1.50E-09	0.008227	0.004897	-3.8741	0.680104
4.2	5.17	4.52E-06	1.60E-09	0.008611	0.004892	-3.8541	0.760087
4.4	5.19	4.31E-06	1.68E-09	0.008993	0.004888	-3.8441	0.84007
4.6	5.21	4.12E-06	1.76E-09	0.009375	0.004883	-3.8141	0.920054
4.8	5.23	3.94E-06	1.84E-09	0.009756	0.004878	-3.8041	1.000039
5.0	5.24	4.22E-06	1.72E-09	0.010136	0.004873	-3.7940	1.080018
5.2	5.26	3.68E-06	1.97E-09	0.010516	0.004869	-3.7650	1.160002
5.4	5.27	3.59E-06	2.02E-09	0.010895	0.004864	-3.7440	1.239987
5.6	5.29	3.43E-06	2.12E-09	0.011273	0.004859	-3.7240	1.319966
5.8	5.31	3.28E-06	2.21E-09	0.01165	0.004854	-3.7040	1.39995
6.0	5.32	3.24E-06	2.27E-09	0.012027	0.00485	-3.7340	1.479928
6.2	5.36	3.21E-06	2.48E-09	0.012403	0.004845	-3.6793	1.559906
6.4	5.38	2.78E-06	2.60E-09	0.012778	0.00484	-3.6693	1.639883
6.6	5.41	2.60E-06	2.79E-09	0.013153	0.004836	-3.6501	1.719847
6.8	5.42	2.54E-06	2.85E-09	0.013527	0.004831	-3.6301	1.799821
7.0	5.43	2.48E-06	2.92E-09	0.0139	0.004826	-3.6210	1.879779
7.2	5.45	2.37E-06	3.06E-09	0.014272	0.004822	-3.5810	1.959741
7.4	5.46	2.32E-06	3.13E-09	0.014644	0.004817	-3.5619	2.039682
7.6	5.48	2.21E-06	3.28E-09	0.015014	0.004812	-3.5319	2.119624
7.8	5.50	2.12E-06	3.43E-09	0.015385	0.004808	-3.5228	2.199548
8.0	5.51	2.07E-06	3.51E-09	0.015754	0.004803	-3.5137	2.279419

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8.2	5.53	1.97E-06	3.68E-09	0.016123	0.004798	-3.4937	2.35931
8.4	5.56	1.84E-06	3.94E-09	0.016491	0.004794	-3.4837	2.439143
8.6	5.59	1.76E-06	4.12E-09	0.016858	0.004789	-3.4837	2.518915
8.8	5.50	2.12E-06	3.43E-09	0.015385	0.004808	-3.4637	2.199548
9.0	5.51	2.07E-06	3.51E-09	0.015754	0.004803	-3.4446	2.279419
9.2	5.53	1.97E-06	3.68E-09	0.016123	0.004798	-3.4346	2.35931
9.4	5.56	1.84E-06	3.94E-09	0.016491	0.004794	-3.4326	2.439143
9.6	5.59	1.76E-06	4.12E-09	0.016858	0.004789	-3.4317	2.518915
Ave ñ = 1.75259							

Table 8: Stability Constant and Gibb's free energy of the complexes

Complex	Stability constant (k)	ΔG (kJ/mol)
[MnL].2H ₂ O	1.29 X 10 ⁵	-63.56
[CuL].2H ₂ O	3.55 X 10 ⁶	-64.45

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