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SYNTHESIS AND ANALYSIS OF Cu(II) AND Co(II) COMPLEXES OF SCHIFF BASE DERIVED FROM GLYCINE AND ISATIN

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ABSTRACT

Reaction of ethanolic solutions of isatin and glycine gave a Schiff base. The reaction of the ethanolic solution of the Schiff base with Cu(II) and Co(II) chloride 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 were high. The Schiff base and its metal (II) complexes were soluble in water, ethanol and methanol. 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 $[ML_2].3H_2O$. The infrared spectral data shows bands observable in the range 494-672 cm^{-1} and 376-494 cm^{-1}in the Schiff base complex indicating metal oxygen (M-O) and metal nitrogen (M-N) bonds respectively, showing the coordination of the ligand to the metals. The stability constant were determined using UV spectroscopy, which were high ($4.0326x10^5$and $5.9615x10^5$) for complexes of Cu and Co respectively, while the Gibbs Free energy (ΔG) were found to be -31978.86 and -38652.19 $Jmol^{-1}$suggesting that the complexes were stable.

Keywords: Schiff base, Metal Complex, Stability constant, Isatin, UV spectroscopy.

INTRODUCTION

Schiff base is a type of ligand formed by condensation of primary amines with a ketone or an aldehyde. The resultant functional group RHC=N-R is called an imine; aldemines for aldehydes and ketoimines for ketones (Cotton, 1994) and is particularly used for binding metal ions via the N-atom lone pair, especially in combination with one or more donor atoms to form polydentate ligand. Schiff base complexes play an essential role in bio-inorganic activity, agriculture, pharmaceutical and industrial chemistry. For example aromatic Schiff bases and their metal complexes catalyse reactions on oxidation, hydrolysis, electro-reduction and decomposition (Kumar *et al.,* 2009). Schiff bases are suitable ligands for the preparation of catalyst due to the easy reaction conditions and the variety of chiral aldehydes used as precursor's example amino acids and peptides are particularly suitable for the creation of effective catalyst as indicated by Hoveyda and Snapper (1996).

Amino acids occur in nature and are classified into essentials i.e those that can be synthesized by the body e.g., Lysine, Methionine, Phenylalanine, Threonine, Valine, Tryptopan, Leucine, Isoleucine etc. and non-essentials amino acids which cannot be synthesized by the body such as Serine, Histidine, Proline, Tyrosine, Glycine, Alanine etc (Na'aliya, 2008).

This work describes the preparation of a Schiff base and its Cu (II) and Co(II) complexes derived from glycine and isatin. The Schiff base ligand was found to be chelating in a tridentate (ONO) manner.

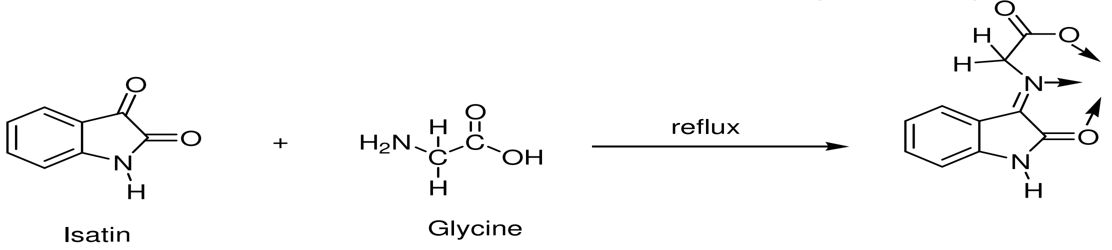
MATERIALS AND METHODS

Reagents of analytical grade purity and distilled water were used directly without further purification. All weighing were carried out on electric metler balance model AB54. Molar conductance was determined using Jenway model 4010.Absorbance measurements were carried out on CECIL CE 7400 UV spectrophotometer.

IR Spectral analysis was recorded on a Fourier Transformed spectrophotometer model IR Genesis series using KBr pellets. Melting point and decomposition temperature were determined on a Straut Scientific Melting Point apparatus Model SMP3.

Preparation of Schiff base

The ligand was prepared by adding 50cm^3 ethanolic solution of isatin (0.01mol) to aqueous solution of glycine (0.01mol) in a round bottom flask. The mixture was refluxed for 1 hour. The reacting mixture was allowed to stand for 24 hours, after which the precipitate obtained was filtered, washed with diethylether and dried in a dessicator over P_2O_5 (Hassan, 1991).



