

Synthesis and Characterization of Schiff base ligand and Its Group IIB Metal II Complexes

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ABSTRACT

Schiff base ligand ($RR^1C=NH$) is formed through condensation of an amine RNH_2 with either aldehyde ($RCHO$) or ketone (RCO). A Schiff base ligand was synthesized from diphenylamine with Cyclohexanone in 1:1mole ratio respectively. The ligand was used to prepare three complexes from group IIB metal salts of. Zn (II), Cd (II) and Hg (II) in 1:2 mole proportion of metal to ligand M:L. The compounds produced were characterized using conductivity, solubility, melting points and infrared spectroscopy. The metal II complexes melted in the range of 109-127 °C. However, the ligand, [DPhACYHEX] melted in the range of 160-162°C. The compounds formed have variable shades of colours ranging from white, teal to gray. The compounds were all soluble in dimethylformamide (DMF). The percentage (%) yields of the compounds are in the range of 75.7-79.7 %. Conductometric test is also observed at $10^{-4}M$ for the compounds and given at the range of 51.2-77.0 Scm^2/mol . The infrared studies indicated the complexes coordinated through the azomethine N ($C=N$) of the ligand. This is evidenced from the appearance of the metal-nitrogen (M-N) bands in the complexes which was absent in the ligands.

Keywords: Schiff base ligand, Diphenylamine, Cyclohexanone, Metal II Complexes, Infrared Spectroscopy.

INTRODUCTION

Group IIB metals consist of Zinc, Cadmium and Mercury, their electronic configurations are $(n-1)d^{10} ns^2$, and are often not classified as transition elements because the completely filled d subshell is not involved in bonding. The characteristic oxidation state for all the element is +2 although mercury exists in the +1 state. Compared to copper, silver and gold, the coinage metals, these elements (group IIB) have higher ionization potentials and more tendencies to form complex compounds. [1].

There has been a considerable effort in recent years towards the preparation of new materials containing polyfunctional units (ligands) able to bind metallic ions. The Schiff base [2] are synthesized from the reaction of aldehydes or ketones and amino compounds through condensation. ($RCHO + R_1NH_2 \rightarrow RR_1C=NH + H_2O$) Given that these materials from stable

complexes, they provide the opportunity to design new systems selective to specific metallic ions. These materials could be applied in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes and environmental chemistry among others [3].

General structure of an azomethines

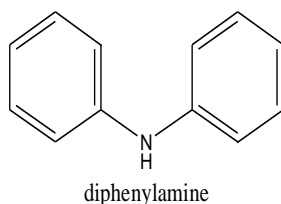
A Schiff base, named after Hugo Schiff, is a compound with a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, not hydrogen. Schiff bases in a broad sense have the general formula $R_1R_2C=NR_3$, where R is an organic side chain. In this definition, Schiff base is synonymous with azomethine. Some restrict the term to the secondary aldimines (azomethines where the carbon is connected to a hydrogen atom), thus with the general formula $RCH=NR'$. [4].

Uses of Schiff base ligands

In Chemistry Schiff bases are used as basic units in the manufacture of certain dyes while others are used as liquid crystals. Schiff bases are also used in the making of carbon nitrogen bonds.

In biology Schiff compounds have many applications including; drug preparations, identification, detection and determination of aldehyde or ketone, purification of carbonyl or amino compounds or protection of these groups during complex reactions [5].

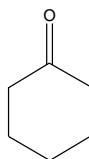
Diphenylamine



Diphenylamine is an organic compound with the formula $(C_6H_5)_2NH$. The compound is a derivative of aniline, consisting of an amine bound to two phenyl groups. The compound is a colourless solid, but commercial samples

are often yellow due to oxidized impurities. Diphenylamine dissolves well in many common organic solvents, but is insoluble in water. It is used mainly for its antioxidant properties [6].

Cyclohexanone



Cyclohexanone

Cyclohexanone is the organic compound with the formula $(CH_2)_5CO$. The molecule consists of six-carbon cyclic molecule with a ketone functional group. This colorless oil has an odor reminiscent of peardrop sweets as well as acetone. Over

time, samples assume a yellow color due to oxidation. Cyclohexanone is slightly soluble in water, but miscible with common organic solvents. Billions of kilograms are produced annually, mainly as a precursor to nylon. [7].

