Arabian Journal of Chemical and Environmental Research
Vol. 08 Issue 2 (2021) 275–286

Synthesis and binding mode of N, N'-bis(4-methoxybenzylidene)ethan-1,2-diamine with Co(II), Ni(II) and Hg(II)

Abubakar Abdullahi Ahmed[1]*, Kamal Usman Hamidu [1],
and Kabir Ibrahim Muduru,[1]

[1] *Department of Pure and Applied Chemistry, Faculty of Science, University of Maiduguri, P.M.B. 1069, Maiduguri, Borno State, Nigeria.*

Received 01 July 2021, Revised 26 xxx 2021, Accepted 26 xxx 2021

Abstract

The Schiff base ligand, N, N'-bis(4-methoxybenzylidene)ethan-1,2-diamine and its metal complexes of Co(II), Ni(II) and Hg(II) have been successfully synthesized and characterized physicochemically and infrared spectroscopically. The ligand was obtained in excellent yield of 90.38 % whereas the complexes showed low yield (29.54 – 32.95 %). The ligand and complexes were solid, air and moisture stable with high melting points (180 -320 °C) which further proved their thermostability. The low values of their molar conductance indicate non-electrolytic nature. The infrared spectroscopic data shows appearance of the azomethine peak at 1623.89 cm^{-1} in the spectrum of the Schiff base which shifted to lower wavenumber by 33-55 cm^{-1} in the spectra of the complexes indicating inferentiality of bidenticity of the Schiff base upon interaction with the metal ions having the two azomethine nitrogen atoms as the coordination sites. The empirical formula determination revealed the formation of the complexes in 1:2:2 metal-ligand-chloride ratio which could be represented as $[ML_2Cl_2].nH_2O$ (where M=Co^{2+}, Ni^{2+} or Hg^{2+}, n= 2, 6, 4 for the complexes respectively). An octahedral structure has been proposed for the complexes.

Keywords: thermostabilty, octahedral, bidenticity, infrared spectra, non-electrolyte

---

*Corresponding author. aaahmed.chem@unimaid.edu.ng
E-mail address:

1. Introduction

The condensation of a carbonyl moiety RR'C=O (R, R' = alkyl or aryl group for ketones, R' = H for aldehydes) with a primary amine R"NH_2 (R" = alkyl or aryl group) forms an iminic group RR'C=NR" bond which is referred to as azomethine or secondary aldimine when R'= H [1]. The term Schiff base is now commonly applied to these compounds since the first report by Hugo Schiff more than one and half century ago, and the lone pair of the iminic nitrogen makes Schiff bases popular as ligands for metal centres [2]. Schiff bases that contain aryl substituents having effective conjugation are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable [3]. Two symmetrical Schiff bases, N, N-bis(2-hydroxybenzylidene)ethylene diamine and N,N-bis (2,4-dimethoxybenzylidene)ethylene diamine, have been prepared by the condensation of ethylenediamine with benzaldehyde derivatives; 2-hydroxybenzaldehyde and 2,4-dimethoxybenzaldehyde, as well as Fe(III) complexes with mentioned Schiff bases. The Schiff base ligands and their iron complexes were characterized by elemental analysis, ultraviolet visible spectroscopy (UV-Vis.), proton nuclear magnetic resonance (^{1}H NMR) and infrared (IR) Spectroscopy [4]. In recent years, concerted efforts have been made in the synthesis of Schiff bases derived from ethylene diamine and its metal complexes [5-9]. Similarly, lot of work has been reported on Schiff base metal complexes containing 4-methoxybenzaldehyde [10-12]. For example; Co(II), Ni(II) and Zn(II) complexes of Schiff bases derived from condensation of 4-anisaldehyde with anisidine, (AAN) or 2,4-dinitrophenylhydrazine, (ADN) have been prepared in 1:2 molar ratio (metal:ligand). The compounds have been characterized using elemental analysis, electronic spectra, infrared with molar conductance measurements [13].

Search into the available literature reveals paucity of information on the synthesis of Schiff base derived from 4-methoxybenzaldehyde and ethylene diamine and its metal(II) complexes, hence this research work on the synthesis and complexation behaviour of the ligand towards metal(II) ions.

2. Materials and methods

2.1. Physical measurements

All measurements were carried out using Electronic balance Metra, Model = XY2002C, No = 15055 15. Water of crystallization was determined using thermostat oven: DHG-93030A. The electrical conductivity was recorded using LIDA instrument model DDS-307 conductivity meter. The IR spectrum for each compound was obtained using the Fourier transform infrared (FT-IR) spectrophotometer BUCK Scientific model 530 in the range 600-4000 cm^{-1} and the results were recorded at the Department of Chemistry, Yobe State University, Damaturu, Nigeria. Melting point was recorded on melting point apparatus at the Faculty of Pharmacy, University of Maiduguri. The metal content was gravimetrically determined subsequent to acid decomposition of the complexes [14].

2.2. Synthesis of N, N'-bis(4-methoxybenzylidene)ethan-1,2-diamine

The ligand was prepared by modification of the procedure reported in the literature [15]. This was achieved by addition of 2.44 ml (0.03 mol) of ethylenediamine to 60 ml ethanolic solution of 4-methoxybenzaldehyde (7.29 ml, 0.06 mol) and then few drops of NaOH. The resultant mixture was magnetically stirred under reflux at 70 °C for 3 hours. The reaction is depicted in **figure 1**.

