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STUDIES OF MN (II) AND NI (II) COMPLEXES WITH SCHIFF BASE DERIVED FROM 2-AMINO BENZOIC ACID AND SALICYLALDEHYDE

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ABSTRACT
The complexes of Mn (II) and Ni (II) with Schiff base derived from salicylaldehyde and 2-aminobenzoic acid have been prepared and characterized by gravimetry, potentiometry, molar conductance and infrared analyses. The solubility test on the Schiff base and its nickel(II) complex revealed their solubility in most organic solvents except ether, acetonitrile and tetrachloromethane. However, manganese(II) complex is insoluble in most organic solvents but soluble in dimethylsulphoxide (DMSO). The molar conductance of the complexes measured are, indicating their non-electrolytic nature. The potentiometric and spectrophotometric studies of the complex compounds revealed 1:1 metal to ligand ratio.

Keywords: Schiff base, azomethine, salicylaldehyde, potentiometry, spectrophotometry, 2-amino benzoic acid

INTRODUCTION

A Schiff base is a compound formed from the condensation of either an aldehyde or a ketone (Holm *et al.,* 1966; Hobday and Smith, 1972; 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 (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. Then 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-dimetylamino benzaldehyde and primary amines. The chemical analysis data showed the formation of (1:1) metal - ligand ratio and a square planar geometry was suggested for Co(II) and Ni(II) complex while an octahedral structure was suggested for Cr(III) and Fe(III) complexes. Ben Saber et al. (2005), reported the synthesis of a Schiff base derived from salicylaldeyde, 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 used in petroleum refining (John et al, 1976). Schiff base formed by the condensation of 1-formyl-2-hydry-3-naphtholic arylamide with O-hydroxyl or O-methoxy aniline complexes of Co(II), Ni(II), Cu(II) and Zn(II) are useful as figments (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 salicyaldehyde and 2-amino-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 of manganese (II) and nickel (II) complexes of Schiff base derived from 2-amino benzoic acid and salicylaldehyde due to paucity of information.

MATERIALS AND METHODS

Chemicals of analytical grade purity were used. Melting point and decomposition temperature were determined on Gallenkamp melting point apparatus. IR spectra measurements were recorded using Fourier Transformed IR Genesis series model in Nujol in the region 40000 – 400cm^{-1}. electrical conductivity measurements were carried out using conductivity meter model 4010. UV-visible spectral measurements were done on a Pye Unicam UV-visible spectrophotometer.

Preparation of the Schiff base

The Schiff based formed from salicylaldehyde and 2-amino benzoic acid was prepared by adding 25cm^3 of salicylaldehyde ethanolic solution (1.22g, 0.01mol) to the same volume of ethanolic solution of 2-amino benzoic acid (1.37g, 0.01mol). The mixture was refluxed for two hours. The product that formed was collected by filtration, washed several times with ethanol and recrystallized from hot ethanol. The orange colour product was then dried in dissicator over phosphorous pentoxide (EL-Ajialy *et al.,* 2006).

Preparation of Schiff base metal complexes

The metal complexes were prepared by adding 25cm^3 of ethanolic solution of metal chloride (0.01 mole) with ethanolic solutions of the prepared Schiff base (0.01 mole) followed by drop wise addition of aqueous ammonia. The resulting mixture was refluxed for two hours and the metal complex compounds that precipitated out were filtered and then washed repeatedly with hot ethanol until the washing was colourless. The product was air dried over phosphorus pentoxide. (El-Ajaily, 2006).

Determination of Dissociation Constant of Schiff Base

To a 400cm^3 beaker were added 90cm^3 of distilled water, 100cm^3 of 0.2M KNO_3, 10cm^3 of 0.4M Schiff base and a magnetic stirring bar before the electrodes of a standardized meter were introduced. A 10cm^3 of standardized aqueous NaOH was added dropwise with stirring. After each 0.5cm^3 addition, the amount of NaOH solution and the corresponding pH were recorded. Points in the 20 to 80 percent titration range were used to calculate the pKa (Gregory *et al.,* 1978).

