American Journal of Analytical Chemistry, 2016, 7, 446-451
Published Online May 2016 in SciRes. http://www.scirp.org/journal/ajac
http://dx.doi.org/10.4236/ajac.2016.75041

A New Schiff Base Derivatives Designed to Bind Metal Ion (Cu, Co): Thermodynamics and Biological Activity Studies

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Received 26 March 2016; accepted 10 May 2016; published 13 May 2016

Abstract

Schiff base synthesis is usually acid catalyzed and it usually requires refluxing the mixture of aldehydes and amine in ethanolic solution. Synthesis and characterization of Schiff base ligands derived from substituted amine and salicylaldehyde and their complexes (Cu^{2+}, Co^{2+}) are reported. The ligands and ligand-complexes were characterized by melting point, FTIR, CHN-elemental analysis and UV-Visible analysis. The UV-Visible and elemental analysis of complexes established (1:2) mole ratio (M:L). The stability constant and thermodynamic parameters (K, ΔG, ΔH, ΔS) were determined at different temperature (30 - 40)˚C which established that the metal-complexes were very stable. The review describes the promising biological activities of Schiff base and their metal complexes.

Keywords

Schiff Base Derivatives, Complexes, Thermodynamic Parameters, FTIR-Spectra, Mole Ratio Method, CHN Analysis, Biological Activity Studies

1. Introduction

Schiff base derived from an amine and carbonyl compound is an important class of ligands that coordinate to metal ions via azomethine nitrogen and has been studied extensively [1]. The characterization bond of Schiff base (C=N) has reversible nature which allows by hydrolysis, obtaining the initial corresponding aldehyde and amine compound [2] [3]. Schiff bases are known to be good chelating agents and easily prepared and characterized. Little interest has been given to their use for analytical purpose because of two serious drawbacks:

1) They are insoluble in aqueous solution.

How to cite this paper: Haddad, H.H. (2016) A New Schiff Base Derivatives Designed to Bind Metal Ion (Cu, Co): Thermodynamics and Biological Activity Studies. *American Journal of Analytical Chemistry*, **7**, 446-451.
http://dx.doi.org/10.4236/ajac.2016.75041

2) They decompose easily in acidic solution limiting their use to basic solution [4].

The chemistry of (C=N) double bond based complexes plays a vital role in the progress of chemistry and it has been found to possess the pharmacological activities such as malarial [5], anticancer [6], antibacterial [7]. Schiff base appears to be an important intermediate in a number of enzymatic reactions involving interaction of enzyme with an amino or carbonyl group of substitutes [8]. The aim of the study is the preparation of Schiff base derived from salicylaldehyde with a series of aniline derivatives. The structure of all Schiff bases was characterized by using FTIR spectra, CHN elemental analysis and UV-Visible. Their stability constant and their thermodynamic parameters such as (ΔE, ΔG, ΔH, and ΔS) were studied in different temperatures spectrophotometrically.

2. Experimental

2.1. Material and Instrumentation

All chemicals and solvents were purchased from Fluka and BDH chemical companies. Cobalt and copper acetate were dried over P_4O_{10} under vacuum for several days before use. Melting point was recorded on VeeGO Digital model VMP-D. Jenway. Elemental analyses (CHN) were performed by Perkin Elemer TGA. IR spectra used in the characterization of products were recorded Shimadzu, FTIR-8400S-JAPAN. UV/Vis absorption studies were measured in the region (200 - 800) nm using (10^{-4}) M solution in ethanolic solution using U.V-9200 BIOTECH ENGINEERN MANAGEMENT CO. LTD (UK) Single beam.

2.2. Preparation of Ligands

The Schiff base was synthesized by refluxing ethanolic solution of (2.44 gm - 0.02 mol) salicylaldehyde with (2.74 gm - 0.02 mol) of substituted (o-benzoic, m-benzoic, p-benzoic) aniline in 20 ml warm ethanolic solution (40˚C - 50˚C, to speed up the reaction), the ratio is (1:1) for two hours [9]. The ligand formed was filtered, washed, recrystallized from ethanol and then dried.

2.3. Preparation of Schiff Base Metal Complexes

An ethanolic solution of (2×10^{-2} M) Schiff base was added to (10^{-2} M) of metal ions (as dehydrated acetate salts). The mixture was stirred and refluxed for two hours. The solid coloured product obtained was filtered, washed and recrystallized from ethanol and then dried.