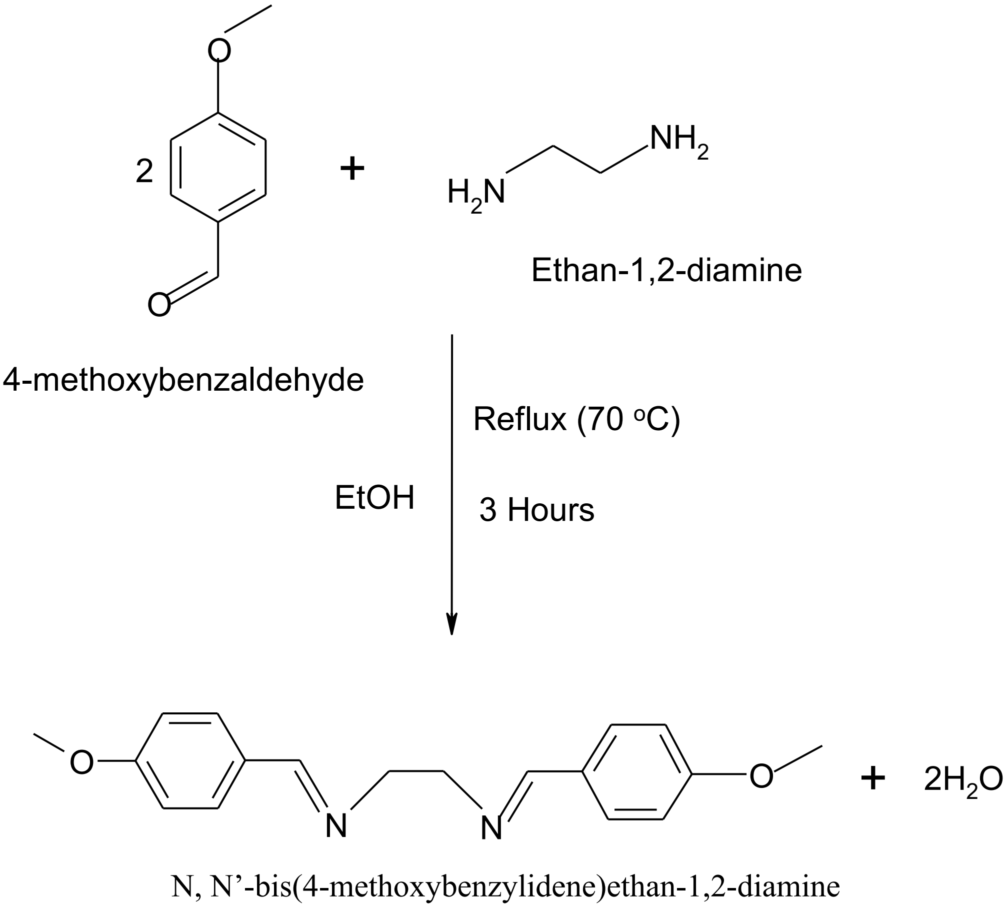


Figure 1. Schematic Depiction of synthesis of N, N'-bis(4-methoxybenzylidene)ethan-1,2-diamine

2.3. Generic Procedure for Synthesis of Metal(II) Complexes

To 1.788 g (0.006 mol) of the synthesized ligand dissolved in 50 ml of ethanol, an equivalent of 0.003 mol of the metal salts ($NiCl_2.6H_2O$, 0.7131 g; $CoCl_2.6H_2O$, 0.7139 g; $HgCl_2$, 0.543 g) was added and heated on water bath for 2 hours at 70 °C. The resultant solution was allowed to stand for 48 hours; thence the products formed were filtered, washed several times and dried in vacuum over calcium chloride [16]. The formation of the complexes is depicted in equation 1:

$$MCl_2.nH_2O + 2L \longrightarrow ML_2.\ yH_2O + 2HCl \tag{1}$$

Where M = Co(II), Ni(II) or Hg(II); n = 0 or 6 and y = 2, 4 or 6

2.4. Estimation of Water of Crystallization

The water of hydration was determined by separately placing 0.2 g of each of the complexes on a watch glass of known weight, which was placed in an oven at 110 ^{o}C until constant weight was obtained. The net weight loss was recorded after cooling as weight of water of hydration. The percentage of water of hydration was calculated using equation 2 [17]. The results are presented in table 3.

$$\%\text{ of water of hydration} = \frac{\text{weight loss}}{\text{weight of sample taken}} \text{ x } 100 \qquad (2)$$

2.5. Molar Conductance Measurements

The 0.001 mol of each of the complex was dissolved in 10 ml of ethanol and the corresponding conductance value was recorded using LIDA instrument model DDS-307 conductivity meter at 33±1 ^{o}C. From the observed conductance recorded, the specific conductance and the molar conductance of the metal complexes were calculated using equations 3 and 4 respectively [18]. The results obtained are shown in **Table 1**:

$$\text{Specific Conductance} = \text{Observed conductance} \times \text{Cell constant} \times \text{Correction factor} \qquad (3)$$

$$\text{Molar conductance} = \frac{1000\text{ K}}{\text{Molar concentration}} \qquad (4)$$

where k = specific conductance

2.6. Fourier transform infrared spectroscopy

In the absence of a powerful technique such as X-ray crystallography, IR spectroscopy is the most suitable technique to obtain information in order to elucidate the nature of the binding of the ligand to the metal ions [24].