MATERIALS AND METHODS

The metal (II) salts were obtained in the form of their chlorides for cadmium and mercury, and nitrate for zinc. They were of analar grade and were used as supplied. They are:

Zinc nitrate hexahydrate, cadmium chloride and mercuric chloride. The other special chemicals used are diphenylamine, dimethylglyoxime (DMG).tetraoxosulphate (VI) acid, trioxonitrate (v) acid, hydrogen peroxide, ethanol, methanol, diethylether,

ammonia/ammoniumchloride, solochrome black T. distilled water.

Preparation of the ligands

The ligands and their metal (II) complexes were prepared according to a literature procedure, [8].

The ligand was prepared by condensation of a Cyclohexanone with diphenylamine in 1:1 molar ratio in an alcoholic medium

(methanol). In a typical reaction 25.9ml of a Cyclohexanone was react with 22.8ml of Diphenylamine to give a Schiff base ligand in an alcoholic (methanol) medium. The general equation for the preparation of the ligand is shown below;
 $RCHO + RNH_2 \rightarrow HL_1 + H_2O$

L = HL_1 , HL_2 , or HL_3 (Schiff base ligands 1, 2 or 3).

Synthesis of the metal complexes

The metal complexes of the Schiff base were prepared according to a modifications of literature procedure, [9]. A hot solution of the appropriate metal chloride and nitrate, (0.59g), to the hot solution of the Schiff base ligand (6.88g) prepared in an alcoholic medium (methanol) (100 ml), in a molar ratio (1:2) of the metal to ligand.

The resulting mixture was stirred under reflux for 3 hours for the complexes to be formed. The mixture was then filtered and washed with a 50% ethanol mixture and diethyl ether. The same procedure was applied to each metal salt and Schiff base ligand prepared.

Equation for the reaction

$MX_2 \cdot nH_2O + 2HL_1 \rightarrow [ML_2X] + nH_2O$
 Where M = Zn (II), Cd (II) and Hg (II).

L = SBL (Schiff base ligand).

X = Halide, NO_2 or Cl

Analysis for purity

The complexes formed were characterized using solubility, melting point, conductivity and infrared spectroscopy.

Conductivity

Conductivity measurement was done using an electrolytic conductivity set model DDSJ- 308A at a concentration 10^{-4} M solution of the complexes.

Melting point

Melting point was determined using a stuart model SMP 3 digital melting point apparatus

Solubility tests

The solubility of the complexes were determined in some polar and non-polar

solvents, and the results are presented in table 4

Metal analysis

Complex metric EDTA Titration

This method is used to determine the percentage of the metal ion that has coordinated to the ligand in a complex compound. [10].

The titration was carried out using the standardized EDTA in a burette and metal ion in a conical flask.

Preparation of solutions for analysis

- (i) 50 % HNO_3 was prepared in 100 ml flask
- (ii) 50% H_2SO_4 was prepared in a 100 ml flask
- (iii) 0.030g of a sample i.e. metal ion was weighed accurately using sensitive digital balance and was transferred into a suitable beaker.
- (iv) 50% HNO_3 was added to the metal ion solution and was heated until the fumes evolved
- (v) The solution was allowed to cool to a room temperature and then 2-3 ml of the 50% H_2SO_4 was added and heat until the fumes evolved. Digestions were all done in a fume cupboard.
- (vi) A little distilled water was added to the solution and transferred quantitatively to a 100 ml volumetric flask and make it to the mark.

Procedure

10ml of the sample i.e. metal ion was pipetted and 2-3 drops of solochrome black T as an indicator was added and NH_3/NH_4Cl was used as a buffer (PH 10). The sample solution was titrated against the standardized EDTA. Color change was noted at the end point. The titre value was recorded in three times and the average was calculated. The % metal that has coordinated to the ligands was also calculated in the formation of the complex. The same procedure was repeated for each metal complex that has been prepared.

Infrared

The infrared spectra wave recorded on a Perkin- Elmer chart model 2400 series 11 CHN/O Elemental analyzer in the range

400 - 4000 cm^{-1} at KBr disc at Abubakar Tafawa Balewa University, Bauchi (ATBU). Spectra wave recorded for both the ligand and the complexes.

