

Synthesis, Spectroscopic Studies and Coordination mode of three Schiff Bases, N-benzylidene-(*o*-, *m*- and *p*-)nitroimine complexes of Zn(II).

*Emmanuel E. Duke Okon¹ (Scopus Author ID 55580458000), V. N. Osabor¹ and G. E. Iniama¹

¹Department of Pure and Applied Chemistry University of Calabar, Nigeria.

* Correspondence Author email: orokinang65@yahoo.com

Abstract: The Coordination mode of three Schiff Base ligands viz ; N-benzylidene-2-nitroimine, N-benzylidene-3-nitroimine and N-benzylidene-4-nitroimine and their Zn(II) ion complexes; synthesized under reflux from catalyzed condensation of Benzaldehyde with corresponding nitroamine, have been investigated. The derived C, H and N elemental analyses data revealed a coordination mode of 1:2 [ML₂Cl₂] metal to ligand mole ratio. The metal complexes showed no indication of electrolytic tendency but points towards diamagnetism. The coordination mode of the metal ion with the Schiff Base ligands occurred via the azomethine nitrogen with differential electron shift attributed to stereochemical properties of the different ligands which in turn distorts the regular tetrahedral geometry of the metal complexes respectively.

Key words Coordination mode, Schiff Base Ligands, Benzaldehyde, 2-, 3-, 4-nitroaniline complexes.

Introduction:

The versatility of Schiff Base and its derived metal complexes in a wide range of fields such as ease and flexibility in modality of synthesis [1] biological and industrial application [2], catalysis [3], medicine [4,5,6] as well as corrosion control [7] cannot be over emphasized. Above these Zn(II) complexes bearing N or O donor imine (Schiff Base) ligands have been reported as more stable and efficient optoelectronic emitters [8]. Borne out of these endearing but challenging attributes of Schiff Base Ligands and corresponding metal complexes, this paper is conceived and aimed at Synthesizing the Schiff Base ligands viz ; n-benzylidene-2-nitroimine, n-benzylidene-3-nitroimine and n-benzylidene-4-nitroimine and Zn(II) complexes under reflux from catalyzed condensation of Benzaldehyde with corresponding nitroamine and investigating

the coordination modes and elucidating their geometry from physico-chemical and spectroscopic data obtained.

Experimental

Materials and Methods

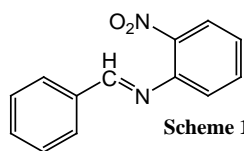
The reagents employed in this studies were AnalaR grade *o*-, *m*- and *p*- (2-, 3- and 4-) nitroaniline, benzaldehyde, zinc chloride, absolute ethanol from Aldrich procured through Lajard (Nig) Ltd. Calabar and used as supplied devoid of further purifications. The doubly distilled water was obtained from the Department of Pure and Applied Chemistry, University of Calabar – Calabar.

Synthesis of Schiff Base Ligands

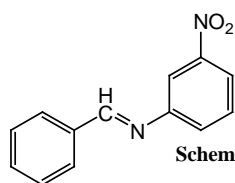
The Schiff Base Ligands for these studies were synthesized from equimolar condensation reaction of 6.9g (0.05M) of the various substituted nitroaniline with 5.3g (0.05M) benzaldehyde. 20 ml ethanolic solution of each

of the substituted nitroaniline was added to same volume of equimolar ethanolic solution of benzaldehyde in a 500 ml round bottom flask (Pyrex). Three drops of glacial acetic acid was added to the resultant exothermically reacting mixture in the flask, to catalyze the reaction. The mixture in flask was refluxed at 450 K on hot plate with constant stirring using magnetic stirrer for three hours. Each was then left to cool in air, the crystals formed were filter in Buchner funnel, recrystallized in ethanol, filtered and dried in a desicator over calcium chloride with percentage yield of approximately 80 - 86% of each ligand.