3. Results and discussion

3.1. Physicochemical Data

The molecular formulae, weights, colours, percentage yields, melting points and molar conductance values of the synthesized compounds are shown in Table 1. The milk crystalline Schiff base, N, N'-bis (4-methoxybenzylidene)ethan-1,2-diamine was afforded in excellent yield of 90.38 % *via* the condensation reaction between 4-methoxybenzaldehyde and ethylenediamine in 2:1 ratio in ethanolic medium. The Schiff base has a melting point of 180 ^{O}C. This sharp value is indicative of the high purity of the synthesized ligand [19,20]. Moreover, the interaction of the Schiff base with Co(II), Ni(II) and Hg(II) chlorides gave orange, silver and canary coloured metal(II) complexes respectively, with percentage yield range 29.54 – 32.95 %. The colour of the complexes is due to the electronic excitation from t_2g to higher eg by absorption of visible light [21,28]. The decomposition temperatures of the complexes were found to be in the range 300-320 ^{O}C, their values indicate that the metal complexes are thermostable [22] and are in good agreement with values of similar metal complexes [4,13,16].

Table 1. Analytical Data of the Schiff Base and its Metal(II) Complexes

Compound	**Molecular weight (g/mol)**	**Colour**	**Yield (%)**	**M.P/D. T (^{o} C)**	**Molar conductance ($\Omega^{-1}cm^{2}$ mol^{-1})**
Ligand	296.40	Milk	90.38	180	-
$Co(L)_2]Cl_2.6H_2O$	830.73	Orange	31.81	300	5.19
$[Ni(L)_2]Cl_2.2H_2O$	758.49	Silver	29.54	310	21.58
$[Hg(L)_2]Cl_2.4H_2O$	936.39	Canary	32.95	320	*

M.P = Melting point, D.T = Decomposition Temperature, (L) = $C_{18}H_{20}N_2O_2$, *= Insoluble.

3.2. Solubility Profile of the Synthesized Compounds

The solubility of the synthesized Schiff base and metal(II) complexes was tested in common polar and non-polar solvents. The results are shown in Table 2. The Schiff base was found soluble in all the solvents used including water. Similarly, Ni(II) and Co(II) complexes showed solubility or slight solubility in ethanol, methanol and tetrachloromethane. This signifies that there is an interaction between the metal chelates and these solvents.

Table 2. Results of the Solubility Test

Compounds	Solvents													
	D. H_2O		Ethanol		Methanol		CCl_4		Diethyl ether		Acetone		DMF	
	C	H	C	H	C	H	C	H	C	H	C	H	C	H
L	SS	S	S	S	S	S	S	S	IS	IS	S	S	S	S
$[Co(L)_2]Cl_2.6H_2O$	SS	SS	S	S	IS	SS	SS	SS	IS	IS	SS	IS	SS	SS
$[Ni(L)_2]Cl_2.2H_2O$	SS	S	SS	S	SS	S	SS	SS	IS	IS	IS	IS	SS	SS
$[Hg(L)_2]Cl_2.4H_2O$	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS

Keys: L = $C_{18}H_{20}N_2O_{2,}$ IS=Insoluble, S=Soluble, SS=slightly soluble, C=Cold, H=Hot

Therefore, it is assumed that the chemical structure of the metal complexes compose partly of hydrophobic and hydrophilic portions [29]. Their solubility in both polar and non-polar solvent is due to the fact that the complexes have low polarities and similar attractive forces therefore dissolved in the mentioned solvents which have both polar and non-polar ends [23]. In contrast, the Hg(II) complex was insoluble in all the solvents used including DMF. The insolubility and very high decomposition temperature could be due to the strong coordinate bond as a result of chelate formation [30]. The metal content of the complexes has been gravimetrically determined. The observed values are in good harmony with calculated values consistent with 1:2 metal-ligand ratio. The water of crystallization has been determined and expressed as percentage. The observed percentages for the Ni(II), Co(II) and Hg(II) complexes were 4 %, 13 % and 8 % respectively. These experimental percentages are in good agreement with calculated values. It could be inferred that metal(II) complexes under investigation are hydrated with 2, 6 and 4 water molecules respectively (Table 3).