RESULTS**Analytical Data**

The physical properties of the complexes and the ligand are shown in table 1 below

Table 1: Some physical properties of the complexes

S/N	compound	Molar mass (g)	Colour	Yield(g) (%)	M.pt/d ($^{\circ}\text{C}$)	Δm (Scm^2/mol)	%M found calc.
1.	[Zn(DPhACYHEX) ₂ (NO ₃) ₂]	685.5	Gray	78.7	126-127	66.8	9.5
2	[Cd(DPhACYHEX) ₂]Cl ₂	679.4	Gray	77.0	118-120	77.0	16.5
3	[Hg(DPhACYHEX) ₂]Cl ₂	767.1	White	79.7	109-110	59.2	26.1
4	[DPhACYHEX]	172	teal	75.7	160-162	51.2	-

Where, [DPhACYHEX]=Diphenylamine- cyclohexane ligand, d= decomposition temperature, M.pt = melting point in $^{\circ}\text{C}$, S = siemen and Δm = molar conductivity.

Table 2: The Solubility of the ligand/complexes in various polar and non-polar solvents are shown in a table below

Table 2: Solubility of the complexes

Compound	water		MeOH		EtOH		Acetone		CHCl ₃		Diethylether		Benzene		DMF		Formaldehyde	
	C	H	C	H	C	H	C	H	C	H	C	H	C	H	C	H	C	H
1 [Zn(DPhACYHEX) ₂ (NO ₃) ₂]	SS	SS	SS	I	S	S	S	S	SS	SS	I	I	I	I	S	S	SS	SS
2 [Cd(DPhACYHEX) ₂]Cl ₂	I	I	SS	SS	SS	SS	I	I	SS	SS	I	I	SS	SS	S	S	SS	SS
3 [Hg(DPhACYHEX) ₂]Cl ₂	SS	I	SS	SS	S	S	I	I	SS	SS	SS	I	SS	SS	S	S	SS	SS
4 [DPhACYHEX]	I	I	I	I	SS	SS	I	I	SS	SS	I	I	SS	SS	S	S	SS	I

Where; I=insoluble S=soluble, SS=slightly soluble C=cold solvent and H=hot solvent

Table 3: Infrared Spectra

The relevant vibrational frequencies of the ligand and complexes proposed assignments of the fundamental modes at the spectral range of 200-4000 cm^{-1} are presented in table 4 below

Table 4: Relevant infrared frequencies for the ligand/complexes

S/N	Compound	$\sqrt{\text{C=N}}$	$\sqrt{\text{C=C}}$	$\sqrt{\text{NO}_2}$	$\sqrt{\text{M-N}}$	$\sqrt{\text{M-Cl}}$
2	[Zn(DPhACYHEX) ₂ (NO ₃) ₂]	1600w	1419m	1330s	620m	-
5	[Cd(DPhACYHEX) ₂ Cl ₂]	1500m	1410w	-	695w	-
6	[Hg(DPhACYHEX) ₂ Cl ₂]	1450s	1370m	-	645m	-
8	[DPhACYHEX]		1430s	-	-	-

Where m=medium, s=strong, w=weak

DISCUSSION

Physical Properties

The compounds obtained have variable colours ranging from white, gray to teal. The metal ions forming these complexes have d^{10} configurations. The colours observed may be due to the ligand or charge transfer transitions. The compounds have sharp melting points; this indicates they are probably pure (Table:1). The complexes with DPhACYHEX have high melting points than free ligands. The melting point recorded for the ligand is between 160-162°C and for the complexes: 109-127°C.

The ligand and the metal complexes showed varying degrees of solubility. Both the ligand and the complexes are soluble in DMF which is a coordinating solvent. They are all insoluble or slightly soluble in water (Table: 2) some are soluble in hot methanol or ethanol. The percentage (%) yields of the complexes are commendable. Hg (II) of DPhACYHEX has the highest (%) yield of 79.7 and Cd (II) complex [Cd(DPhACYHEX)₂Cl₂] has the lowest yield of 77.0 %.