3. Result and Discussion

3.1. Physical Measurement

Physical measurements of the synthesized ligand and their metal complexes and their expected formula are shown in **Table 1**. Melting point gives an impression that the synthesis from Schiff base and their complexes are without any contaminated material.

Table 1. Physical properties of synthesized ligand and their metal complexes.

Compound	Colour	Yield	M.p.
L_1	yellow	78%	120
$Cu(L_1)_2$	sapphire	56%	187
$Co(L_1)_2$	mustard	71%	274
L_2	Yellow-green	82%	141
$Cu(L_2)_2$	Indigo	69%	263
$Co(L_2)_2$	Rose	62%	226
L_3	Silver	87%	101
$Cu(L_3)_2$	Azure	63%	190
$Co(L_3)_2$	Gray	52%	185

L_1 = o - position, L_2 = m - position, L_3 = p - position.

3.2. The Elemental Analyses (CHN) of Ligand and Their Metal Complexes

The data of element analysis (CHN) have shown that the results obtained are in good agreement with those calculated for suggested formula (**Table 2**).

3.3. IR Spectrum of Ligand and Their Ligand Metal Complexes

Table 3 shows the absence of band at 1735 cm^{-1} (C=O) due to carbonyl and 3315 cm^{-1} for NH_2 stretching vibration of strong new band appeared at 1630 cm^{-1} assigned to azomethine (HC=N) which indicates that amine and aldehyde of starting material are absent and have been converted into the new ligand. The IR spectra of complexes exhibited ligand bands with the appropriate Shifts due to complex formation (C=N) at (1630 cm^{-1}) in free ligand shift to (1620 cm^{-1}). The reduction in band order upon complexation can be attributed to delocalization of metal electron density to the π-system of the ligand. These Shifts confirm the coordination of the ligand via nitrogen of the azomethine to the metal ions (**Figure 1**). All lower frequency of complexes exhibited band around (400 - 600 cm^{-1}) assigned to the υ (M-N) [10] [11].

3.4. UV-Visible Spectrum of Ligand and Their Metal Complexes

Spectrophotometrically from the wide studied range of molar concentration (10^{-5} - 10^{-3} M) of the mixed solution only concentration of (10^{-4} M) obey Beer-lambert law and showed intense colour, A calibration curve was plotted on absorbance against molar concentration in the range of (1×10^{-4} - 3×10^{-4} M), best fit straight line, were obtained. The composition of complexes formed in solution has been established by mole ratio and continuous variation methods, in both cases the result reveals (1:2) (M:L) ratio.

Table 2. Elemental analysis data for schiff bases and their complexes.

Compound	Founded (calculated)		
	%C	%H	%N
L_1	69.91 (70)	4.11 (4.16)	5.75 (5.83)
$Cu(L_1)_2$	62.24 (62.27)	2.82 (2.96)	5.09 (5.18)
$Co(L_1)_2$	62.90 (62.81)	3.05 (2.99)	5.14 (5.23)
L_2	70.09 (70)	4.22 (4.16)	5.94 (5.83)
$Cu(L_2)_2$	62.26 (62.27)	2.93 (2.96)	5.25 (5.18)
$Co(L_2)_2$	62.89 (62.81)	2.89 (2.99)	5.18 (5.23)
L_3	69.83 (70)	4.25 (4.16)	5.87 (5.83)
$Cu(L_3)_2$	62.22 (62.27)	2.85 (2.96)	5.12 (5.18)
$Co(L_3)_2$	62.20 (62.81)	3.07 (2.99)	5.22 (5.23)

L_1= o - position, L2 = m - position, L_3 = p - position.

Table 3. IR spectra of Schiff base and its metal complexes.

Compound	CH *alphatic*	CH *aromatic*	C=O	C=N	C-N	C=C	OH
L_1	3400	3068	-	1616	1598	1425	1558
$Cu(L_1)_2$	3275	3115	2922	1598	1543	1357	1467
$Co(L_1)_2$	3307	-	-	1597	1541	1300	1448
L_2	3500	3055	2995	1622	1678	1365	1463
$Cu(L_2)_2$	3392	3066	2879	1614	1560	1305	1469
$Co(L_2)_2$	3396	3070	2881	1614	1598	1390	1477
L_3	3450	3074	2879	1680	1570	1431	1570
$Cu(L_3)_2$	3400	3018	2885	1614	1589	1398	1442
$Co(L_3)_2$	3433	-	2881	1602	1556	1409	1436

L_1 = o - position, L_2 = m - position, L_3 = p - position.