Table 3. Results of metal content and water of Crystallization in the Metal(II) Complexes

Complexes	Molar mass (g/mol)	% Found (Calculated)			Equivalent Number of H_2O Molecule
		Metal	Cl	H_2O	
$[Co(L)_2]Cl_2.6H_2O$	830.73	6.86(7.09)	7.94(8.54)	13.00(13.00)	6
$[Ni(L)_2]Cl_2.2H_2O$	758.49	7.23(7.74)	9.73(9.41)	4.00(4.75)	2
$[Hg(L)_2]Cl_2.4H_2O$	936.39	21.89(21.42)	7.16(7.58)	8.00(7.69)	4

L = $C_{18}H_{20}N_2O_2$

3.3. Infrared Spectral Data of the Synthesized Compounds

The selected bands of the Schiff base ligand and its metal(II) complexes are presented in **Table 4**. and spectra as **figures 2-5**. In the spectrum of the Schiff base ligand, the strong band at 1623.89 cm^{-1} is due to the (C=N) stretching vibration [25]. No peak related to unreacted primary amine or carboxyl groups were observed in the spectrum of the Schiff base. On complex formation, the IR band due to azomethane group got shifted to lower wave number by 33- 55 cm^{-1}, indicating coordination through the nitrogen atom of the azomethine group to the metal ions [16,24]. Furthermore, the band appearing at 800.84 - 814.63 cm^{-1}in the spectra of the complexes supported the coordination through the azomethine nitrogen atom [15].

Table 4. Selected IR Spectra (cm^{-1}) of the Schiff Base and its Metal(II) Complexes

Compound	**ν(OH)H_2O**	**ν(C=N)**	**ν(M-N)**
Ligand	-	1623.89s	-
$Co(L)_2]Cl_2.6H_2O$	3212.92b	1571.70s	802.53s
$[Ni(L)_2]Cl_2.2H_2O$	3288.04b	1568.53 s, sh	814.63w
$[Hg(L)_2]Cl_2.4H_2O$	3188.74b	1590.91m	800.84w