Determination of Stability Constant of Complexes

Into a 400cm^3 beaker 100cm^3 of 0.2M KNO_3, 1mmole of metal (II) chloride, 0.1M HNO_3 and 90cm^3 of distilled water were added, respectively. A magnetic stirring bar and sodium salt of the Schiff base, prepared by neutralizing a known quantity of the Schiff base with calculated amount of standardized NaOH solution. After each 0.2cm^3 aliquot addition, the corresponding pH of the stirred reaction mixture was recorded. From the results obtained, stability constant of the complex compound and the number of the coordinated ligands per metal ion were determined (Gregory, *et al* 1978).

RESULTS AND DISCUSSION

The ligand prepared is crystalline orange, it is soluble in common organic solvents but insoluble in water. The manganese (II) and nickel (II) Schiff base complexes prepared are crystalline brown and have decomposition temperatures 206^{o}C and 245^{o}C, respectively. These high decomposition temperatures revealed the stability of the complex compounds (Table 1), which is common with such complexes. The solubility tests carried out on the ligand and its nickel(II) complex showed that they are soluble in most common organic solvents but insoluble in water, indicating that the compounds are not ionic. However, the manganese(II) schiff base complex is insoluble in such solvents except dimethyl sulphoxide (Table 2). The molar conductance measurements of the complexes in 10^{-3}M dimethylsulphoxide is in the range 17.39 – 18.12cm^2 ohm^{-1} mol^{-1}, which are relatively low, indicating their non-electrolytic nature (Table 3). The IR spectral data of the ligand showed a band at 1619cm^{-1}, which is assigned to ν(C=N) stretching vibration, a feature found in Schiff bases (Jezowska et al, 1988). This band is also observable in the complex compounds, suggesting that the ligand is coordinated to the respective metal ions, resulting in the formation of the two complexes (Prabhu and Dodwad, 1986). The bands in the regions 511-556cm^{-1} and 450-485cm^{-1} are attributed to ν(M-O) and ν(M-N) stretching vibrations respectively, confirming the coordination of the Schiff base to the respective metal ions. The broad band in the region 3350-3560cm^{-1} is accorded to ν(O—H) stretching vibrations, a feature indicating the presence of water (Table 4). The water analysis of the complexes suggested two water molecules per complex compound. According to a similar work by Morad et al. (2007), one of the two water molecules is coordinated to the metal ion, and the other is water of hydration. The dissociation constant (pKa) of the Schiff base is 5.95, suggesting weak acid (Table 5). The stability constants of Mn (II) and Ni (II) Schiff base complexes are 1.0 x 10^{13} and 3.98x10^{14}, respectively, indicating reasonable stability of the complexes, supported by high decomposition temperatures shown in Table 1. The potentiometric studies also suggested 1:1 metal – ligand ratio for the manganese (II) and nickel (II) complexes, respectively (Tables 6 and 7).

From the analyses of the complexes the general molecular structure has been proposed below:

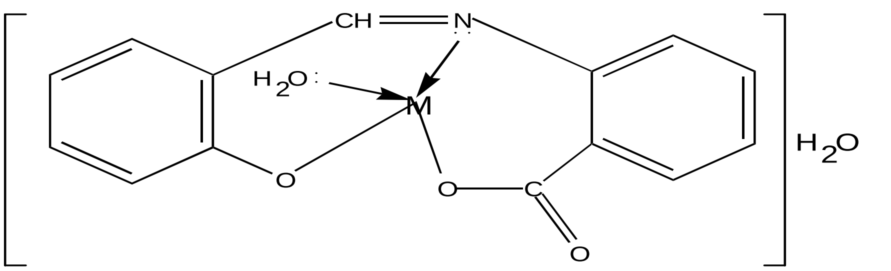

Fig. 1: The molecular structure of the complexes, where M is Mn(II) or Ni(II)

Table 1: The percentage yield, colour, decomposition temperature of the compounds

Compound	Colour	% yield	Decomposition Temp (^0C)
$[MnLH_2O]H_2O$	Pale brown	61.50	206
$[NiLH_2O]H_2O$	Pale brown	83.64	215

Table 2: The Solubility of the compounds in some common organic solvents.