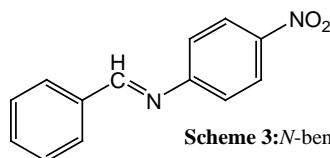
The molecular structures of the different substituted Ligands



Scheme 1: *N*-benzylidene-2-nitrobenzenimine



Scheme 2: *N*-benzylidene-3-nitrobenzenimine



Scheme 3: *N*-benzylidene-4-nitrobenzenimine

Synthesis of Complex

The metal complexes were synthesized by refluxing 2:1 molar ethanolic solutions of each

of the Schiff Base ligands (4.25 g) and (1.36 g) zinc(II) chloride for 2 hours in a water steam bath. The reflux condenser was disconnected whilest the steam heating continued for another 30 minutes to derive slurry. The slurry was cooled in air to obtain pink, yellow and brown dichloro*bis*-*N*-benzylidene-2-nitrobenzeniminezinc(II), dichloro*bis*-*N*-benzylidene-3-nitrobenzeniminezinc(II) and dichloro*bis*-*N*-benzylidene-4-nitrobenzeniminezinc(II) crystals of the corresponding ligands. The complexes were washed, filtered and dried in desicator over calcium chloride. The percentage yield ranged between 74 – 80 % with 4- substituted ligand being the least.

Table 1: Physical Measurements

Sample	% C Found (calcd)	% H Found (calcd)	% N Found (calcd)	% M (Ash) Found	Melting Point (K)
<i>o</i> - C ₁₃ H ₁₀ N ₂	69.63 (69.02)	4.61 (4.46)	12.53 (12.38)	===	312.18
<i>m</i> - C ₁₃ H ₁₀ N ₂	70.01 (69.02)	4.88 (4.46)	12.17 (12.38)	===	322.44
<i>p</i> - C ₁₃ H ₁₀ N ₂	68.52 (69.02)	4.71 (4.46)	12.44 (12.38)	===	310.23
<i>o</i> -ML ₂ Cl ₂	53.00 (53.06)	3.50 (3.53)	9.50 (9.52)	11.0 (11.05)	585.13
<i>m</i> -ML ₂ Cl ₂	53.07 (53.06)	3.48 (3.53)	9.47 (9.52)	11.0 (11.05)	588.48
<i>p</i> -ML ₂ Cl ₂	53.10 (53.06)	3.50 (3.53)	9.50 (9.52)	11.0 (11.05)	596.43

Fig 1: ir spectroph of *o*-BND (Ligand)

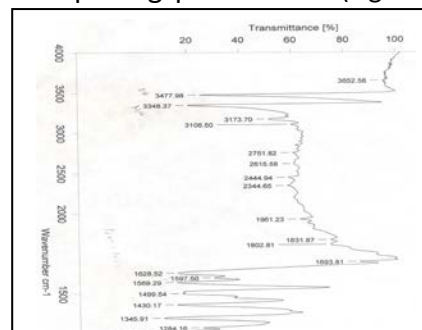


Fig 2: ir spectograph of *m*-BND (Ligand)