Preparation of Schiff base Metal (II) complex

The complexes were prepared by adding a hot aqueous solution of Metal chlorides (0.005mol) to an ethanolic solution of the Schiff base (0.01mol) in a round bottom flask. The reaction mixture was refluxed for 1 hour after which the hot solution was concentrated to one third of its total volume, which was cooled and allowed for crystallization to occur. Dark green and black crystals were formed on cooling which were filtered, washed with diethylether and dried over P_2O_5 in a desiccator (Hassan, 1991).

$$MCl_2.XH_2O + 2(L^-) \xrightarrow{\qquad} [M(L)_2]_{(s)} + XH_2O_{(L)}$$

Determination of the Metal to Ligand Ratio in the Complex Compounds Using Job's Method of Continuous Variation.

The number of coordinated ligands in the complex compounds were determined using Job's method of continuous variation in which one millimolar solution of the ligand and the metal (II) chloride were separately prepared. By mixing these solutions to make a total volume of 10cm^3 in which the mole fraction of the ligand, x is $0.1 \le x \ge 0.9$. The absorbance of each mixture was measured at the wave length of maximum absorbance of the metal (II) chloride solution.

A plot of absorbance against mole fractions was made by taken the triangular shape of the plot, mole fraction (x) at maximum absorbance was recorded, which was the point where the metal ion and the ligand were in stoichiometric ratio. The number of coordinated Schiff base ligand to metal ion was calculated using the relation,

$$n = \frac{x}{1-x}$$

Where n = the number of coordinated ligand.

x=corresponding mole fraction of the ligand at maximum absorbance (Angelici, 1971).

Determination of Stability Constant of the Complex Compounds

Equilibrium constant of the compounds were determined by taking absorbance of 5 solutions of known concentration of the complex compounds. The concentrations taken were 0.001, 0.002, 0.003, 0.004 and 0.005moldm^{-3} respectively.

The stability constants were obtained using Beer's Lambert law. A Beer's law plot was made from which the molar absorptivity of the complex was calculated. Using the calculated molar absorptivity, the equilibrium concentration of each complex compound was calculated from Beer's law and dilution formula, using the expression below;

$$[M(L)_2] = \frac{Absorbance}{Molar\ Absorptivity}\ X\ 1\ cm \qquad (I)$$

Where 1cm is the path length of the cell that hold the sample.

$$[M^{2+}]_0 = \frac{(\text{volume of the metal ion used})(0.001\text{M})}{\text{Total volume of solution}} \qquad (II)$$

$$[L]_0 = \frac{(\text{volume of ligand used})(0.001M)}{Total\ volume\ of\ solution} \qquad (III)$$

Equilibrium Concentration of metal ion and ligand was calculated from the following expression

$[M^{2+}]_{eqm} = [M^{2+}]_0 - [\text{complex}]$ (IV)

$[L]_{eqm} = [L]_0 - x[\text{complex}]$ (V)

Therefore equilibrium constant, K_f was calculated from the relation;

$$K_f = \frac{[\text{complex}]}{[M^{2+}]_{eqm}\,[L]^{x}_{eqm}} \qquad (VI)$$

(mst.edu. 2009)

Similarly the Gibb's Free energy of the complexes was obtained using the expression,

$$\Delta G = -\,nRT\ln K$$

RESULTS AND DISCUSSION

The Schiff base prepared was brickred crystalline solid. It has relatively high melting temperature with high yield of 83.17%. The high melting point ($170^{O}C$) might be associated to the strong attractive force between the particles and high molecular mass. The complexes formed from the interaction of isatin Schiff base ligand and the respective metal (II) chloride also shows high percentage yield as seen in table 1.

Both the Schiff base ligand and the corresponding metal (II) complexes were found soluble in ethanol, methanol and DMSO (Table 3). This is due to the fact that the complexes have low polarity and have similar attractive forces therefore dissolved in the mentioned solvents which have both polar and non-polar ends (Satya *et al.,* 2006). The empirical formulas for the complex compounds were determined from known values of percentage compositions of metal, ligand and water of crystallization (Table 2). The result of 1: 2 for the metal – ligand ratio was in agreement with the result obtained from Job's method, which also suggests a 1:2 metal to ligand ratio. The complexes were established to possess molecular formula $[(ML_2)].3H_2O$, where L= Schiff base.

