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Microwave Preparation and Spectroscopic Investigation of Binuclear Schiff Base Metal Complexes Derived from 2,6-Diaminopyridine with Salicylaldehyde

Hasan A. Mohammed*, Nihad Ismeal Taha

Department of Chemistry, College of Science, University of Kirkuk, Kirkuk, Iraqi
Email: *Hassanahmed88@yahoo.com

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Abstract

The binuclear Schiff base complexes prepared by condensation 2,6-diaminopyridine and salicylaldehyde (LH) by using microwave and adding metal salts to ligand by same ratio. The Schiff base ligand was checked by infrared, electronic spectra and ^{1}HNMR spectroscopy and prepared complexes characterized by molar conductivity, infrared, electronic spectra and susceptibility measurements. The values of molar conductivities reveal that the complexes are non-electrolytes, from obtained data of electronic spectra and magnetic moment, an octahedral geometry was suggested, coordinated to the metal ions in a manner with N donor sites of imine groups, and oxygen of phenolic OH group.

Keywords

Schiff Base, Binuclear Metal, Complexes, 2,6-Diaminopyridine, Salicylaldehyde

1. Introduction

The reactions of aldehyde or ketone with primarily amine in which carbonyl group is replaced by imine group is called Schiff bases, are widely used in organic synthesis [1]. Schiff bases' importance increased due to a wide range of applications [2]: Exhibit antimicrobial activity, fungicidal activity [3], pharmacological applications [4]. Salicylaldehyde is an important precursor to a variety of chelating agents [5]. Schiff bases of salicylaldehyde are well known as the polydentate ligands, coordinating as a deprotonated or neutral forms. Schiff bases

used as a ligand in coordination chemistry because its donor ability that deals with Schiff bases and their metal complexes due to synthetic flexibility and sensitivity toward a variety of metal atom and there are many studies [6] which prove this situation [7] [8]. Recently, synthesized Cu(II), Ni(II) and Co(II) complexes show the current interest of researchers in the field of coordination chemistry of these metal ions [9]. Microwave is one of the modern green synthetic methodologies for Schiff bases [10] [11]. Many features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields reactions under solvent free or less solvent conditions are attractive offering reduced pollution. In this paper, we prepare ligand (LH) (2,2'-((1E,1'E)-(pyridine-2,6-diylbis(azanylylidene)) bis (methanylylidene))diphenol) resulting from the condensation of salicylaldehyde with primary amines 2,6-diaminopyridine with some binuclear transition metals that the general formula $[M_2(LH)_2Cl_4]$.

2. Experimental

2.1. Materials and Methods

Higher grade reagents and solvents were commercially available (Fluka A.G., Merck, BDH) and used as received. Infrared spectra were recorded on a Nicolet 100 FTIR spectrophotometer in the 400 - 4000 cm^{-1} range using KBr discs. NMR spectroscopy recorded by Av 300 instrument. Conductivity measurements were carried out on 10^{-3} M solution of the complexes in DMF using conductivity meter Jenway PCM3 at an ambient temperature. The electronic spectra were recorded on a PgT92+ UV-visible spectrophotometer for 10^{-3} M solutions of complexes in DMF as solvent at 25˚C using 1 cm quartz cell. Melting points were recorded on an Electrothermal 9300 apparatus. The magnetic susceptibility measurements were carried out at 25˚C on the solids by Gouy's method using Sherwood Scientific instrument.

2.2. Syntheses of the LIGAND (2,2'-((1E,1'E)-(pyridine-2,6-Diylbis(Azanylylidene)) Bis(Methanylylidene))Diphenol) (LH)

To a mixture of 2,6-diaminopyridine (0.109 g, 0.001 mol) and 2-hydroxybenzaldehyde (0.2442 g, 0.002 mol) add drop of glacial acetic acid were placed in the microwave oven and irradiated at 400 W for 1 min. Then left to cool to room temperature. The solid so formed was filtered and recrystallized from ethanol.

2.3. Synthesis of the Complexes $[M_2(LH)_2Cl_2]$ M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II)

To an ethanoic solution of (LH) (0.317 g, 0.001 mol) was added dropwise to each ethanoic solution of $CoCl_2 \cdot 6H_2O$ (2.30 g, 0.001 mol), $NiCl_2 \cdot 6H_2O$ (2.36 g, 0.001 mol), $CuSO_4$ (0.167 g, 0.001 mol), $ZnCl_2$ (0.136 g, 0.001 mol) and $CdCl_2$ (0.183, 0.001 mol) with a stirring at a room temperature the precipitate formed was filtered off, washed with 10 ml of water and dried under vacuum.