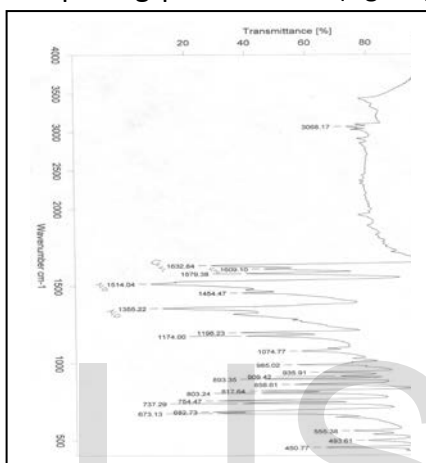
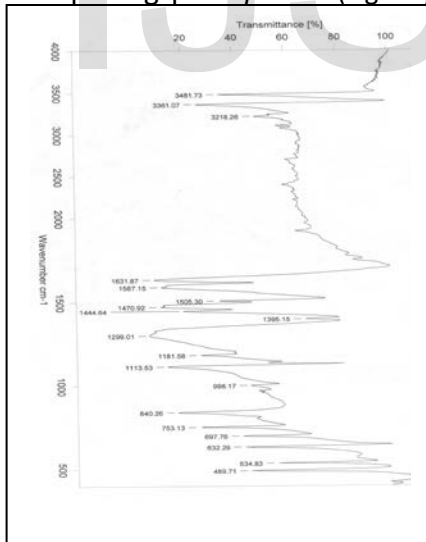
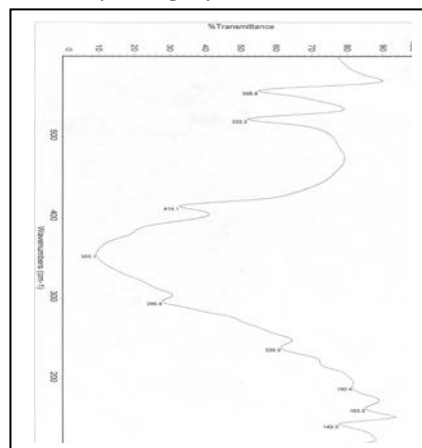


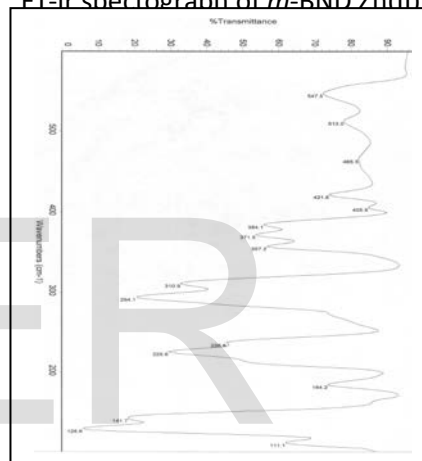
Fig 3: ir spectograph of *p*-BND (Ligand)



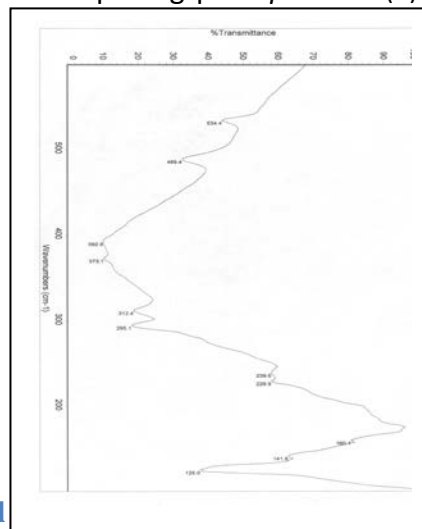
FT-ir spectograph of *o*-BND Zn(II)



FT-ir spectograph of *m*-BND Zn(II)



FT-ir spectograph of *p*-BND Zn(II)



Physical

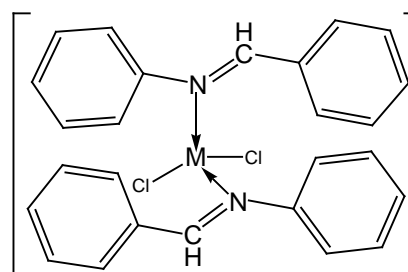
analyses were carried out with Perkin-Elmer 240C Foss Heraeus CHN-O-Rapid at the Center of Materials Analysis, Nanjing University, China.

Determination of the insoluble metal (Zn^{2+}) ion content was conducted *via* FT-IR after standard pre treatment. The spectra at $500-200\text{ cm}^{-1}$ and percentage Transmittance range of 0 – 100 were recorded on Nexus 870 FT-IR at the same Center. Uv-Visible spectrograms of the various ligands were obtained in the range of 200 - 500 nm on Jenway 6500 Uv-Visible Spectrophotometer to elucidate the Electronic Spectra of the products [9].