The % metal ions obtained from experiment were found to agree closely with theoretical values obtained from proposed structures (Table 1). The results of the conductivity measurements in DMF revealed that the complexes are non electrolytes [11].

Infrared

The infrared spectra of the ligand and complexes are shown in Figure 3 (Appendix II). Tentative assignments of the bands are made base on similar studies [12] and also by comparing the spectra of the complexes with the spectra of the ligands [13]. Very strong band at 1569 cm^{-1} is characteristics of the azomethine nitrogen present in the Schiff base ligand. This was shifted to 1553-1595 cm^{-1} in the complexes, which indicates the coordination of the metal to the azomethine nitrogen.

In DPhACYHEX, C=N was found at 1600, 1500 and 1450 cm^{-1} for Zn, Cd and Hg complexes respectively. The shift to lower wave numbers or frequencies indicates coordination of the metal ions to the azomethine nitrogen]. A similar study has been reported [14] the band appears at 1534 cm^{-1} is assigned to C=N stretching in the spectrum of free ligand which has been shifted to 1658 cm^{-1} in the spectrum of the metal complex due to structural changes.

The C=C mode was also observed base on the study [15]. The Zn complex was seen at 1419 cm^{-1} , while the complex of Cd was given a spectra at 1410 cm^{-1} for [Cd(DPhACYHEX)₂Cl₂]. The band appeared at 1370 for the complex of Hg. The ligand (DPhACYHEX) was given a spectra band at 1430 cm^{-1} . M-N spectra appeared at 620

cm^{-1} for $\text{Zn}(\text{DPhACYHEX})_2(\text{NO}_3)_2$, while the complex appeared $[\text{Cd}(\text{DPhACYHEX})_2]\text{Cl}_2$ at 645 cm^{-1} .

M-NO₂ spectra band appeared for the complex of Zn at 1330 cm^{-1} .

The compounds produced are air stable and are all anhydrous. They have variable colours.

The complexes have lower melting points than the ligand [17]. Microanalysis could not be done due to instrument limitation in order to ascertain the stoichiometric compositions of the compounds. However, infrared studies have shown

$[\text{Zn}(\text{DPhACYHEX})_2]\text{Cl}_2$. For the M-Cl, bands could not be observed due to instrument limitation; M-Cl bands are expected below 400 cm^{-1} [16].

CONCLUSION

that the azomethine N of the Schiff base ligands coordinated to the metal ions. This evidenced by the appearance of M-N bands in the complexes in the range of $620\text{-}695 \text{ cm}^{-1}$. Also metal-chloro (M-Cl) absorption bands could not be recorded due to instrument limitation. The complexes were all non-electrolytes in DMF.