Molar conductance value of the metal(II) Schiff base complexes in 10^{-3}moldm^{-3} DMSO solution determined, were relatively low; 7.6 and 8.9 ohm^{-1}cm^{2}mol^{-1}. By comparing with the molar conductance values of strong electrolytes like NaCl (123.7ohm^{-1}cm^{-2}mol^{-1})and $AgNO_3$ (130.5ohm^{-1}cm^{-2}mol^{-1}) it shows that the complexes are non-electrolyte (Geary, 1971 and Parnau*et al.*, 2004).

Equilibrium constant depend on the size of the metal ion and the complex formed (Satya *et al.,* 2006), the results obtained were relatively high which suggest good thermodynamic stability for the complexes. The change in Gibb's free energy of the complexes were -31978.86 and -38652.19 Jmol^{-1} suggesting good stability (Table 5), this is because the larger the negative value of Gibb's free energy the greater the stability of the complex compound (Satya *et al.,* 2006).

The IR spectral data of Schiff base ligand showed a sharp band in the region of 1621.22cm^{-1} due to C=N stretching frequency. As the vibration frequency for C=N is 1500cm^{-1} to 1700cm^{-1} (Pretsch *et al.,* 2000). This confirmed the condensation reaction between isatin and amino acid. The spectral band of the metal (II) Schiff base complexes assignable to (C=N) shifted to a lower valueof 1618cm^{-1} and1620 cm^{-1} for Cu and Co complexes respectively. New bands appeared in the range of 494cm^{-1} - 672cm^{-1} and 376 - 494cm^{-1} which are attributed to υ(M-O) and υ(M-N) respectively, confirming coordination of the ligand to the respective metal ions (Table 6).This result is in agreement the result obtained by Bello (2008) and Sulaiman (2010) respectively.

Table 1: Percentage yield and Some Physical properties of the ligand and complexes

Ligand/Complex	Colour	% Yield	Melting point/°C	Decomposition temperature /°C
Ligand	Brickred	83.17	170	-
$[CuL_2]$	Dark Green	90.88	-	230
$[CoL_2]$	Black	87.55	-	240

Key: L =isatin-glycine Schiff base

Table 2: Empirical formula of the Complexes

Complex	%Metal	%Ligand	%Water of Crystallization	Empirical Formula	Metal Ligand Ratio
$[CuL_2]$	13.90	75.10	11	$[CuL_2].3H_2O]$	1:2:3
$[CoL_2]$	12.80	77.20	10	$[CoL_2].3H_2O$	1:2:3

Key: L = Isatin-Glycine Schiff base

Table 3: Solubility of the Ligand and its Complexes in Some Common Solvent

Compounds	Water	Acetone	Diethylether	Methanol	Ethanol	Isopropanol	Benzene	DMSO
Ligand	S	SS	IS	S	S	SS	IS	S
$[CuL_2].3H_2O$	SS	SS	IS	S	S	SS	IS	S
$[CoL_2].3H_2O$	SS	SS	IS	S	S	SS	IS	S

KEY: S – Soluble, SS – slightly Soluble, IS – insoluble.

L= Isatin-Glycine Schiff base ligand

Table 4: Molar conductance of the Complexes in 10^{-3} moldm^{-3} DMSO solution

Complex	Concentration 10^3[C]	Electrical conductivity (Ohm^{-1} cm^{-1})	Molar conductivity Ohm^{-1} cm^{-2} mol^{-1}
$[Cu(L)_2]$.$3H_2O$	1.0	7.6x 10^6	7.6
$[Co(L)_2]$.$3H_2O$	1.0	8.9 x 10^6	8.9

Key: L = Isatin-Glycine Schiff base ligand

Table5: Stability Constant and Gibbs free energy of the Metal Complexes

Complex	K_f	ΔG Jmol^{-1}
$[CuL_2]$.$3H_2O$	4.0326 x10^5	-31978.86
$[CoL_2]$.$3H_2O$	5.9615 x10^5	-38652.19

Key: L = isatin-glycine Schiff base

Table 6: Infrared Spectral Data of the Schiff Base Ligand and its Metal (II) Complexes

Compounds	υ(C=N) (cm^{-1})	υ(C=O) (cm^{-1})	υ(N-H) (cm^{-1})	υ(M-O) (cm^{-1})	υ(M-N) (cm^{-1})
Ligand	1621	1716	3337	_	_
$[CuL_2]$.$3H_2O$	1618	1720	3238	494	376
$[CoL_2]$.$3H_2O$	1620	1717	3294	672	494

