Biokemistri
Vol. 22, No. 2, December 31, 2010
Printed in Nigeria

0795-8080/2010 $5.00 + 0.00

http://www.niseb.org/bkr
Also available online at http://www.bioline.org.br/bk

BKR 2010146/22204

Spectroscopic and Potentiometric Studies of N-(2-Hydroxybenzyl)-L-α-Valine Cobalt (II) Complex

H. N. Aliyu and S. Isyaku

Department of Chemistry Bayero University, P. M. B. 3011, Kano, Nigeria
E-mail: hnuhu2000@yahoo.com

(Received September 16, 2010; Accepted November 4, 2010)

ABSTRACT: A Schiff base was prepared from the reaction of 2-hydroxybenzylaldehyde and L-valine. The reaction of the Schiff base and cobalt (II) chloride formed 2-hydroxybenzylaldehyde and L-valine cobalt (II) complex. The Schiff base is crystalline white and has a yield of 66%. The prepared complex is pale brown, has a yield of 68% and decomposition temperature of 274^oC. The Schiff base and its cobalt (II) complex are insoluble in most common solvents however they are soluble in ethanol-water mixture. The molar conductance of the cobalt (II) Schiff base complex compound determined is 5.2 ohm cm^2 mol^{-1}. The infra-red spectra of the Schiff base showed band in the range 1480 -1520cm^{-1}, assignable to v(C=N) stretching vibrations, the same band is observable in the cobalt (II) Schiff base complex. The broad band in the range 3270 - 3420cm^{-1} observed in Schiff base is assigned to v(O-H) stretching vibrations. The dissociation constant (pKa) of N – (2 – hydroxybenzyl) - L - α - valine Schiff base determined is 8.84. The average number of the Schiff base to cobalt (II) ion is 1 (one).

Key Words : Schiff base; Cobalt (II) complex; 2-Hydroxybenzaldehyde; L-valine; **S**tability constant; Potentiometry.

Introduction

N – (2 – hydroxybenzyl) - L - α - valine belongs to a group of chemical compounds called, Schiff bases, which are compounds containing the azomethine (-C=N-) group. They are usually obtained by the condensation of an aldehyde or ketone with primary amine (Holm *et al*., 1966). Schiff base 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 $R_1R_2C=NR_3$, where R_3 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, however, there was no comprehensive, systematic study until the preparative work of Pfeiffer and associates (1931), in which they reported a series of complexes derived from Schiff bases of salicylaldehyde and its substitution products. Delephine (1898) prepared complexes by reacting metal acetate, salicyladehyde and a primary amine in alcohol and demonstrated 2:1 stoichiometry (Holm *et al*., 1966). Recently, Gupta *et al*. (2002) reported the synthesis and characterization of cobalt (II) N, N' - bis(acetylacetone)ethylenediiminato complex from the interaction of cobalt (II) salt and N, N'- bis(acetylacetone)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-methoxylphenylamine) and salicylic aldehyde.

Schiff bases and their complex compounds have been studied for their important properties, for example, thiazole and benzothiazole Schiff bases show effective antifungal activity (Dash et al., 1984). Some Schiff bases derived from quinazolinones show antifungal activity against *Candida albicans, Trichophyton rubrum, T. mentagrophytes, A. niger and Microsporum gypseum* (Rao et al., 1987). metal complexes of molybdenum (IV) and manganese (II) with Schiff base ligands derived from hydrazine carboxamide and hydrazine carbothiaamide show antibacterial activity against *S. aureus and xanthomonas compestris* (Singn *et al*., 1999). In another report, Guar (2003) explained that Schiff base complexes of copper (II) and nickel (II) show antibacterial activities to *Colibacillus and pseudomonas aeruginosa*.

This paper reports the Spectroscopic and Potentiometric Studies of N-(2-Hydroxybenzyl)-L-α-Valine Cobalt (II) Complex

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 Schiff Base

To a solution of the L-valine (1.17g, 10mmol) in 10cm^3 of water containing sodium hydroxide (0.40g, 10mmol) was added salicylaldehyde (1.22g, 10mmol) in ethanol (10cm^3). 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 KBH_4 (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 (H_2O – EtOH)(1:1).

