

SYNTHESIS, CHARACTERIZATION AND CONDUCTIVITY STUDIES OF SCHIFF BASE LIGAND DERIVED FROM ISATIN AND O-PHENYLENEDIAMINE WITH ITS COBALT(II) METAL COMPLEX AND LITHIUM-SCHIFF BASE COMPOUND

(Sintesis, Pencirian dan Kajian Kekonduksian Terhadap Ligan Bes Schiff yang Terhasil Daripada Isatin dan O-Phenylenediamina dengan Kobalt(II) Kompleks Logam Peralihan serta Litium-Bes Schiffnya)

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Abstract

In this study, a Schiff base ligand, (*E*)-3-(2-aminophenylimino)indolin-2-one (APIISA) was synthesized *via* condensation reaction of *o*-phenylenediamine with isatin. Metal complex and Lithium-Schiff base of this ligand were prepared. Metal complex bis[*(E)*-3-(2-aminophenylimino)indolin-2-one]Co(II), [Co(APIISA)₂] was synthesized from Schiff base ligand with Cobalt acetate tetrahydrate in 2:1 ratio. While Lithium-Schiff base was prepared by using Lithium acetate dihydrate produced Lithium[*(E)*-3-(2-aminophenylimino)indolin-2-one], [Li(APIISA)]. All the synthesized compounds were characterized by variety of physicochemical techniques such as melting point, elemental analysis, infrared spectroscopy, ¹H nuclear magnetic spectroscopy, magnetic susceptibility and X-ray diffraction. Conductivity studies of the ligand, metal complex and Lithium-Schiff base were investigated by impedance analyzer which the samples were prepared in the form of pellets. The electrical conductivities of the prepared compounds were measured by applying alternating current (ac) voltage. The conductivity values were calculated and Lithium-Schiff base showed higher conductivity value followed by Cobalt metal complex and Schiff base ligand.

Keywords: Isatin, Schiff base, Cobalt(II) metal complex, Lithium-Schiff base, Conductivity studies

Abstrak

Dalam kajian ini, ligan bes Schiff, (*E*)-3-(2-aminophenylimino)indolin-2-one (APIISA) telah disintesis melalui tindak balas kondensasi *o*-phenylenediamina dengan isatin. Kompleks logam dan Litium-ligan bes Schiff ini telah disediakan. Metal kompleks bis[*(E)*-3-(2-aminophenylimino)indolin-2-one]Kobalt(II), [Co(APIISA)₂] telah disintesis daripada ligan bes Schiff dengan Kobalt tetrahidrat asetat dalam nisbah 2:1. Manakala Litium-bes Schiff telah disediakan dengan menggunakan Litium asetat dihidrat menghasilkan Litium-[*(E)*-3-(2-aminophenylimino)indolin-2-one] [Li(APIISA)]. Semua sebatian yang disintesis telah dicirikan oleh pelbagai teknik kimia-fizikal seperti menentu takat lebur, analisis unsur, spektroskopi inframerah, ¹H spektroskopi resonan magnet nuklear, kerentanan magnet dan pembelauan sinar-X. Kajian kekonduksian ligan, kompleks logam dan Litium-bes Schiff dianalisis dengan analisis impedans dimana sampel telah disediakan dalam bentuk pelet. Kekonduksian elektrik sebatian yang telah disediakan diukur dengan menggunakan arus ulang-alik (ac). Nilai konduktiviti dikira dan Litium-bes Schiff menunjukkan nilai kekonduksian tertinggi diikuti oleh kompleks logam Kobalt dan ligan bes Schiff.

