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SYNTHESIS AND INVESTIGATIONS ON IRON (II) SCHIFF BASE DERIVED FROM 2-HYDROXYBENZYLALDEHYDE AND L-VALINE**H. N. Aliyu and S. Isyaku**

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*Correspondence author: hnuhu2000@yahoo.com**ABSTRACT**

A Schiff base was prepared from the reaction of 2-hydroxybenzylaldehyde and L-valine as reported. The reaction of the Schiff base with iron (II) chloride gave N – (2 – hydroxybenzyl) - L - α - valine iron (II) complex compound. The Schiff base is a crystalline white, has a yield of 66 percent and a melting point of 225°C. The complex compound is pale brown, has a yield of 62% and decomposition temperature of 278°C. The ligand and its iron (II) complex compound are insoluble in most common solvents but are soluble in ethanol-water mixture. The molar conductance of the complex compound determined is 6.4 ohm cm² mol⁻¹. The infra-red spectral measurement of the ligand and its iron (II) complex compound showed bands in the range 1510 -1530cm⁻¹, assignable to ν (C=N) stretching vibrations. The broad bands in the range 3271 - 3415cm⁻¹ observed in the ligand and iron (II) Schiff base complex are assigned to ν (O-H) stretching vibrations. The dissociation constant (pKa) of the Schiff base determined is 8.84. The ratio of the Schiff base to the iron (II) ion in the complex determined using pH measurements is 1:1.

Keywords: N – (2 – hydroxybenzyl) - L - α - valine, Ligand, Schiff base, complex, 2-hydroxybenzaldehyde, stability constant, potentiometry.

INTRODUCTION

Schiff bases are compounds containing the azomethine group, -C=N-, which are usually obtained by the condensation of an aldehyde or ketone with primary amine (Holm *et al.*, 1966). Schiff base named after Hugo Schiff (1864) is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by a carbon – nitrogen double bond (C=N) with the nitrogen atom connected to an aryl or alkyl group (Schiff bases are of the general formula R₁R₂C=NR₃, where R₃ is an aryl or alkyl group that makes the Schiff base a stable imine (Henry and Lange, 1977). 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). Recently, Gupta *et al.* (2002) reported the synthesis and characterization of cobalt (II) N, N' - bis(acetylacetonate)ethylenediiminato complex from the interaction of cobalt (II) salt and N, N' - bis(acetylacetonate)ethylenediimine Schiff base ligand. In another report, Xishi *et al.* (2003) described the synthesis and spectroscopic properties of manganese (II), cobalt (II) and copper (II) complexes with novel Schiff base ligand derived from 2, 2' bis(p-methoxyphenylamine) and salicylic aldehyde.

Transition metal Schiff base complexes are used as catalysts, e.g. synthetic iron (II) schiff base complex exhibits catalytic activities towards electro-reduction of oxygen (Chakraborty *et al.*, 1994). Some metal complexes of polymer bound Schiff base show catalytic activity on decomposition of hydrogen peroxide and oxidation of ascorbic acid (Sreekala *et al.*, 2004). Schiff base derived from furylglyoxal and p-toluidene shows antibacterial activity against *Escherichia coli*, *staphylococcus aureus*, *bacillus*

subtilis and *proteus vulgaris* (Bhardwaj and Singh, 1994).

This paper reports the studies on complex compound formed by Schiff base derived from 2-hydroxybenzylaldehyde and L-valine with cobalt (II) ion

MATERIALS AND METHODS

All glass wares used were well washed with a detergent, rinsed with distilled water and dried in an oven before use. Weightings were carried out on digital balance model, AB 54 to four decimal places. Infrared spectral analyses were recorded using a Nicolade IR 100 model in Nujol in the range 400 – 4000cm⁻¹. pH measurements were also carried out using Jenway pH Meter model 3320 and electrical conductance using conductivity meter, model 4010-Jenway.