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

0.01mol of cobalt (II) chloride solution was treated separately with H_2O – EtOH (1:1) solution of Schiff base in the ratio of 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 cobalt (II) was separated out, filtered and washed with methanol followed by ether and dried in an oven at 50^{0}C.

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

To 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 bar before the electrodes of a standardized meter were introduced. 10cm^3 of standardized 0.4M NaOH solution was added dropwise with constant stirring. After each 0.5cm^3 additions, the amount of NaOH solution and the corresponding $_P$H 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 the Cobalt (II) Complex

Into a 400cm^3 beaker were added 90 cm^3 of distilled water, 100cm^3 0.2M KNO_3, 10cm^3 of 0.1M HNO_3 acid, and one millimole of cobalt (II) chloride hexahydrate, respectively. 0.2cm^3 of 0.4M sodium salt of the Schiff base was added and after each addition with stirring the corresponding pH reading was recorded. The sodium salt of Schiff base was prepared by exactly neutralizing a weighed solid 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 cm^3 (Gregory *et al.,* 1978).

Results and Discussion

The interaction of L-valine and salicyladehyde gave a white crystalline N–(2 – hydroxybenzyl) - L - α - valine Schiff base. The reaction of the prepared N–(2 – hydroxybenzyl) - L - α - valine Schiff base with cobalt (II) chloride gave a pale brown N–(2 – hydroxybenzyl) - L - α - valine cobalt (II) complex, with percent yield of 68 and decomposition temperature 274°C, which is very high, indicating a stable compound (Table 1). The N–(2 – hydroxybenzyl) - L - α - valine Schiff base and its cobalt (II) complex compound are insoluble in common solvents, but are soluble in ethanol/water mixture (Table 2). The molar conductance of the complex compound determined is 5.2 ohm cm^2 mol^{-1}, suggesting that the complex is non electrolyte (Table 3).

The infra-red spectral analysis of the schiff base showed a band in the range 1480 - 1520cm^{-1}, assignable to *v*(C=N) stretching vibrations. This same band is observable at lower frequency within 1475 - 1510cm^{-1} in the complex compound, revealing coordination of the Schiff base to the cobalt (II) ion ((Jezowska et al, 1988; Abdulsamath *et al.*, 1992). The far infrared spectra of the complex showed bands in the range 335 - 350cm^{-1} and 380 - 450cm^{-1}, which are assigned to *v*(Mn-O) and *v*(Mn-N) stretching vibrations respectively, establishing coordination of the N–(2 – hydroxybenzyl) - L - α - valine Schiff base to the cobalt (II) ion (Silverstein and Bassler, 1967; Koji, 1977). The broad band in the Schiff base observed in the range 3270 - 3420 cm^{-1} is attributable to *v*(O-H) stretching vibrations, which is visible within lower frequency range 3245 – 3370cm^{-1} in the Schiff base cobalt (II) complex, suggesting water presence in the complex (Table 4). The dissociation constant (pKa) of the Schiff base determined is 8.84, indicating that it is a weak acid (Table 5). The ratio of cobalt (II) ion to N–(2 – hydroxybenzyl) - L - α - valine Schiff base determined potentiometrically is 1:1 (Table 6).

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

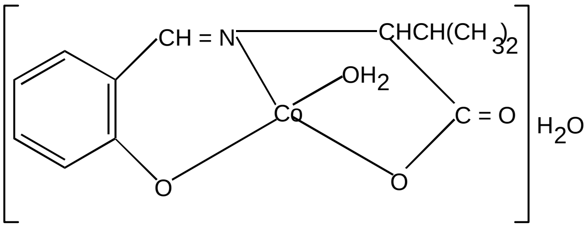

Fig.1: Molecular structure of N–(2 – hydroxybenzyl) - L - α - valine cobalt (II) complex