Kata kunci: Isatin, Bes Schiff, Kobalt(II) logam peralihan, Litium-Bes Schiff, Kajian kekonduksian

Introduction

Schiff base ligand is a compound that contains a carbon-nitrogen double bond, with the nitrogen atom connected to an aryl or alkyl group. The general formula of Schiff base is R-CH=N-R' where R and R' is an alkyl or aryl group

that makes the Schiff base a stable amine [1]. It can be synthesized by condensation of aliphatic or aromatic primary amine with carbonyl compound [2]. Schiff base ligands and transition metal ions are the two parents and necessary components for designing stable complexes and play an important role in the development of coordination chemistry [1,3]. In 1967, Schrauzer and Windgassen found that inorganic metal complexes might exhibit conducting properties. Until now, there are very rare reports on Schiff base complexes that have such properties [3]. For this reason, the major aims for this report are to synthesis, characterization of Schiff base ligand derived from isatin and *o*-phenylenediamine with cobalt(II) metal complex. To extend the investigation, Schiff base ligand has been reacted with lithium salt to produce Lithium-Schiff base compound. These three compounds were analyzed on their conductivity value by using electrochemical impedance spectroscopy method (EIS).

Materials and Methods

General considerations

Isatin, *o*-phenylenediamine, cobalt(II) acetate tetrahydrate, lithium acetate dihydrate and all other reagents were used without further purification.

Physical measurement

Elemental analyses were performed using CHNS Analyzer Flash EA 1112 series, IR spectra were recorded on KBr discs using FTIR Perkin Elmer 100 Spectrometer. ^1H NMR spectrum was recorded on Bruker instrument using DMSO- d_6 as solvent. Magnetic susceptibility at room temperature was performed using Sherwood Magnetic Susceptibility Balance (Auto), calibrated with mercury tetrakis(isothiocyanato) cobaltate(II). X-Ray Diffraction were using Shimadzu XRD-600 diffractometer with nickel-filtered copper-K α radiation ($\lambda=1.54\text{\AA}$) at 40 kV and 200 mA. Electrochemical impedance spectroscopy measurement was done by using WEIS510 Multichannel EIS System.

Synthesis of Schiff base ligand

Solution of isatin (5mmol) in absolute ethanol was added to equimolar solution of *o*-phenylenediamine in of the same solvent. The mixture was refluxed for 3 hours. Precipitate of Schiff base was filtered, washed with cold ethanol and dried *in vacuo* over silica gel. The yellow product form was (*E*)-3-(2-aminophenylimino)indoline-2-one [4].

Synthesis of Schiff base metal complex and Lithium-Schiff base

Cobalt(II) acetate tetrahydrate (5mmol) was dissolved in ethanol. The solution was treated with solution containing Schiff base (10mmol) in ethanol. The mixture was refluxed for 6 hours. The product was filtered, washed with cold ethanol and dried *in vacuo* over silica gel.

Synthesis of Lithium-Schiff base

The mixture of *o*-phenylenediamine (10mmol) and lithium acetate dihydrate (5mmol) in absolute ethanol was refluxed for 1 hour. After cooled the resulting solution at room temperature, a solution of isatin (10mmol) in absolute ethanol was added slowly. The mixture was stirred until 10cm³ of the solution reduced. The product was filtered and dried *in vacuo* over silica gel [5].

Results and Discussion

Physico-Chemical Data Analysis of the Schiff Base, Its Metal Complexes and Lithium-Schiff base

The physical characteristics of the Schiff base ligand, its metal complex and Lithium-Schiff base compound are shown in Table 1. Quantitative elemental analysis of carbon, hydrogen and nitrogen were carried out in order to determine the elemental content of the synthesized compounds. The results were found to be in acceptable range compared with calculated values.