Preparation of N – (2 – hydroxybenzyl) - L - α - valine

To a solution of the L-valine (1.17g, 10mmol) in 10cm³ of water containing sodium hydroxide (0.40g, 10mmol) was added salicylaldehyde (1.22g, 10mmol) in ethanol (10cm³). The yellow solution was stirred for 30 minutes at room temperature prior to cooling in an ice bath. The intermediate Schiff base solution was carefully adjusted to pH range 6.0 – 7.0 with hydrochloric acid, then excess potassium borohydrate KBH₄ (0.46g, 12mmol) was added drop wise with gentle stirring. The resultant yellow solution was acidified to pH 3.0 – 5.0 with concentrated hydrochloric acid and it was left to stand for one hour. The resulting solid was separated, washed with methanol and diethylether, dried and then re-crystallized from water – ethanol (H₂O – EtOH)(1:1).

Preparation of N-(2-hydroxybenzyl)-l-α-Valine Iron (II) Complex

0.01mol of iron (II) chloride solution was treated separately with H₂O – EtOH (1:1) solution of Schiff base in the ratio 1:1, followed by drop wise addition of ammonia. The mixture was refluxed for 3 – 4 hours. Upon standing for 48 hours, the N-(2 – hydroxybenzyl) - L - α - valine iron (II) was separated, filtered and washed with methanol followed by ether and dried in an oven at 50°C.

Determination of Dissociation Constant of N-(2-hydroxybenzyl)-l-α-Valine

To 400cm³ beaker were added 90cm³ of distilled water, 100cm³ of 0.2M KNO₃, 10cm³ of 0.4M N-(2-hydroxybenzyl)-l-α-Valine Schiff base and a magnetic bar before the electrodes of a standardized meter were introduced. 10cm³ of standardized 0.4M NaOH solution was added dropwise with constant stirring. After each 0.5cm³ addition, the amount of NaOH solution and the corresponding pH were recorded; points in 20 to 80 percent titration range were recorded and the pK_a calculated as reported by Gregory (1972).

Determination of Stability Constant of N-(2-hydroxybenzyl)-l-α-Valine Iron (II) Complex

Into a 400cm³ beaker were added 90 cm³ of distilled water, 100cm³ 0.2M KNO₃, 10cm³ of 0.1M HNO₃ acid, and one millimole of iron (II) chloride tetrahydrate, respectively. 0.2cm³ of 0.4M sodium salt of N-(2-hydroxybenzyl)-l-α-Valine Schiff base was added and after each addition with stirring the corresponding pH value was recorded. The sodium salt of Schiff base was prepared by exactly neutralizing a weighed solid N-(2-hydroxybenzyl)-l-α-Valine Schiff base with a calculated amount of standardized 0.48M NaOH and diluting the solution with ethanol-water mixture to a total volume of 20 cm³ (Gregory *et al.*, 1978).

RESULTS AND DISCUSSION

Reaction of the solutions of L-valine in water and salicylaldehyde in ethanol formed N-(2 –