L = $C_{18}H_{20}N_2O_2$, S=strong, sh= sharp, b= broad, m=medium, w= weak

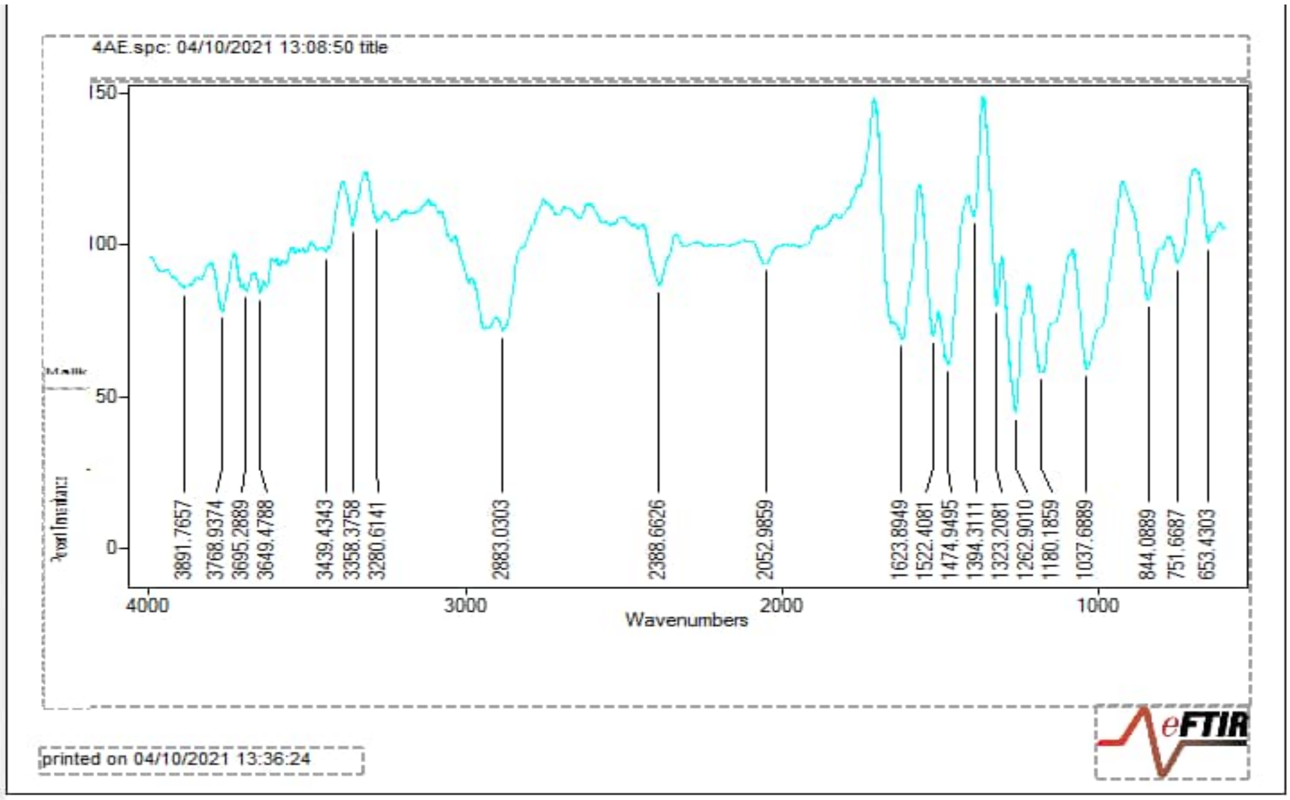


Figure 2. IR Spectrum of Schiff Base Ligand

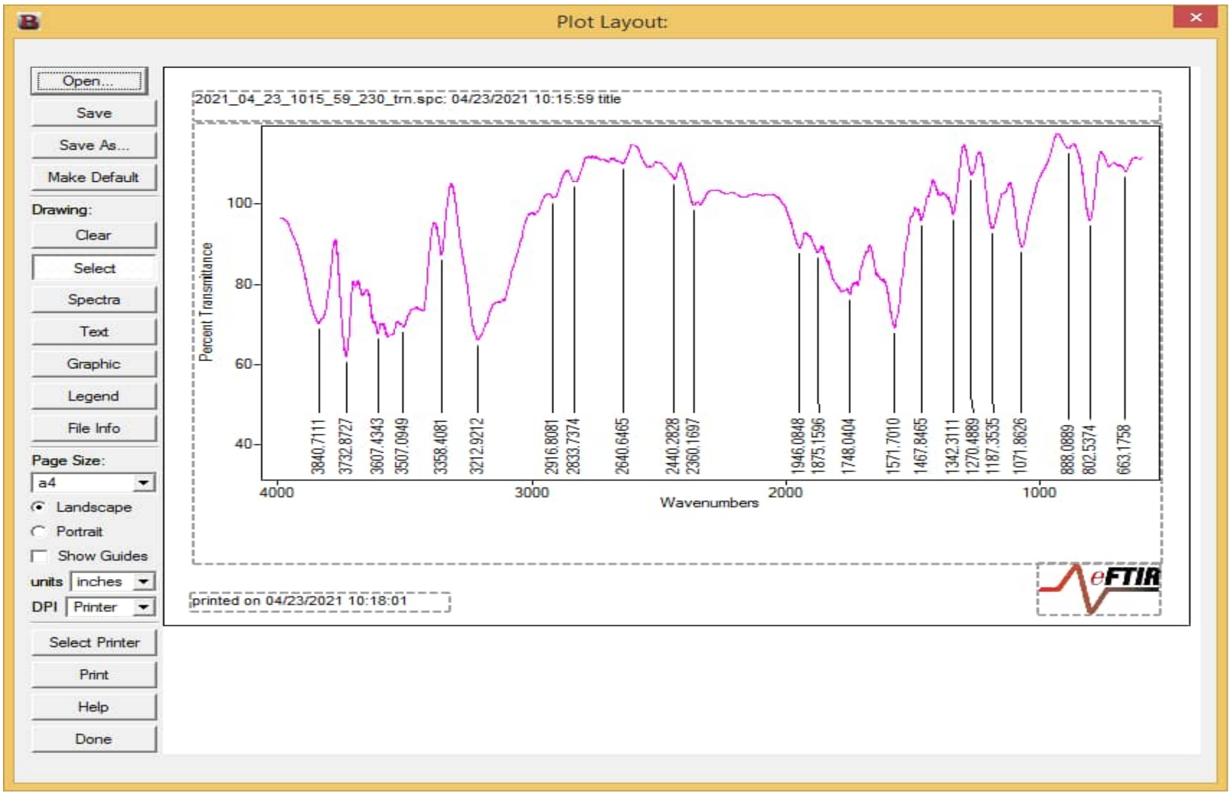


Figure 3. IR Spectrum of Co(II) Complex

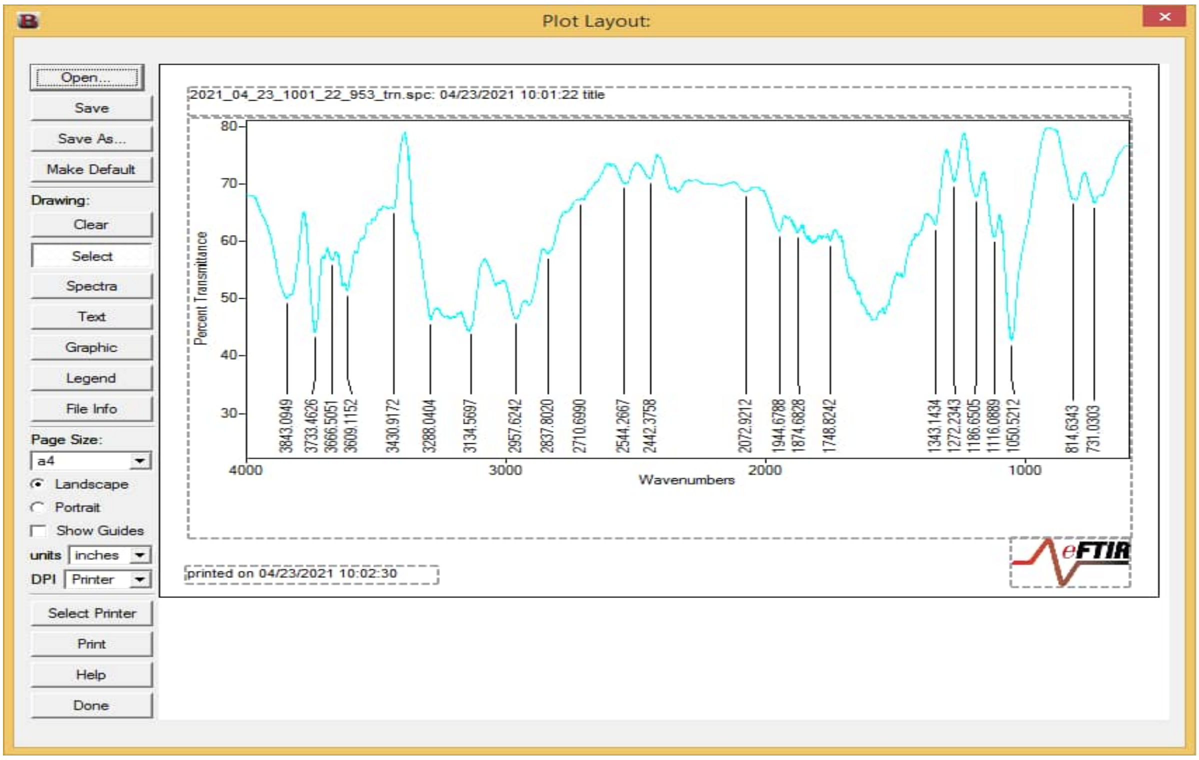


Figure 4. IR Spectrum of Ni(II) Complex

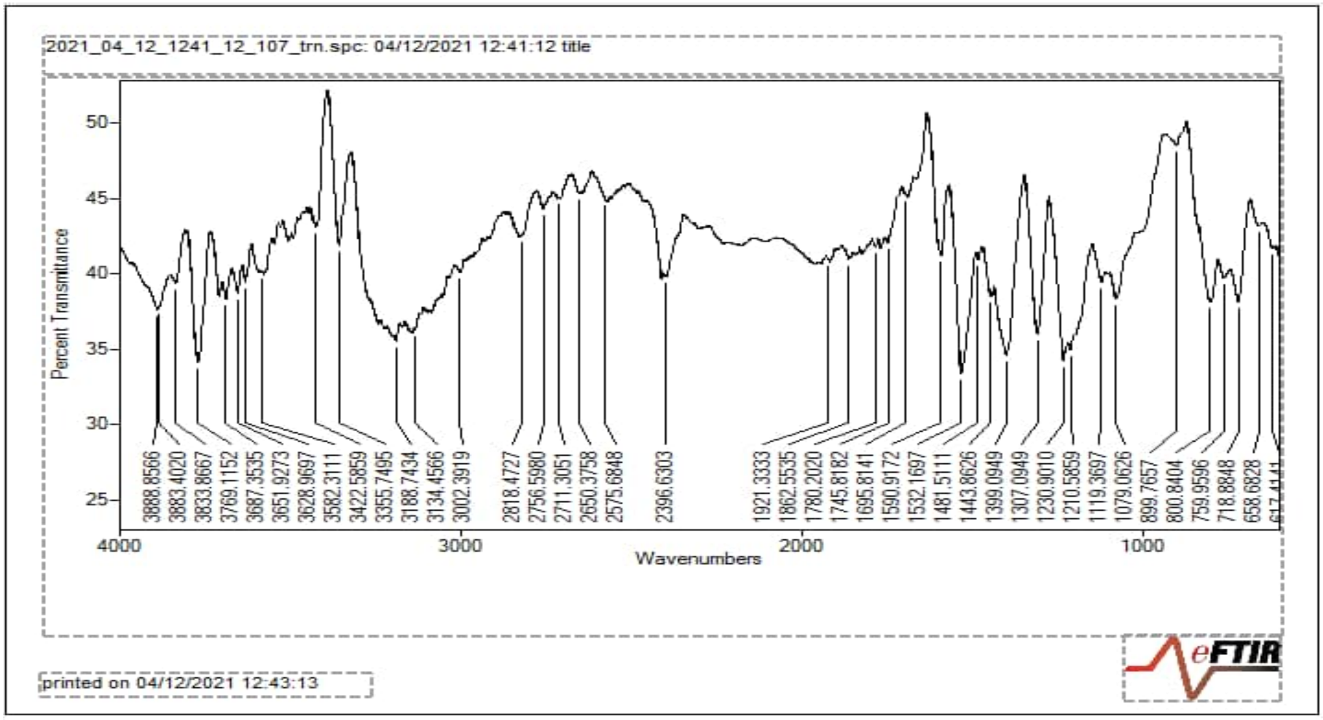
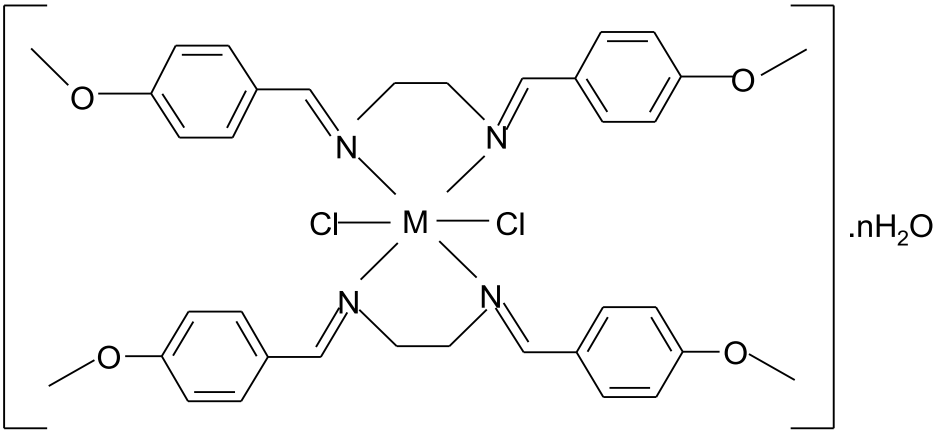


Figure 5. IR Spectrum of Hg(II) Complex

The spectra of the complexes showed broad bands in the region 3188.74 - 3288.04 cm^{-1} arising due to water lattice in the complexes [26,27]. The coordinated chloride ions could not be detected since they occur out of scale of the instrument used [19]. Silver nitrate test only gave white precipitate when aciddigested solution of the complexes where used indicated that the chloride ions are inside the coordination sphere as supported by molar conductance values [12]. From the results and information from the literature [13, 24] the structure of the complexes is proposed as shown in figure 6.