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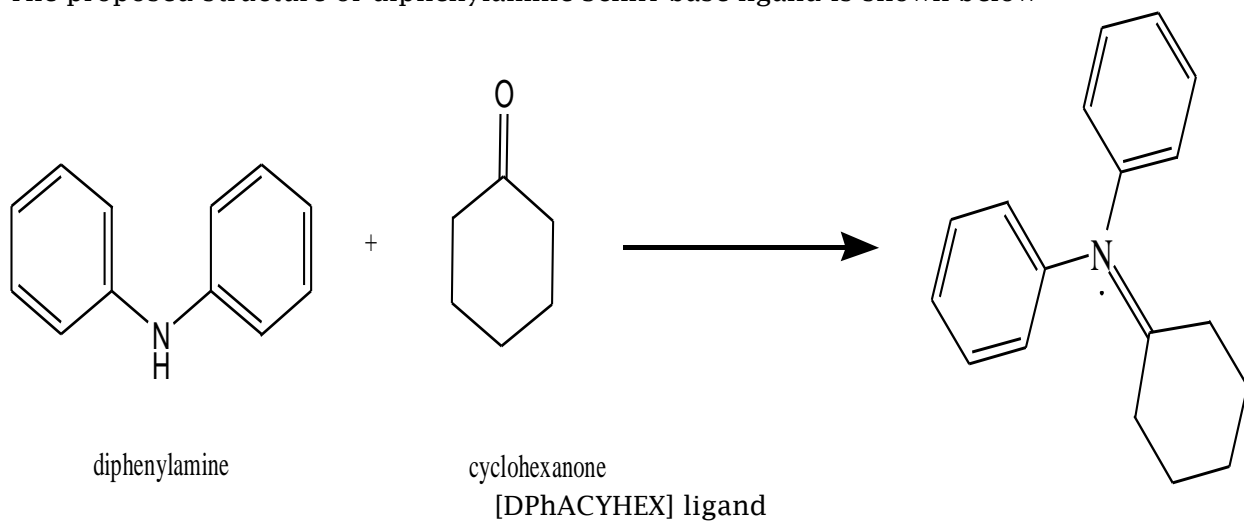
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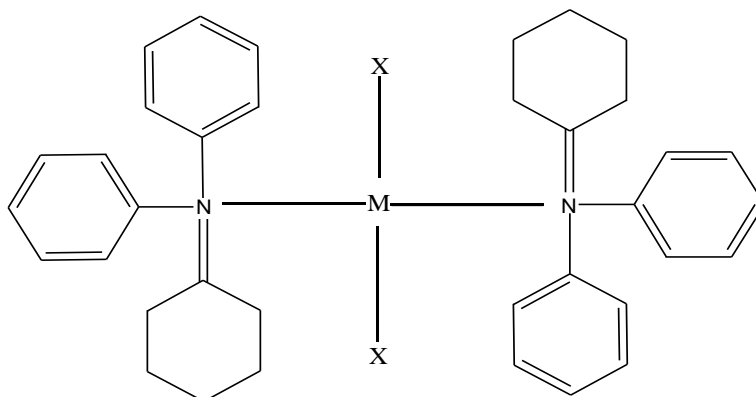
APPENDIX

Proposed structure of [DPhACYHEX] Schiff base ligand

The proposed structure of diphenylamine Schiff base ligand is shown below



The proposed structure of the complex with diphenylamine Schiff ligand is shown below



[DPhACYHEX]₂] Schiff base complex

Where: M = Zn (II), Cd (II) or Hg (II).

X = NO₃⁻ or Cl⁻

Infrared spectra of the ligand and the metal (ii) complexes Infrared spectrum of [PhACYHEX] ligand