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

Compound	Colour	Melting Point (^oC)	Decomposition Temp. (^oC)	Per cent Yield (%)
Schiff base	White	225	-	66
$[CoL(H_2O)].H_2O$	Brown	-	242	65

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

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

Compound	Water	Methanol	Ethanol	Acetone	Nitrobenzene	Chloroform	DMSO
Schiff base	SS	IS	IS	IS	IS	IS	IS
$[CoL(H_2O)].H_2O$	SS	IS	IS	IS	IS	IS	IS

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

Compound	Molar Conductance ($Ohm^{-1}cm^2mol^{-1}$)
$[CoL(H_2O)].H_2O$	6.7

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

Compound	v(C=N) (cm^{-1})	v(O-H) (cm^{-1})	v(M-O) (cm^{-1})	v(M-N) (cm^{-1})
Schiff base	1495 – 1530	3257 - 3400	-	-
$[CoL(H_2O)].H_2O$	1470 - 1500	3260 - 3390	320- 345	366 - 430

Table 3.8: 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 cobalt (II) ion

S./No	Vol (cm^3)	pH	$[H^+]$	$[OH^-]$	$Log[A^-]$	M_{tot}	n
1.	2.2	3.18	$0.442x10^{-3}$	$36.534x10^{-12}$	-2.346	$4.946x10^3$	0.031
2.	2.4	3.38	$0.279x10^{-3}$	$57.903x10^{-11}$	-2.331	$4.941x10^3$	0.016
3.	2.6	3.79	$0.109x10^{-3}$	$1.488x10^{-10}$	-2.316	$4.936x10^3$	0.062
4.	2.8	5.70	$1.335x10^{-6}$	$1.210x10^{-8}$	-2.307	$4.931x10^3$	0.120
5.	3.0	6.27	$3.593x10^{-7}$	$4.495x10^{-18}$	-2.308	$4.926x10^3$	0.200
6.	3.2	6.45	$2.374x10^{-7}$	$8.564x10^{-8}$	-2.308	$4.921x10^3$	0.280
7.	3.4	6.55	$1.886x10^{-7}$	$8.564x10^{-8}$	-2.308	$4.916x10^3$	0.360
8.	3.6	6.64	$1.533x10^{-7}$	$10.537x10^{-8}$	-2.309	$4.912x10^3$	0.440
9.	3.8	6.70	$1.335x10^{-7}$	$12.098x10^{-8}$	-2.309	$4.907x10^3$	0.520
10.	4.0	6.75	$1.190x10^{-7}$	$13.574x10^{-8}$	-2.310	$4.902x10^3$	0.600
11.	4.2	6.79	$1.085x10^{-7}$	$14.883x10^{-8}$	-2.310	$4.900x10^3$	0.679
12.	4.4	6.83	$0.990x10^{-7}$	$16.319x10^{-8}$	-2.311	$4.892x10^3$	0.760
13.	4.6	6.86	$0.924x10^{-7}$	$17.486x10^{-8}$	-2.311	$4.888x10^3$	0.840
14.	4.8	6.90	$0.842x10^{-7}$	$19.173x10^{-8}$	-2.311	$4.883x10^3$	0.920
15.	5.0	6.93	$0.786x10^{-7}$	$20.545x10^{-8}$	-2.312	$4.878x10^3$	1.000
16.	5.2	6.95	$0.751x10^{-7}$	$21.513x10^{-8}$	-2.312	$4.873x10^3$	1.080
17.	5.4	6.98	$0.701x10^{-7}$	$23.051x10^{-8}$	-2.313	$4.869x10^3$	1.156
18.	5.6	7.00	$0.669x10^{-7}$	$24.138x10^{-8}$	-2.313	$4.864x10^3$	1.240
19.	5.8	7.02	$0.639x10^{-7}$	$25.276x10^{-8}$	-2.313	$4.859x10^3$	1.320
20.	6.0	7.03	$0.624x10^{-7}$	$25.864x10^{-8}$	-2.314	$4.854x10^3$	1.400
21.	6.2	7.05	$0.596x10^{-7}$	$27.083x10^{-8}$	-2.314	$4.850x10^3$	1.480
22.	6.4	7.08	$0.557x10^{-7}$	$29.020x10^{-8}$	-2.315	$4.845x10^3$	1.560
23.	6.6	7.10	$0.531x10^{-7}$	$30.388x10^{-8}$	-2.315	$4.840x10^3$	1.640
24.	6.8	7.13	$0.496x10^{-7}$	$32.561x10^{-8}$	-2.316	$4.836x10^3$	1.720
25.	7.0	7.15	$0.474x10^{-7}$	$34.096x10^{-8}$	-2.3159	$4.831x10^3$	1.800
26.	7.2	7.18	$0.442x10^{-7}$	$3.653x10^{-7}$	-2.3164	$4.826x10^3$	1.880
27.	7.4	7.20	$0.422x10^{-7}$	$3.826x10^{-7}$	-2.3169	$4.822x10^3$	1.960
28.	7.6	7.22	$0.403x10^{-7}$	$4.006x10^{-7}$	-2.3172	$4.817x10^3$	2.040
29.	7.8	7.25	$0.376x10^{-7}$	$4.292x10^{-7}$	-2.3177	$4.812x10^3$	2.120
30.	8.0	7.28	$0.351x10^{-7}$	$4.599x10^{-7}$	-2.3181	$4.808x10^3$	2.200