Where M = Ni(II), Hg(II) or Co(II) and n = 2, 4 or 6 respectively

Figure 6: Proposed geometric structure of the Metal(II) Complexes

Conclusion

The Schiff base ligand, N, N’-bis(4-methoxybenzylidene)ethan-1,2-diamine and its transition metal complexes of Ni(II), Co(II) and Hg(II) have been successfully synthesized and characterized physicochemically as well as spectroscopically. The ligand and complexes characterized as solid, air and moisture stable with high melting point which further proof their thermostability. The complexes were non-electrolytic in nature. From the data collected from IR, the Schiff base ligand displayed bidenticity upon interaction with the metal ions with the two azomethine nitrogen atoms being the donor sites. The empirical formulae of the synthesized complexes were $[ML_2Cl_2].nH_2O$. The complexes possess six coordinate octahedral geometry.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

[1] R. Mazzoni, F. Roncaglia, and L. Rigamonti, When the metal makes the difference: Template syntheses of tridentate and tetradentate Salen-type Schiff base ligands and related complexes, *Crystals* 11: 483-503 (2021).

[2] H. N. Aliyu and R. S. Zayyan, Synthesis and Characterization of Biologically Active N, N-Bis(4-benzene azo salicylidene-o-phenylenediiminato cobalt(II) Complex, *Bayero Journal of Pure and Applied Science* 6(2): 127-131 (2013).

[3] T. I. Hussein, M. A. Ahmed, I. A. Arbab, A. S. Ibrahim, M. Al-Bratty and H. A. Alhazimi, Synthesis, characterization and biological activity of a Schiff base derived from o-aminobenzoic acid and its Co(II), Cd(II) and Ni(II) complexes, *European Journal of Chemistry* 11(1): 15-20 (2020).

[4] R. Rafeye and A. Anita, Synthesis and Characterization of New Schiff Bases of Ethylenediamine and Benzaldehyde Derivatives, Along with Their Iron Complexes, *Journal of Applied Chemical Research* 9(2): 59-65 (2015).

[5] M. S. Iorungwa, A. R. Wuana, L. Tyagher, Z. M. Agbendeh, P. D. Iorungwa, N. Surwa and Q. M. Amua, Synthesis, characterization, kinetics, thermodynamics and nematicidal studies of Sm(III), Gd(III) and Nd(III) Schiff base complexes, *ChemSearch Journal* 11(2): 24-34 (2020).

[6] A. Prakash, M. P. Ganwar and K. K. Singh, Synthesis, Spectroscopy and biological studies of nickel(II) complexes with tetradentate Schiff bases having N_2O_2 donor group, *Journal of Development, Biology and Tissue* 3(2) : 13-19 (2011).

[7] M. S. Islam, M. R. S. Ansary, M. A. Farooque and M. A. Asraf, Synthesis and characterization of Schiff base complexes of Cu(II), Co(II) and Cd(II) derived from ethylene diamine and benzaldehyde derivatives, *Asian Journal of Applied Chemistry Research* 6(1): 34-46 (2020).

[8] S. H. Sumra, M. Ibrahim, S. Ambreen, M. Imran, M. Danish and F. S. Rehmani, Synthesis, spectral characterization and biological evaluation of transition metal complexes of bidentate N, O donor Schiff bases, *Bioinorganic Chemistry and Applications* 6:1-10 (2014).

[9] A. A. Osowole, Synthesis and characterization of some tetradentate Schiff base complexes and their heteroleptic analogues, *e-Journal of Chemistry* 5(1): 130-135 (2008).

[10] Y. Ma, H. Li, S. Peng and L. Wang, Highly Selective and Sensitive Fluorescent Paper Sensor for Nitroaromatic Explosive Detection, *Analytical Chemistry* 84: 8415–8421 (2012).

[11] V. K. Gupta, A. K. Singh and L. K. Kumawat, Thiazole Schiff Base Turn-on Fluorescent Chemosensor for Al^{3+} ion, Sensors Actuators B. *Journal of Chemistry* 195: 98–108 (2014).

[12] I. T. Siraj and B. U. Sambo, Synthesis, Characterization and Antimicrobial Activities of Schiff base Derived from Thiourea and Anisaldehyde and its Mn(II), Fe(II) and Co(II) complexes, *Bayero Journal of Pure and Applied Sciences* 11(1): 20-24 (2018).

[13] N. P. Ndahi and Y. P. Nasiru, Complexes of Cobalt(II), Nickel(II) And Zinc(II) With Schiff Bases Derived from 4-Anisaldehyde, *International Journal of Pharmaceutical and Science* 3(12): 5116-5120 (2012).