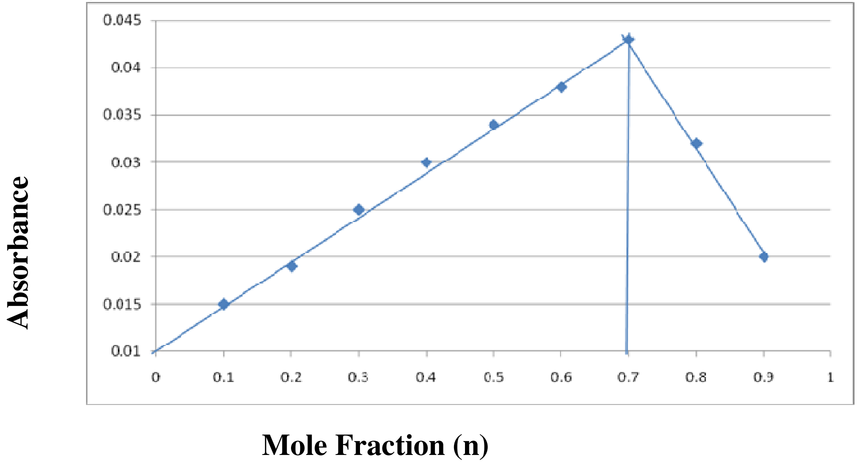
Key: L = isatin-Glycine Schiff base

Table 7: Determination of Number of Ligands Coordinated to Metal Ion using Job's Method of Continuous Variation

$[CuL_2]$ Absorbance at various mole fractions

Mole fraction	Absorbance
0.1	0.015
0.2	0.019
0.3	0.0 25
0.4	0.030
0.5	0.034
0.6	0.038
0.7	0.043
0.8	0.032
0.9	0.020

n = 2.33

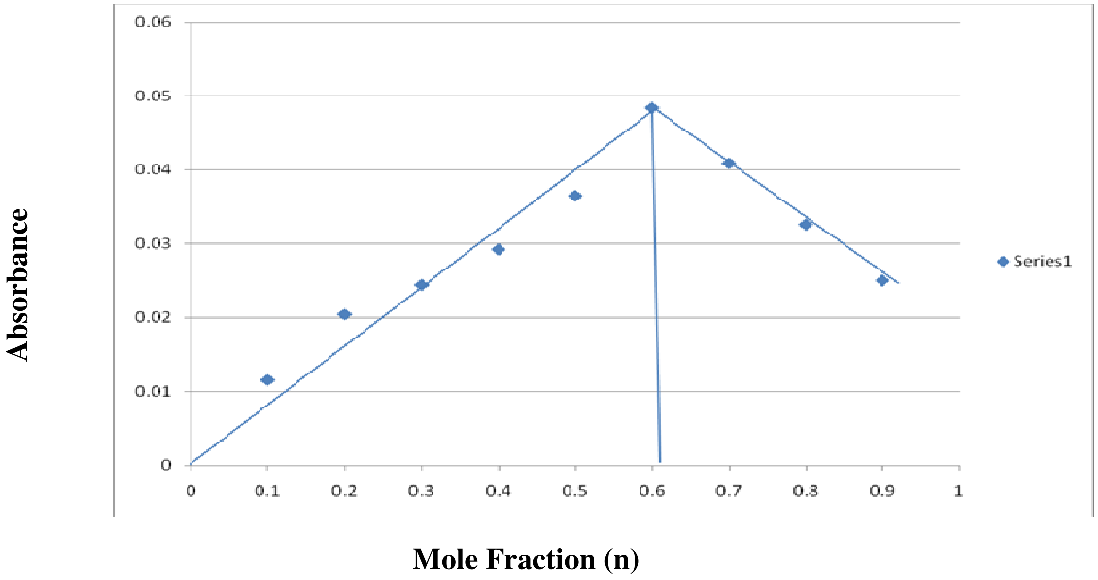


Plot of Absorbance against Mole Fraction of [CuL_2] Complex

[CoL_2] Absorbance at various mole fractions

Mole fraction	Absorbance
0.1	0.0115
0.2	0.0204
0.3	0.0244
0.4	0.0292
0.5	0.0365
0.6	0.0484
0.7	0.0409
0.8	0.0326
0.9	0.0250

n = 1.5



Plot of Absorbance against Mole Fraction of [CoL_2] Complex

CONCLUSION

It can be concluded that stable complexes have been characterized from the Infrared, UV spectroscopy and elemental analysis results in which the metal - ligand ratio is 1:2. Thus having molecular formula of $[(ML_2)].3H_2O$ Where L=isatin-glycine Schiff base. Therefore octahedral stereochemistry could be proposed for the complexes.