hydroxybenzyl) - L - α - valine Schiff base, which is crystalline white, has a yield of 66% and melting point of 225°C. The interaction of the prepared N-(2 – hydroxybenzyl) - L - α - valine schiff base with iron (II) tetrahydrate gave a pale blue crystalline N-(2 – hydroxybenzyl) - L - α - valine iron (II) complex, has a yield of 68% and a decomposition temperature of 282°C, indicating a stable compound (Table 1). The N-(2 – hydroxybenzyl) - L - α - valine Schiff base and its iron (II) complex are insoluble in common solvents, but are soluble in ethanol/water mixture (Table 2). The molar conductance of the complex compound determined is 6.4 ohm cm² mol⁻¹, suggesting that it is a non electrolyte (Table 3). The infra-red spectral data of the N-(2 – hydroxybenzyl) - L - α - valine schiff base showed a band in the region 1510 - 1530cm⁻¹, attributable to ν(C=N) stretching vibrations. In the complex, this same band is observable at lower frequency in the rage 1480 - 1510cm⁻¹, revealing coordination of the Schiff base to the iron (II) ion ((Jezowska *et al.*, 1988; Abdulsamath *et al.*, 1992). The far infrared spectra of the complex showed bands in the range 364 - 395cm⁻¹ and 437 - 463cm⁻¹, which are assigned to ν(Fe-O) and ν(Fe-N) stretching vibrations respectively, confirming coordination of the N-(2 – hydroxybenzyl) - L - α - valine Schiff base to the iron (II) ion (Silverstein and Bassler, 1967; Koji, 1977). The broad band in the Schiff base observed in the range 3285 - 3415 cm⁻¹ is attributable to ν(O-H) stretching vibrations, which is visible within lower frequency range 3271 – 3403cm⁻¹ in the Schiff base iron (II) complex, suggesting presence of water in the complex (Table 4). The dissociation constant (pKa) of N-(2 – hydroxybenzyl) - L - α - valine Schiff base determined is 8.84, revealing a weak acid (Table 5). The ratio of iron (II) ion to the Schiff base determined potentiometrically is 1:1 (Table 6).

From the analytical results of the iron (II) complex and a published structure from similar work, the following molecular structure is proposed.

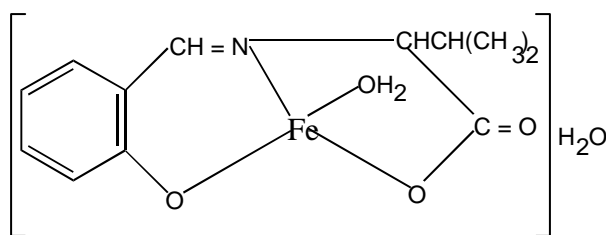


Figure 1: The proposed molecular structure of N-(2 – hydroxybenzyl) - L - α - valine iron (II) complex

Table 1: Some physical properties of the schiff base and its iron (II) complex

Compound	Colour	Melting Point (°C)	Decomposition Temp. (°C)	Per cent Yield (%)
Schiff base	White	225	-	66
[FeL(H ₂ O)].H ₂ O	Blue	-	278	62

Key: L = N-(2 – hydroxybenzyl) - L - α - valine Schiff base

Table 2: Solubility of the Schiff base and its iron (II) complex in some solvents

Compound	Water	Methanol	Ethanol	Acetone	Nitrobenzene	Chloroform	DMSO
Schiff base	SS	IS	IS	IS	IS	IS	IS
[FeL(H ₂ O)].H ₂ O	SS	IS	IS	IS	IS	IS	IS

Key: S = Soluble, IS = Insoluble, SS = Slightly soluble

Table 3: Conductivity measurement of the Schiff base and its iron (II) complex

Compound	Molar Conductance (Ohm ⁻¹ cm ² mol ⁻¹)
[FeL(H ₂ O)].H ₂ O	6.4

Table 4: Infra red spectral data of the Schiff base and its iron (II) complex

Compound	$\nu(\text{C=N})$ (cm ⁻¹)	$\nu(\text{O-H})$ (cm ⁻¹)	$\nu(\text{M-O})$ (cm ⁻¹)	$\nu(\text{M-N})$ (cm ⁻¹)
Schiff base	1510 – 1530	3285 – 3415	-	-
[FeL(H ₂ O)].H ₂ O	1480 - 1510	3271 - 3403	364- 395	437 – 463