3. Results and Discussion

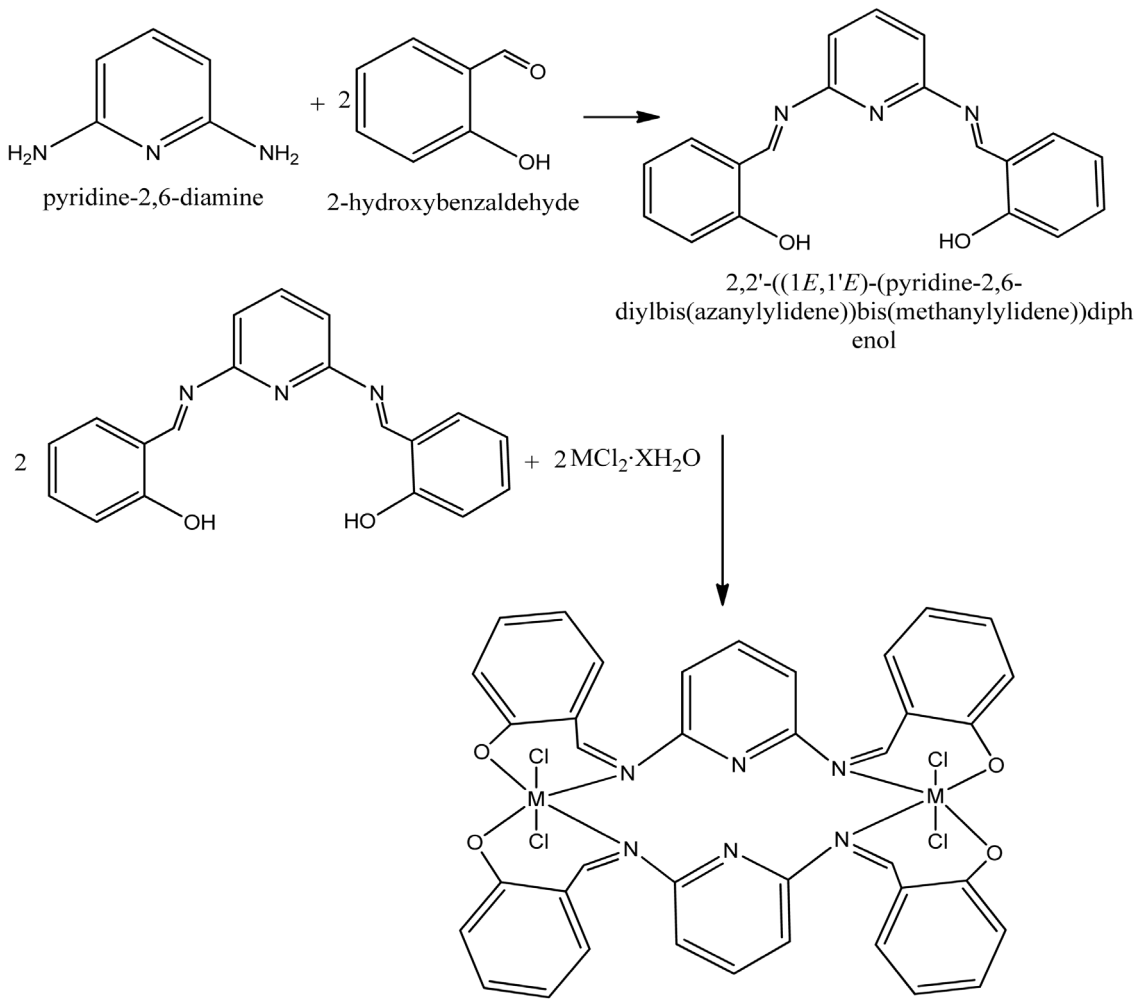
The ligand was prepared by condensation of primary amine and aldehyde under microwave irradiated the complexes were prepared by direct addition of the ethanoic solution of the metals salts (Scheme 1).

The physical properties and analytical data for ligand and complexes are given in Table 1. The values of molar conductivities of the complexes in DMF (12 - 26 $ohm^{-1}\cdot cm^{2}\cdot mol^{-1}$) indicate that all the prepared complexes are non-electrolytes [12].

Table 1. Analytical and some physical properties of the ligand and prepared complexes.