Average number of Schiff base coordinated to cobalt (II) = 1.047 (one)

References

Abdulsamath S., Raman M., Raman N., (1992), Complexes of Copper (II) cinnamalidene Transition Metal Chem. 17:13

Dash B., Mahapatra P. K., and Patnaik J. M., (1984). Fungicidal activities of Schiff base derived from p-hydroxobenzaldehydes and their derivatives, J. Indian chem. Soc., 61(2): 1061 – 1064.

Gregory, S., Thomas, B. R., Robert, J. A. (1978) "Synthesis and Techniques in Inorganic Chemistry" 3rd edition, Longman Publishers, London, 119-126.

Guar S. (2003). Physico-chemical and biological properties of manganese (II), cobalt (II), nickel (II) and copper (II chelates of Schiff bases, Asian Journal of chemistry, 15(2): 250-254.

Gupta S.K. Hitchcock and Kushwah Y.S. (2002), Synthesis, characterization and crystal structure of a Ni (ii) shiff base complex derived from acetylacetone and ethylene diamine; J. of coord. Chem...,55 (12), 1401-1407.

Henry P. M. and Lange G. L. (1977), The chemistry of double bonded functional groups, S. Patai , Interscience, New York, suppl. A, part 2, Pp 1067.

Holm R. H., Everett G. W., and Chakravorty A. (1966), Metal complexes of Schiff bases and β – ketoimines, Progr. Inorg. Chem., 7: 83 – 214.

Jezowska, B. Lisowski, J. and Chemielewski P. (1988) synthesis and spectroscopic studies of Schiff base complexes polyhedron, 7(5), 337-340.

Koji N., (1977); Infrared Absorption Spectroscopy, 2nd Edition, Holden-Day Inc, Sanfrancisco, 20-49

Rao N. R., Rao P. V., Reddy G. V. and Ganorkar M. C., (1987), Metal chelates of a physiologically active O:N:S tridentate Schiff base, Indian J. chem., 26(1): 887 -890.

Silverstein, S. M. and Bassler, G. C., (1967); "Spectrophotometric Identification of Organic Compounds", Willey, New York, pp. 12-23.

Singh R., Gupta N. and Fahmi S, (1999). Biochemical aspects of dioxomolybdenum (IV) and manganese (II) complexes, Indian Journal of Chemistry, 38A: 1150-1158.

Xishi, T., Xian, H. Y., Qiang, C. and Minyu, T., (2003), "Synthesis of Some Transition Metal Complexes of a Novel Schiff Base Ligand Derived from 2, 2' – Bis(p-Methoxy Phenylamine) and Salicylic Aldehyde", Molecules, 8: 439-443.