RECOMMENDATIONS

Physical and analytical measurements carried out in this work were used in proposing the general molecular structure of the complex. However, further analysis such as ^{1}Hand ^{13}C NMR, X-ray crystallography, and thermogravemetry should be carried out to fully establish the proposed structure. There is also a need to test for the microbial activities of the complexes.

REFERENCES

Angelici R. J. (1971). Synthesis and Techniques in inorganic chemistry, W. B. saunders company, New York, 2nd ed. Pp 115-130.

Asemave, K.,Yiase, S.G., Adejo, S.sO. and Anhwange, B. A. (2012). Kinetics and Mechanism of Subsituted Reactions of Trans-Dichlorobis (Ethylenediamnine) Cobalt (III) Chloride with Aspartic acid, *Int. J. Inorg. and Bioinorg. Chem.*, 2(1):11-14.

Bello I. (2008) synthesis and characterization of Cu (II) complexes with some amino acid Schiff base unpublished thesis submitted to the Department of Pure and Industrial Chemistry, Bayero University, Kano.

Cotton F. A. and Wilkinson G. (1994). Advanced inorganic Chem., Inter science, New York, 3rded. Pp 624.

David T. S., Balakumar S., Suganthi S. (1999). Effect of complexation on the ions mobility of some 3-d metal ions. *Int. J. App. Chem.* 12:38-49.

"Determining an equilibrium constant using spectrophotometry and Beer's law" last updated 9/11/19. Available at https://www.mst.edu/Datasheet/spectrophotometry

Geary W. J., (1971).The use of conductivity measurement in organic solvent for the characterization of coordination compound. *Chem, Review,* 7(I) : 81 – 122

Hassan A., Aly M., (1991), Co(II) and Fe(III) complexes of Schiff bases derived from isatin with some Amino Acids. *Journal of Islamic Academic of sciences,* 4 : 4, 271 – 274

Hovenda A. H., Cole B. M., Snapper M. L., Shimizu K. D., Krueger C. A., Harrity J.P.A.,(1996). Synthesis of some New bis-Schiff base of isatin and 5-fluoroisatin in a water suspension medium.*Angew.chem.,Int.Ed.Engl.*,35,1668.

Kumar S., Dhar D. N., Saxena P. N., (2009). Applications of metal complexes of Schiff bases. A review, *J. Sci. Ind. Res.* 68:181-187.

Na'aliya J.(2008) Potentiometric studies of some Essential Amino Acid complexes. Unpublishedn Ph.D Dissertation submitted to Department of Pure and Industrial Chemistry, Bayero University Kano.

Parnau C., Zalaru F., Angela F.K., Kirza A.,(2004).Complexes of Ti(IV) and Zr(IV)with some bidentate Schiff bases derived from isatin, *Anal. Univ. Buc., Ser. Chem.* XI(I): 38-43.

Pretsch E., Buhlmann and Affolter C. (2000). Structure Determination of organic compounds. "Table of Spectral Data." Third completely revised and enlarged English ed. Springer. Pp 13-69.

Satya P., Tuli G. D., Basu S. K., Madan R. D. (2006). Advanced inorganic chemistry. Chand and company India.2:46-48.

Siham, A. L., Reda, A.A.; Mona F. A. and Eman M. S.(2012).Mixed Ligand Complex of Cu(II) with 1,2-Diphenylethylenediamine as primary Ligands and Amino Acids as Secondary Ligands, *Int. J. Electrochem. Sci.,*7699-7711.

Sulaiman Z. (2010). Potentiometric and spectroscopic Determination of metal (II) complexes with Schiff bases ligand derived from Isatin and Benzene-1-hydroxy-2-Amine.Unpublished M.Sc Dissertation, Department of Pure and Industrial Chemistry, Bayero University Kano.

Zahid, H., Chohan, M., Praveen, A. and Ghaffar, A. (1997). Structural and Biological Behavior ofCo(II), Cu(II) and Ni(II) Metal Complexes of Some Amino Acid Derived Schiff-Base Ligands,*Metal Based Drugs.* 4(5):267-272.