Comp. no.	Chemical formula	Color	m.p ˚C	Λ $ohm^{-1}\cdot cm^{2}\cdot mol^{-1}$	Yield %
1	LH	Light yellow	210	-	85
2	$[Co_2(LH)_2Cl_4]$	Dark green	240 Dec	22	80
3	$[Ni_2(LH)_2Cl_4]$	Light green	245 Dec	23	76
4	$[Cu_2(LH)_2Cl_4]$	Black	285 Dec	26	90
5	$[Zn_2(LH)_2Cl_4]$	Light yellow	221 Dec	18	82
6	$[Cd_2(LH)_2Cl_4]$	Light yellow	235 Dec	12	78

Dec = decompose.



Scheme 1. Preparation of ligand and complexes. M = Co, Ni, when x = 6; M = Cu, Zn, Cd, when x = 0.

3.1. Infra-Red Spectroscopy

The most important of infrared frequencies of Schiff base and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II) complexes are recorded in Table 2. The spectrum of ligand showed the absence of C=O absorption band at 1850 - 1650 cm^{-1}. And appearance of a new band at (1601) cm^{-1} due to azomethine spectra, suggest the formation of ligand [13] [14]. The ligand spectra show a broad band at 3375 cm^{-1} due to stretching vibration of υ (O-H), as well as the C-N band at 1454 cm^{-1}, the band at 1601 cm^{-1} assign to υ (C=N), and the υ (C-O) band at 1277 cm^{-1} [15]. The prepared complexes exhibited very comparable IR features, suggesting that they are of similar structure [16]. In the complexes the absorption band of stretching vibrations υ (O-H) disappeared which is assigned to the complexes formation [17]. The complexes shown absorption bands (1608 - 1613) cm^{-1} due to υ (C=N) shifted to higher frequency compared with ligand [18] [19]. And absorption band of υ (C-N) shows a shifted to lower frequency assign to coordination [7]. The bands in the region of (586 - 421) cm^{-1} confirm the nature of the metal-ligand bonding [20].

3.2. ^{1}HNMR Spectroscopy

The ^{1}HNMR spectrum of ligand (LH), Figure 1 in DMSO–d^6 solvent shows a signal at (δ = 10.27 ppm) equivalent to two protons assigned to (O–H) group of carbon [21]. Two protons of (N=C–H) imine group appears as a signal at (δ = 9.31, 9.96 ppm). The multiplet signals at (δ = 6.11 ppm), (6.68), (6.9), (7.0), (7.35), (7.48), (7.53), (7.95) ppm are due to aromatic hydrogen of carbon [22].

Table 2. FT-IR spectral data of ligand and complexes.

Compound	υ (O-H)	υ (C-N)	υ (C=N)	υ (C-O)	υ (M-N)	υ (M-O)
LH	3375	1454	1601	1277		
$[Co_2(LH)_2Cl_4]$	-	1456	1608	1225	568	443
$[Ni_2(LH)_2Cl_4]$	-	1457	1609	1228	586	427
$[Cu_2(LH)_2Cl_4]$	-	1456	1613	1231	512	432
$[Zn_2(LH)_2Cl_4]$	-	1454	1612	1234	534	422
$[Cd_2(LH)_2Cl_4]$	-	1458	1610	1227	572	451