Table 1. Analytical Data and Physical Properties of Schiff Base, Metal Complex and Lithium Schiff base

Compound	Abbs	Colour	Melting point (°C)	Experimental Value (Calculated Value) %		
				C	H	N
(<i>E</i>)-3-(2-aminophenylimino)indoline-2-one	APIISA	Yellow	244.8	71.27 (70.87)	4.35 (4.67)	17.99 (17.71)
bis[(<i>E</i>)-3-(2-aminophenylimino)indoline-2-one] Cobalt(II)	Co (APIISA) ₂	Brown	287.7	64.88 (63.28)	4.38 (3.79)	15.92 (15.81)
Lithium-(<i>E</i>)-3-(2-aminophenylimino)indoline-2-one	LI-APIISA	Dark brown	257.0	71.69 (69.85)	4.52 (4.61)	18.36 (17.46)

¹H Nuclear Magnetic Resonance (NMR) Spectroscopy Analysis of the Schiff Base

¹H nuclear magnetic resonance spectroscopy spectrum of the synthesized Schiff base was examined in order to elucidate each distinct type of hydrogen nuclei. The solvent used for the Schiff base was acetone-d₆. The important chemical shifts of the ¹H spectrum of the Schiff base is shown in Figure 1. The spectrum data is tabulated in Table 2.

The ¹H spectrum shows single peak at 3.66 ppm which ascribed as NH₂. Meanwhile signals between 7.24 - 8.28 ppm may be attributed to aromatic-H and isatin ring. NH peak of isatin appear at 10.84 ppm [6].

Table 2. ¹H NMR spectrum data for APIISA

¹ H NMR Assignment	Chemical shift, δ (ppm)
NH ₂ ; H11	3.66 (singlet, 2H)
NH; H1	10.84 (singlet, 1H)
Aromatic-H and pyrrole (isatin ring)-H	7.24 – 8.28 (multiplet, 8H)
H2, H3, H4, H5, H7, H8, H9, H10	

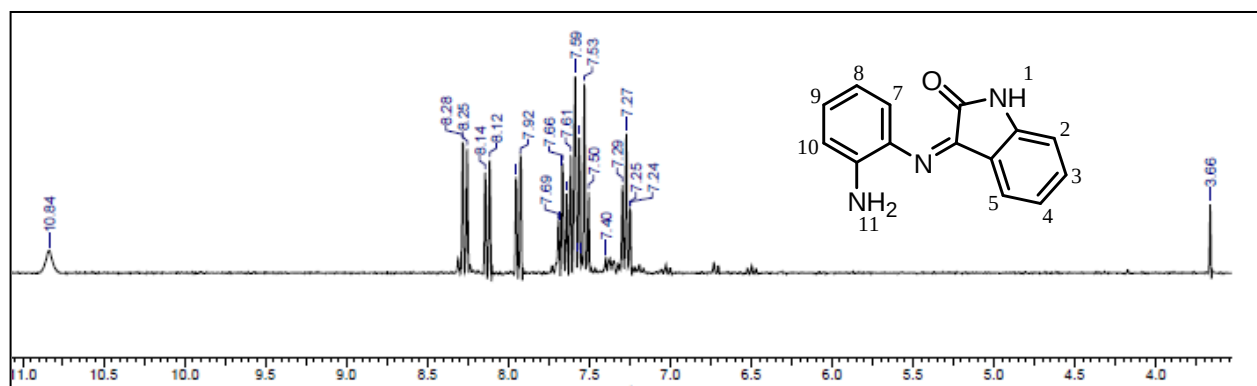


Figure 1. ¹H NMR analysis for (*E*)-3-(2-aminophenylimino)indoline-2-one

Fourier-Transform Infrared Data for the Schiff Base and Its Metal Complexes

Infrared spectroanalysis was carried out in order to determine the functional group of the synthesized compounds. The IR spectra for the Schiff base ligand and its metal complex are shown in Table 3.

Three key functional groups which are the $\nu(\text{C}=\text{N})$, $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{O})$ bands were selected to provide a comparative analysis, as these bands shift either to higher or lower wavenumbers upon complexation with the metal ions.

Table 3. Infrared data of the Schiff base and metal complexes

Compound	Bands (Wavelength, cm^{-1})				
	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
(API)ISA	1665	1617	3391	-	-
$[(\text{API})\text{ISA}]_2\text{Co}$	1663	1570	3381	521	-
Li-(API)ISA	1663	1615	3390	-	-

The lowering $\nu(\text{C}=\text{N})$ on complexation may be attributed to a lowering bond order as a result of coordination of ligand to metal ion *via* azomethine nitrogen. Furthermore, this can be confirmed by the presence of new band 521 cm^{-1} which assignable to $\nu(\text{M}-\text{N})$ band [1,6-8].