Table 5: Determination of dissociation constant (pK_a) of the Schiff base

S/No	Vol of NaOH (cm ³)	pH	Moldm ⁻³ [H ⁺]	Moldm ⁻³ [OH ⁻]	Moldm ⁻³ [Na ⁺]	A _{tot}	pK _a
1.	0.5	7.39	2.7x10 ⁻⁸	2.7x10 ⁻⁸	1.15x10 ⁻³	19.95x10 ⁻³	8.78
2.	1.0	7.76	1.2x10 ⁻⁸	1.2x10 ⁻⁸	2.29x10 ⁻³	19.90x10 ⁻³	8.81
3.	1.5	7.96	7.3x10 ⁻⁹	7.3x10 ⁻⁹	3.42x10 ⁻³	19.85x10 ⁻³	8.80
4.	2.0	8.18	4.4x10 ⁻⁹	4.4x10 ⁻⁹	4.56x10 ⁻³	19.80x10 ⁻³	8.88
5.	2.5	8.34	3.1x10 ⁻⁹	3.1x10 ⁻⁹	5.68x10 ⁻³	19.75x10 ⁻³	8.90
6.	3.0	8.44	2.4x10 ⁻⁹	2.4x10 ⁻⁹	6.80x10 ⁻³	19.70x10 ⁻³	8.90
7.	3.5	8.45	2.4x10 ⁻⁹	2.4x10 ⁻⁹	7.91x10 ⁻³	19.65x10 ⁻³	8.79
8.	4.0	8.54	1.9x10 ⁻⁹	1.9x10 ⁻⁹	9.02x10 ⁻³	19.60x10 ⁻³	8.79
9.	4.5	8.64	1.5x10 ⁻⁹	1.5x10 ⁻⁹	10.12x10 ⁻³	19.55x10 ⁻³	8.79
10.	5.0	8.74	1.2x10 ⁻⁹	1.2x10 ⁻⁹	11.22x10 ⁻³	19.51x10 ⁻³	8.79
11.	5.5	8.84	9.7x10 ⁻¹⁰	9.7x10 ⁻¹⁰	12.31x10 ⁻³	19.46x10 ⁻³	8.77
12.	6.0	9.01	6.5x10 ⁻¹⁰	6.5x10 ⁻¹⁰	13.40x10 ⁻³	19.42x10 ⁻³	8.84
13.	6.5	9.16	4.6x10 ⁻¹⁰	4.6x10 ⁻¹⁰	14.50x10 ⁻³	19.37x10 ⁻³	8.86
14.	7.0	9.36	2.9x10 ⁻¹⁰	2.9x10 ⁻¹⁰	15.56x10 ⁻³	19.32x10 ⁻³	8.91
15.	7.5	9.57	1.8x10 ⁻¹⁰	1.8x10 ⁻¹⁰	16.63x10 ⁻³	19.28x10 ⁻³	8.93
16.	8.0	10.05	6.0x10 ⁻¹¹	6.0x10 ⁻¹¹	17.69x10 ⁻³	19.23x10 ⁻³	9.08
17.	8.5	10.44	2.4x10 ⁻¹¹	2.4x10 ⁻¹¹	18.75x10 ⁻³	19.18x10 ⁻³	9.05
18.	9.0	10.55	1.9x10 ⁻¹¹	1.9x10 ⁻¹¹	19.81x10 ⁻³	19.14x10 ⁻³	8.94
19.	9.5	10.68	1.4x10 ⁻¹¹	1.4x10 ⁻¹¹	20.86x10 ⁻³	19.09x10 ⁻³	8.75
20.	10.0	10.78	1.1x10 ⁻¹¹	1.1x10 ⁻¹¹	21.90x10 ⁻³	19.05x10 ⁻³	8.59

Average dissociation constant (pK_a) = 8.84

Table 6: Determination of the number of Schiff base chelated (n) to iron (II) ion