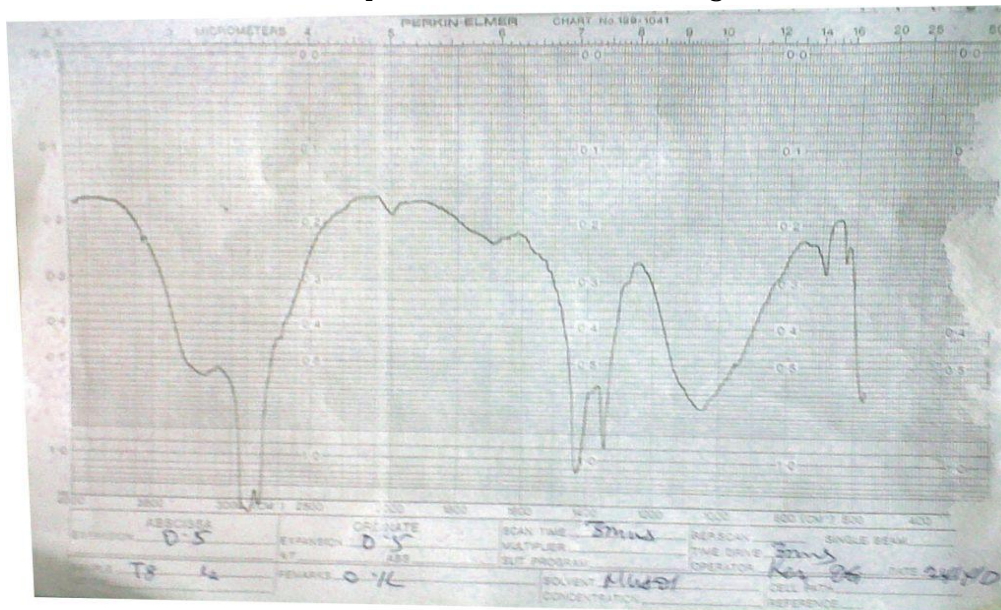


Fig.1 Infrared spectrum of [DPhACYHEX] ligand

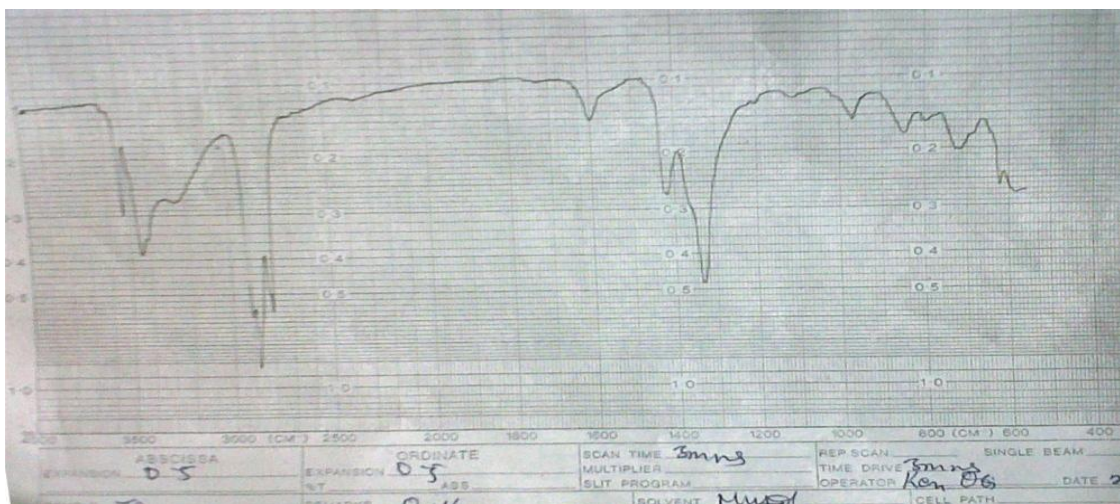


Fig.2. Infrared spectrum of [Zn(DPhACYHEX)₂(NO₃)₂].

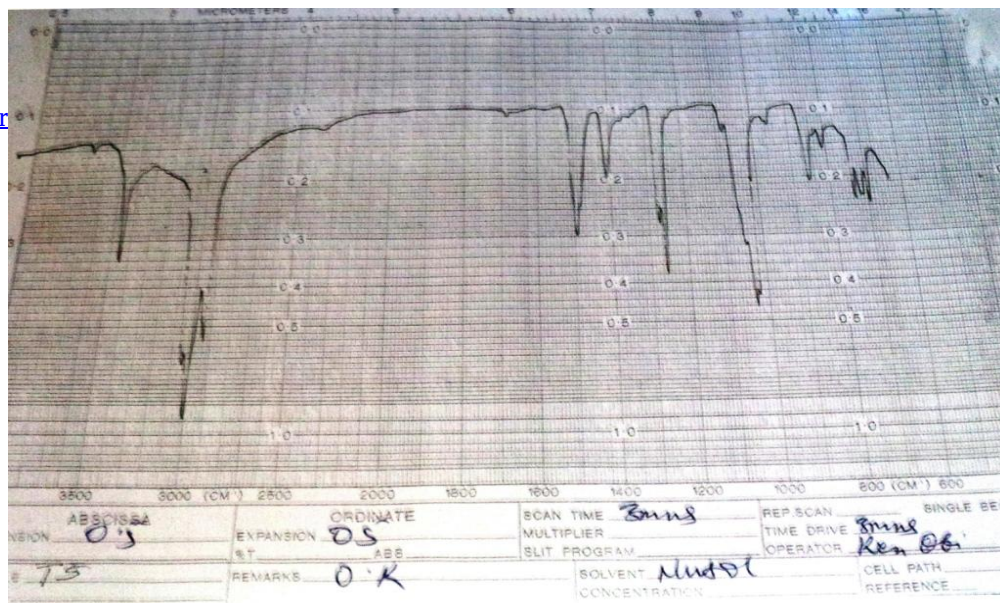


Fig.3. Infrared spectrum of $[Cd(DPhACYHEX)_2].Cl_2$.



Fig.4. Infrared spectrum of $[Hg(DPhACYHEX)_2].Cl_2$.