Other than that, the strong $\nu(\text{N}-\text{H})$ band was shifted toward lower wavelength compared with ligand indicating coordination of the ligand is not only at azomethine nitrogen, but also at imino nitrogen as well. Meanwhile, the $\nu(\text{C}=\text{O})$ band display not much difference wave numbers between ligand and complex clearly showing no participation of carbonyl oxygen in the coordination to the metal ion [9]. The proposed structure of metal complex is shown in Figure 2.

For Lithium-Schiff base, the similarities in values of the three main functional groups prove that there is no bonding between Lithium salt with Schiff base ligand.

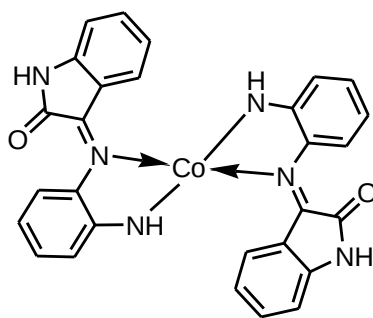


Figure 2. Structure of metal complex

Magnetic Susceptibility Analyses of the Metal Complexes

The molar magnetic susceptibility χ_m which characterizes the extent of paramagnetism of the metal complexes were measured in order to determine the spin properties of the complexes. The complex can either appear in the high spin

state or exist as low spin complex. The measurement is crucial to identify the number of unpaired electrons and therefore to determine their geometric structure.

The cobalt(II) complex reported herein has a room temperature magnetic moment value of 4.58 B.M., which is in the normal range observed for tetrahedral cobalt(II) complex [10].

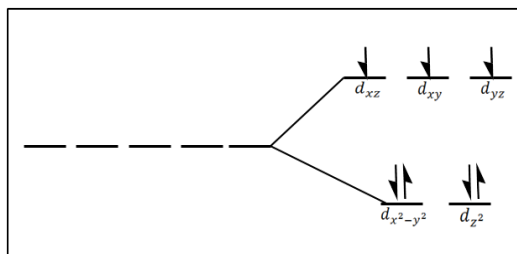


Figure 3. Crystal field diagram of tetrahedral cobalt (II) complex

X-Ray Diffraction of Lithium-Schiff base

X-Ray powder patterns of Schiff base ligand, Lithium-Schiff base and Lithium acetate dihydrate were given in Figure 3. The comparative range of all these compounds was between 0 to 30 2θ . Based on the similarities of some peaks in Lithium acetate dihydrate with Lithium-Schiff base, and Schiff base ligand with Lithium-Schiff base, it may be attested the combination of Lithium ion with Schiff base is successful. However, the type and place of bonding of this compound is still under investigation of study.