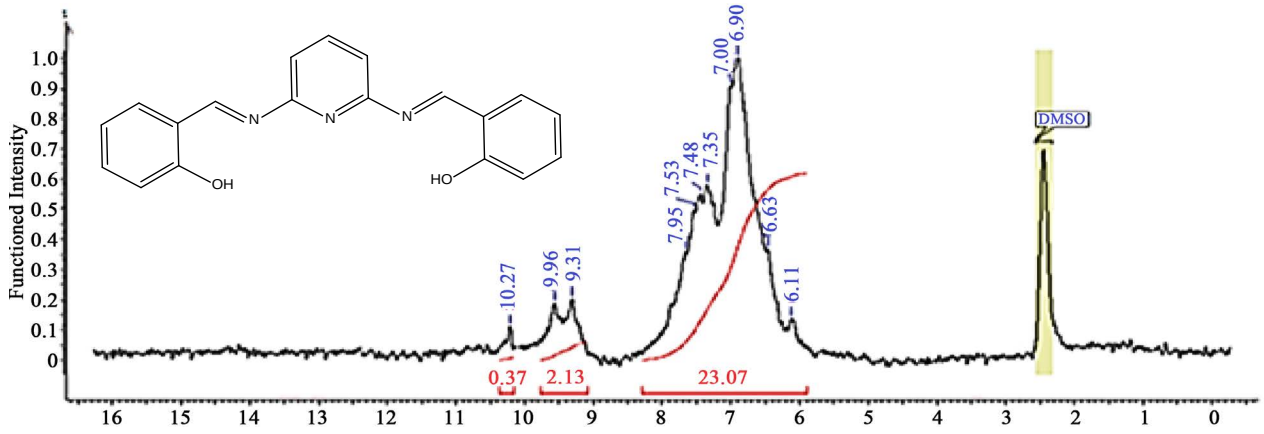


Figure 1. ^{1}HNMR spectrum of the ligand (LH).

3.3. Electronic Spectra

The electronic spectra of ligand appeared two band at (26,455, 35,971) cm^{-1} is assigned to ($n \rightarrow \pi^*$) ($\pi \rightarrow \pi^*$) transition respectively [23]. The cobalt(II) complex displays bands at (13661 cm^{-1}), (13,888 cm^{-1}) and (26,881 cm^{-1}) referring to $^4T_{1g}$ (F) → $^4T_{2g}$ (F), $^4T_{1g}$ (F) → $^4A_{2g}$ (F), $^4T_{1g}$ (F) → $^4T_{1g}$ (P) respectively and other charge transfer bands at (31,645 cm^{-1}) [24]. The nickel(II) complex displays bands at (12,820 cm^{-1}), (14,025 cm^{-1}) and (25,906 cm^{-1}) referring to ($^3A_{2g}$ (F) → $^3T_{2g}$ (F)), ($^3A_{2g}$ (F) → $^3T_{1g}$ (F)), ($^3A_{2g}$ (F) → $^3T_{1g}$ (P)) respectively and other charge transfer bands at (37313 cm^{-1}) [25]. The electronic spectrum of Cu(II) complex shows a band at (12,106 cm^{-1}), referring to (^{2}Eg → $^2T_2$g) and anther charge transfer band at (37,593 cm^{-1}). The electronic spectrum of Zn(II) and Cd(II) shows a bands at (26,178 - 31,645 cm^{-1}), which is assigned to charge transfer as it's shown in the Table 3.

3.4. Magnetic Properties

The cobalt complex exhibit magnetic moment value of 4.80 B.M. this value is greater than spin only due to orbital contribution suggesting octahedral geometry [26]. The Ni(II) complex show magnetic moment value of 2.82 B.M. indicating an octahedral environment. The observed magnetic moment values for the Cu(II) complex are 1.84 suggesting a distorted octahedral geometry [27].

Table 3. Electronic spectral data of the complexes.

Comp. no.	Chemical formula	Band position	Assignments	Geometry	μ_{eff} B.M
1	LH	26,455	$n \rightarrow \pi^*$		--
		35,971	$\pi \rightarrow \pi^*$		
2	$[Co_2(LH)_2Cl_4]$	13,661	$^4T_{1g}$ (F) → $^4T_{2g}$ (F)	octahedral	4.8
		13,888	$^4T_{1g}$ (F) → $^4A_{2g}$ (F)		
		26,881	$^4T_{1g}$ (F) → $^4T_{1g}$ (P)		
		31,645	Charge transfer		
3	$[Ni_2(LH)_2Cl_4]$	12,820	$^3A_{2g}$ (F) → $^3T_{2g}$ (F)	octahedral	2.82
		14,025	$^3A_{2g}$ (F) → $^3T_{1g}$ (F)		
		25,906	$^3A_{2g}$ (F) → $^3T_{1g}$ (p)		
		37,313	Charge transfer		
4	$[Cu_2(LH)_2Cl_4]$	12,106	^{2}Eg → $^2T_2$g	octahedral	1.84
		37,593	Charge transfer		
5	$[Zn_2(LH)_2Cl_4]$	26,315	Charge transfer	octahedral	dia
		28,735	Charge transfer		
6	$[Cd_2(LH)_2Cl_4]$	26,178	Charge transfer	octahedral	dia
		31,645	Charge transfer		

4. Conclusion

The synthesized Schiff base ligand and its binuclear metal complexes were characterized by various techniques. The data obtained from various studies are in good agreement with proposed structure of the Schiff base ligand and its metal complexes. From the above discussion, we suggested that the structure of complexes is octahedral geometry except Cu(II) complex is distorted octahedral.

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