Compound	Water	Methanol	Ethanol	Acetone	DMSO	Ether	Acetonitrile	Nitrobenzene	Tetrachloro methene
$MnL[H_2O]H_2O$	IS	S	S	S	S	IS	IS	S	IS
$NiL[H_2O]H_2O$	IS	IS	IS	IS	S	IS	IS	IS	IS

Key: IS = insoluble, S = soluble

Table 3: The molar conductivity measurements of the compounds in 10^{-3}M DMSO

Complex	Concentration moldm^{-3}	Specific Conductance (Ohm^{-1}cm^2)	Molar conductance (Ohm^{-1}Sm^{2}mol^{-1})
$[MnL\ H_2O]\ H_2O$	$1.0x\ 10^{-3}$	$18.12\ x\ 10^{-6}$	18.12
$[NiLH_2O]\ H_2O$	$1.0x\ 10^{-3}$	$17.39\ x\ 10^{-6}$	17.39

Table 4: The IR spectra of the Schiff base and the complexes

Compound	ν(C=N) (cm^{-1})	ν(O-H) (cm^{-1})	ν(M-O) (cm^{-1})	ν(M-N) (cm^{-1})
Schiff base	1619	3350-3560	-	-
$(MnL\ H_2O)\ H_2O$	1620	3360-3570	511-556	450-485
$[NiL\ H_2O]\ H_2O$	1618	3355-3560	520-560	440-470

Table 5: The dissociation constant (pKa) of the Schiff base

S/N	Vol. of NaOH (Cm^3)	pH	[Na$^+$] x 10^{-3}	[H$^+$]x10^{-5}	[OH]x10^{-10}	pKa
1.	0.5	3.66	1.22	29.2	62.3	4.36
2.	1.0	3.94	2.44	7.68	1.22	4.96
3.	1.5	4.17	4.86	3.35	2.93	4.97
4.	2.0	4.30	5.65	4.52	2.32	4.99
5.	2.5	4.48	6.05	2.22	5.30	5.01
6.	3.0	4.68	7.24	1.32	8.03	5.12
7.	3.5	4.84	8.24	0.583	0.184	5.25
8.	4.0	5.06	8.43	0.583	0.184	5.25
9.	4.5	5.35	9.61	0.299	0.305	5.52
10.	5.0	5.93	10.8	0.0786	0.595	5.90

Average pKa = 5.95

Table 6: Determination of the number of coordinated Schiff base per manganese (II) ion

S/N	Vol. of NaOH (Cm^3)	pH	[H$^+$] x 10^{-3}	[OH$^-$]x10^{-11}	Ň	Log [A$^-$]
1	2.2	2.31	3.35	0.48	0.5	-8.55
2	2.4	2.33	3.13	0.52	0.5	-8.25
3	2.6	2.35	2.99	0.57	0.7	-7.82
4	2.8	2.37	2.85	0.57	0.7	-7.82
5	3.0	2.40	2.66	0.61	0.7	-7.69
6	3.2	2.42	2.54	0.64	0.8	-7.58
7	3.4	2.43	2.48	0.66	0.8	-7.47
8	3.6	2.45	2.37	0.68	0.9	-7.37
9	3.8	2.48	2.22	0.73	0.9	-7.28
10	4.0	2.50	2.12	0.77	1.0	-7.16
11	4.2	2.52	2.02	0.80	1.0	-7.05
12	4.4	2.55	1.89	0.86	1.1	-7.02
13	4.6	2.57	1.80	0.90	1.1	-6.85
14	4.8	2.59	1.72	0.94	1.2	-6.74
15	5.0	2.60	1.68	1.30	1.3	-6.65
16	5.2	2.63	1.57	1.03	1.4	-6.53
17	5.4	2.65	1.50	1.08	1.4	-6.53
18	5.6	2.66	1.43	1.11	1.5	-6.35
19	5.8	2.69	1.37	1.19	1.6	-6.25
20	6.0	2.71	1.31	1.24	1.6	-6.20