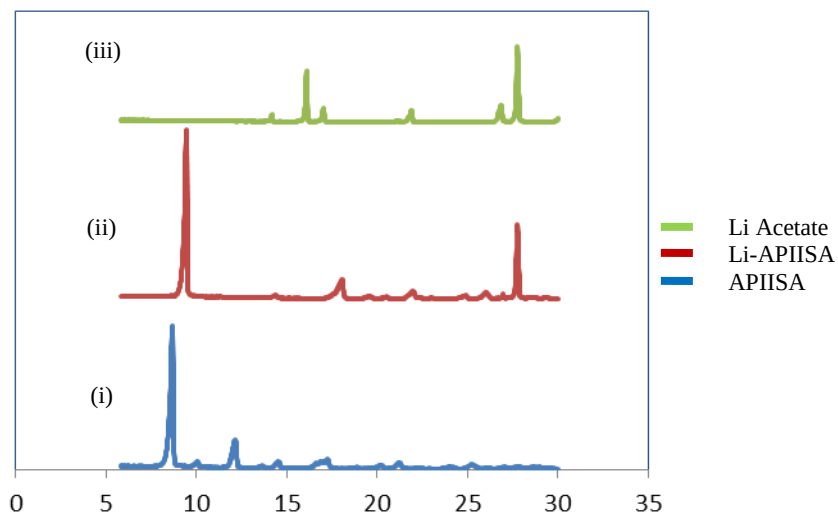


Figure 4: X-Ray Diffraction of (i) Schiff base, (ii) Lithium-Schiff base and (iii) Lithium acetate dihydrate.

Conductivity studies

The samples for electrical conductivity measurements were prepared from the Schiff base ligand, metal complex and lithium-Schiff base in the form of pellets. These pellets were placed between two electrodes and contacts were tested to be ohmic. The impedance diagrams for these compounds are shown in Figure 4. The electrical

conductivities of the prepared compounds were obtained by formula $\frac{T}{R_b A}$ where T denotes thickness of the tablets, R_b is for bulk resistance and A is for surface area of the pellets. Table 4 shown the values calculated. From the result, it shows that Lithium-Schiff base gives highest value of conductivity followed by cobalt(II) metal complex and Schiff base ligand.

Table 4: Conductivity value of Schiff base ligand, metal complex and Lithium-Schiff base

Compound	Conductivity value (Ωcm^{-1})
(API)ISA	7.2371×10^{-10}
$[(\text{API})\text{ISA}]_2\text{Co}$	4.4367×10^{-10}
Li-(API)ISA	3.0941×10^{-10}

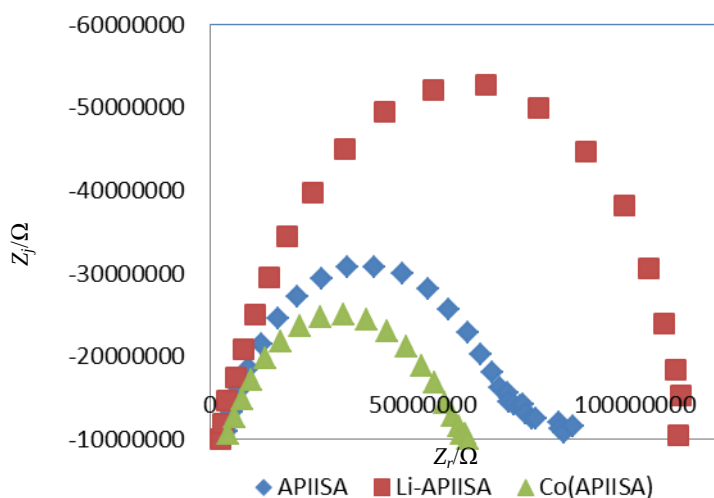


Figure 5: Impedance Data Obtained for Schiff base, Lithium-Schiff base and Metal Comple

Conclusion

The synthesis, characterization and conductivity studies of Schiff base ligand APIISA, cobalt(II) metal complex $\text{Co}(\text{APIISA})_2$, and Lithium-Schiff base Li-APIISA have been described. Schiff base behaves as a bidentate chelating ligand which binds through azomethine and imino nitrogen. ^1H NMR spectrum of Schiff base indicates the structure of the compound. Magnetic moments show that cobalt(II) complex was tetrahedral environment.

The Schiff base, its metal complex and Lithium-Schiff base have been evaluated for their conductivity studies. From the result, it shows that Lithium-Schiff base gives highest conducted values followed by cobalt (II) metal complex and Schiff base ligand.

Acknowledgement

This work is funded by Ministry of Higher Education Malaysia for Fundamental Research Grand Scheme for financing this research (FRGS/1/10/SG/UiTM/03/05) and also MyMaster scholarship, Faculty of Applied Sciences, Institute of Science, Universiti Teknologi MARA and International Education Center (INTEC) for providing research facilities.

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