3.5. Determination the Stability Constant for Complexes

$$\alpha = \frac{A_m - A_s}{A_m} \tag{1}$$

where α = degree of analysis [12] [13], A_m = absorbance of equivalent amount of L:M, A_s = absorbance of excess amount of ligand with constant volume of metal.

$$K = \frac{1-\alpha}{4\alpha^3 C^2} \tag{2}$$

where C = concentration of the ligand which is equal the concentration of the metal.

3.6. The Thermodynamic Parameters

The thermodynamic parameters (**Table 4**) were calculated from their stability constant at different temperatures such as (ΔG, ΔH and ΔS) from the following equation [14] [15]:

$$\Delta G = -RT \ln K \tag{3}$$

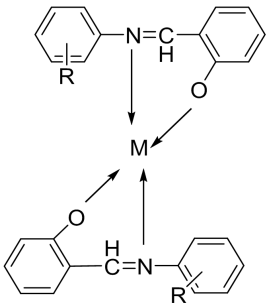
$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4}$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \tag{5}$$

where, K = Stability Constant, G = Free Energy, H = Enthalpy, S = Entropy.

3.7. Biological Activity

The biological activity were studied, the effect of schiff base derivatives and its complexes on two type of



M = Cu &Co
R = O–COOH, m-COOH, P-COOH

Figure 1. Suggest structure of metal—complexes Schiff base.

Table 4. Shows the difference stability at different temperature and then thermodynamic parameter was recorded.

Compound	λ_{max} nm	*at* 303					*at* 313			
		α	$K \times 10^8$	ΔH	ΔG	ΔS	α	K	ΔG	ΔS
L_1	396	-	-	-	-	-	-	-	-	-
$Cu(L_1)_2$	400	0.25	2.30	11.50	12.70	-65	0.27	2.00	10.50	-32
$Co(L_1)_2$	412	0.29	1.90	13.70	11.40	12	0.30	1.80	9.70	25
L_2	380	-	-	-	-	-	-	-	-	-
$Cu(L_2)_2$	391	0.31	1.70	10.90	12.90	24	0.33	1.50	8.70	13
$Co(L_2)_2$	396	0.19	2.70	15.80	13.20	33	0.22	2.10	9.30	-34
L_3	400	-	-	-	-	-	-	-	-	-
$Cu(L_3)_2$	408	0.22	2.60	11.00	14.90	53	0.25	2.30	11.30	41
$Co(L_3)_2$	415	0.31	1.70	13.80	12.30	-41	0.32	1.60	9.80	30

Table 5. The biological activity of ligand and their metal complexes.

Compound	Aeromomas hydrophila (−)	Staphylococcus aureus (+)
L_1	-	-
$Cu(L_1)_2$	-	12
$Co(L_1)_2$	-	10
L_2	-	10
$Cu(L_2)_2$	-	12
$Co(L_2)_2$	-	10
L_3	-	10
$Cu(L_3)_2$	-	12
$Co(L_3)_2$	-	10

L_1 = o - position, L_2 = m - position, L_3 = p - position.

Bacteria *Aeromomas hydrophila* (−) and *Staphylococcus aureus* (+) have been described in **Table 5**. The result show that the complexes have more toxicity against the bacterial species than free ligand. This can be attributed to the tweeds chelation theory [16] according to which the chelation reduces the polarity of metal ions mainly because of the partial sharing of its positive charge with donor group and possible electro delocalization over the whole ring.

4. Conclusion

Schiff base of [o-benzyl, m-benzyl, p-benzyl] aniline with salisaladehyed was synthesized and characterized by analytical and spectral, FTIR, CHN technique. These compounds exhibited significant biological activities.

Acknowledgements

The author thanks the Iraqi Government, Ministry of Higher Education and Basrah University for the financial support provided for this work. The author is thankful of the support of the college of Education and Iraq Marine Science Center, Basrah University in undertaking the antibacterial studies.

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