Table 6 Continue

S/N	Vol. of NaOH (Cm3)	pH	[H+] x 10-3	[OH-]x10-11	Ň	Log [A-]
21	6.2	2.73	1.25	1.03	1.7	-6.18
22	6.4	2.76	1.16	1.40	1.8	-6.14
23	6.6	2.78	1.11	1.46	1.8	-5.76
24	6.8	2.81	1.04	1.57	1.9	-6.06
25	7.0	2.83	0.99	1.64	2.0	-6.03
26	7.2	2.85	0.95	1.72	2.0	-6.00
27	7.4	2.87	0.90	1.80	2.1	-5.97
28	7.6	2.90	0.84	1.93	2.2	-5.97
29	7.8	2.92	0.81	2.02	2.2	-5.96
30	8.0	2.94	0.77	2.11	2.3	-5.96

Average ñ =1.36

Table 7: Determination of the number of coordinated Schiff base per nickel (II) ion

S/N	Vol. of NaOH (Cm^3)	pH	$[H^+] \times 10^{-3}$	$[OH^-] \times 10^{-12}$	Ñ	Log (A^-)
1.	2.2	2.27	3.58	4.51	0.6	-9.61
2.	2.4	2.29	3.43	4.73	0.6	-9.42
3.	2.6	2.31	3.28	4.95	0.7	-8.28
4.	2.8	2.32	3.20	5.	0.7	-9.17
5.	3.0	2.34	3.06	5.30	0.8	-9.05
6.	3.2	2.35	2.99	5.43	0.8	-8.88
7.	3.4	2.37	2.85	5.68	0.9	-8.91
8.	3.6	2.39	2.73	5.95	0.9	-8.83
9.	3.8	2.41	2.60	6.23	1.0	-8.77
10.	4.0	2.43	2.49	6.52	1.0	-8.71
11.	4.2	2.45	2.37	6.83	1.1	-8.60
12.	4.4	2.46	2.32	6.99	1.1	-8.54
13.	4.6	2.48	2.22	7.32	1.2	-8.49
14.	4.8	2.49	2.17	7.49	1.2	-8.41
15.	5.0	2.51	2.07	7.84	1.3	-8.34
16.	5.2	2.53	1.98	8.21	1.3	-8.28
17.	5.4	2.55	1.89	8.60	1.4	-8.19
18.	5.6	2.56	1.84	8.80	1.4	-8.06
19.	5.8	2.58	1.76	9.22	1.5	-7.94
20.	6.0	2.60	1.68	9.87	1.5	-7.78
21.	6.2	2.63	1.57	10.3	1.6	-7.42
22.	6.4	2.64	1.53	10.6	1.6	-7.24
23.	6.6	2.66	1.46	11.1	1.7	-7.10
24.	6.8	2.68	1.40	11.6	1.7	-6.95
25.	7.0	2.71	1.31	12.4	1.8	-7.73
26.	7.2	2.73	1.25	13.0	1.8	-6.65
27.	7.4	2.76	1.16	14.0	1.9	-6/50
28.	7.6	2.79	1.09	15.0	1.9	-6.43
29.	7.8	2.82	1.01	16.0	2.0	-6.36
30.	8.0	2.85	0.945	17.2	2.1	-6.34

Average number of coordinated ligands (ñ) = 1.37

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