S./No	Vol (cm ³)	pH	[H ⁺]	[OH ⁻]	Log[A ⁻]	M _{tot}	n
1.	2.2	2.38	2.789x10 ⁻³	5.790x10 ⁻¹²	-2.6661	4.946x10 ³	0.444
2.	2.4	2.40	2.664x10 ⁻³	6.063x10 ⁻¹²	-2.6426	4.941x10 ³	0.499
3.	2.6	2.41	2.603x10 ⁻³	6.204x10 ⁻¹²	-2.6321	4.936x10 ³	0.567
4.	2.8	2.43	2.486x10 ⁻³	6.497x10 ⁻¹²	-2.6117	4.931x10 ³	0.624
5.	3.0	2.45	2.374x10 ⁻³	6.803x10 ⁻¹²	-2.5931	4.926x10 ³	0.682
6.	3.2	2.47	2.267x10 ⁻³	7.124x10 ⁻¹²	-2.5761	4.921x10 ³	0.741
7.	3.4	2.49	2.165x10 ⁻³	7.459x10 ⁻¹²	-2.5605	4.916x10 ³	0.800
8.	3.6	2.50	2.116x10 ⁻³	7.633x10 ⁻¹²	-2.5535	4.912x10 ³	0.871
9.	3.8	2.52	2.021x10 ⁻³	7.993x10 ⁻¹²	-2.5397	4.907x10 ³	0.932
10.	4.0	2.54	1.930x10 ⁻³	8.370x10 ⁻¹²	-2.5270	4.902x10 ³	0.994
11.	4.2	2.56	1.843x10 ⁻³	8.764x10 ⁻¹²	-2.5151	4.900x10 ³	0.055
12.	4.4	2.58	1.760x10 ⁻³	9.177x10 ⁻¹²	-2.5042	4.892x10 ³	0.120
13.	4.6	2.60	1.681x10 ⁻³	9.609x10 ⁻¹²	-2.4939	4.888x10 ³	0.184
14.	4.8	2.62	1.605x10 ⁻³	10.062x10 ⁻¹²	-2.4844	4.883x10 ³	0.249
15.	5.0	2.63	1.569x10 ⁻³	10.297x10 ⁻¹²	-2.4803	4.878x10 ³	0.322
16.	5.2	2.65	1.498x10 ⁻³	10.782x10 ⁻¹²	-2.4717	4.873x10 ³	0.387
17.	5.4	2.67	1.431x10 ⁻³	11.290x10 ⁻¹²	-2.4637	4.869x10 ³	1.454
18.	5.6	2.69	1.366x10 ⁻³	11.822x10 ⁻¹²	-2.4562	4.864x10 ³	1.521
19.	5.8	2.71	1.305x10 ⁻³	12.379x10 ⁻¹²	-2.4493	4.859x10 ³	1.589
20.	6.0	2.73	1.246x10 ⁻³	12.963x10 ⁻¹²	-2.4427	4.854x10 ³	1.651
21.	6.2	2.75	1.190x10 ⁻³	13.574x10 ⁻¹²	-2.4366	4.850x10 ³	1.725
22.	6.4	2.77	1.136x10 ⁻³	14.213x10 ⁻¹²	-2.4307	4.845x10 ³	1.794
23.	6.6	2.79	1.085x10 ⁻³	14.883x10 ⁻¹²	-2.4254	4.840x10 ³	1.864
24.	6.8	2.82	1.013x10 ⁻³	15.948x10 ⁻¹²	-2.4176	4.836x10 ³	1.929
25.	7.0	2.83	0.990x10 ⁻³	16.319x10 ⁻¹²	-2.4156	4.831x10 ³	2.007
26.	7.2	2.86	0.924x10 ⁻³	17.088x10 ⁻¹²	-2.4087	4.826x10 ³	2.072
27.	7.4	2.88	0.882x10 ⁻³	18.310x10 ⁻¹²	-2.4045	4.822x10 ³	2.143
28.	7.6	2.91	0.823x10 ⁻³	19.620x10 ⁻¹²	-2.3986	4.817x10 ³	2.211
29.	7.8	2.94	0.768x10 ⁻³	21.023x10 ⁻¹²	-2.3932	4.812x10 ³	2.250
30.	8.0	2.99	0.685x10 ⁻³	23.588x10 ⁻¹²	-2.3848	4.808x10 ³	2.362

Average number of Schiff base coordinated to iron = 1.37

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