[14] J. Devi, N. Batra, J. Yadar and S. Pachwania, Synthesis, Characterization and Antimicrobial Evaluation of Transition Metal(II) complexes with Isatinimine Schiff bases & 8-Hydroxyquinoline *Journal of Applicable Chemistry* 8: 97-106 (2019).

[15] A. Uba, M. M. Ladan, U. A. Adamu, B. Magaji, M. N. Ibrahim and M. M. Sani, Synthesis, characterization and antimicrobial assay of some Schiff base metal(II) complexes, *Advances in Research* 21(5): 28-34. (2020).

[16] S. Islam, A. K. M. N. Siddiki, S. Begum and M. Abdussalam, Synthesis, Spectral Characterization and Thermal Behaviour of Newly Derived La(III), Co(III) and Mn(II) Complexes with Schiff base derived from Methionine and salicylaldehyde, *Open Journal of Inorganic Chemistry* 8:55-69 (2018).

[17] A. A. Ahmed, H. N. Aliyu and Y. Yunusa. Synthesis, Characterization and Biocidal Activity of some Schiff Base Metal(II) Complexes. *Jordan Journal of Chemistry,* 15: 95-101 (2020). https://jjc.yu.edu.jo/index.php/jjc/article/view/450

[18] A. K. Ibrahim, B. A. Yusuf and A. Hamisu, Synthesis, Characterization and Antimicrobial Studies of Cu(II) and Zn(II) Complexes with the Schiff Base N-salicylidene-4-chloroanaline, *ChemSearch Journal* 8(2): 68-74 (2017).

[19] N. F. Mahmoud, O. A. Fouad and G. G. Mohammed, Newly synthesized Cu-MOF Based on Schiff base Linker: Structure, Properties, method of synthesis and Characterization, *Journal of Basic and Environmental Sciences* 7: 221-224 (2020).

[20] O. W. Salawu, R. A. Wuana and J. T. Ashimon, Synthesis, Characterization and Corrosion Inhibition of Co(II), Ni(II), Cu(II) and Zn(II) complexes Derived from Nicotinic Acid Hydrazide, *Academic Journals Conference proceedings*, a paper presented at 39th CSN Annual International Conference, Workshop and Exhibition, River State University of Science and Technology, PortHarcout, Nigeria 18th -23rd Sept. 1-5 (2016).

[21] S. Y. Hussaini, A. Ahmed and S. Sani, Studies of Ni(II) and Cu(II) complexes with Schiff Base Derived from Salicylaldehyde and Aniline, *Bayero Journal of Pure and Applied Sciences* 10(2): 245-250 (2017).

[22] B. A. Yusuf, A. K. Ibrahim and A. Hamisu, Synthesis, physiochemical and Antimicrobial Evaluation of Cu(II), Fe(II), Mn(II) complexes with Schiff Base Derived from N-(2-hydroxybenzylidene)-3-(Benzylideneamino) benzensulfonamide, *ChemSearch Journal* 9(1):1-8 (2018).

[23] U. Muhammad and H. N. Aliyu, Synthesis and Charaterization of Bis(3-Hydroxy-3-Phenyl-1-o-carboxyphenyltriazene) manganese(II) complexes, *Chemsearch Journal* 8(1):70-73 (2017).

[24] L. Kafi-Ahmadi, A. P. Marjani and M. Pakdaman-Azari, Synthesis, Characterization and Antibacterial Properties of N, N'-Bis(4-dimethylaminobenzylidene)benzene-1,3-diamine as New Schiff Base Ligand and its Binuclear Zn(II), Cd(II) Complexes, *South African Journal of Chemistry* 71:155-159 (2018).

[25] A. A. Ahmed, Y. Yunusa and H. A. Umar, Synthesis and Characterization of Cu(II) and Zn(II) Schiff base complexes, *International Journal of Science and Applied Research* 2(3):8-16 (2017).

[26] V. D. Bhatt and S. Ram, Synthesis and Characterization of Homo and Heterodinuclear Complexes of Co(II) and Ni(II), *Chemical Science Transaction* 2:1418-1426 (2013).

[27] M. M. El-ajaily, N. S. Al-barki and A. A. Maihub, Mixed Schiff Base Chelates: Synthesis ans Spectroscopic Investigation, *Asian Journal Advanced Basic Science* 4:123-130 (2016).

[28] M. K. Nazeeruddin and M. Gratzel, "Transition Metal Complexes for Photovoltaic and Light Emitting Applications". Photofunctional Transition Metal Complexes, *Structure and Bonding,* 123: 113-175 (2007). Springer, Berlin, Heidelberg.

[29] S. I. Terhemba and J. G. Aondoaver, Chelation Effect of 2,4-pentadione with Ni(II) and Cu(II) Ions, *Chemistry Research Journal* 6(2): 48-57 (2021).

[30] A. O. Sobola and G. M. Watkins, Antimicrobial Activity and Cu(II) Complexes of Schiff bases Derived from Ortho-aminophenol and Salicylaldehyde Derivatives, *Journal of Chemical and Pharmaceutical Research* 5(10): 147-154 (2013).

(2021) ; www.mocedes.org/ajcer