Results and discussions

The Schiff bases *N*-benzylidene-2-nitroimine, *N*-benzylidene-3-nitroimine and *N*-benzylidene-4-nitroimine were synthesized under reflux from catalyzed condensation of Benzaldehyde with corresponding nitroamine in equimolar (1:1) ratio. The structures were investigated and established *via* elemental analyses, infrared, Uv-vis and ^1H nmr spectroscopic methods; the data gathered informed of the structural representations shown in schemes 1, 2 and 3. The ligands and complexes were air stable and displayed characteristic (yellow, pink and brown) coloration attributable to the ligands as Zn^{2+} in its d^{10} state depicts no chromophores. The structure of the ligands and corresponding complexes were established through elemental analyses, Ir, and UV-Visible spectra. The data obtained from physical measurements are as presented in Table 1. On the other hand the spectrographs bearing the respective precursors are as presented in Figs 1 – 3 followed by respective Ft-ir spectrographs of their Zn(II) complexes. The ir and Ft-ir spectra of the ligands and complexes respectively showed marked shift in

frequency from the precursors conforming to the syntheses of the ligands and the complexes hence corollary aided in vibration band assignments. The inherently $1626 - 1618\text{ cm}^{-1}$ (vs) and $1430 - 1514\text{ cm}^{-1}$ (m) stretching vibration modes of $\nu(-\text{C}=\text{N}-)$ and $\nu(-\text{NO}_2)$ respectively were evident in the ligands [10]. The Ft-Ir of the complexes showed significant down shift in frequency to the range of $392 - 414\text{ cm}^{-1}$ (s) but no distortion in $\nu(-\text{NO}_2)$ observed and assigned band to inform of the strong coordination of the ligands to (Zn^{2+}) the metal center *via* the azomethine nitrogen. [11]. ^1H -nmr of the ligands and complexes overtly showed signals at $\sigma 10.14$ and $\sigma 7.39$ ppm (s) to indicate the presence of methyl and aromatic ^1H respectively [12]. In the same vein ^{13}C -nmr spectra of the ligands showed strong signals at $\sigma 129.5$, $\sigma 130.6$ and $\sigma 136.2$ ppm to signal the presence of sp^2 , aromatic and azomethine carbon atoms respectively [13]. The data so gathered informs the tetrahedral structure proposed for the complex.



Generalized proposed tetrahedral structure of n-benzylidene(2-,3- and 4-)nitrobenzeneaminozinc(II) (not showing positions of the nitro group)

Conclusion

The Schiff ligands n-benzylidene(2-,3- and 4-)nitrobenzeneamine have been successfully synthesized and coordinated to Zn(II) to

derive neutral ZnL_2Cl_2 showing bonding to the metal *via* the azomethine nitrogen of the ligand. The two ligands locates in differential planes of the regular tetrahedron; one situates in-plane of the Cartesian axes while the other and two

covalently bonded Cl^- occupy the three dorsal vertices of a regular tetrahedron but with a slight distortion attributable to the bulky nature of the Schiff base ligand compare to the size of the chloride in the coordination sphere.

References

1. Blagus, A., Cincic, D., Friscic, T., Kaitner, B. & Stilimovic V. (2010). Schiff Bases Derived from Hydroxyaryl Aldehydes: Molecular and Crystal Structure, Tautomerism, Quinoid Effect and Coordination Compounds. *Macedonian Journal of Chemistry and Chemical Engineering*; Vol. 29, (2) 117 – 138.
2. Abdelrazaq, E. A., Omar, M. A. & Al-Numa, K. S. (2010). Synthesis and Characterization of Dinuclear Metal Complexes Stabilized by Tetradentate Schiff Base Ligands. *American Journal of Applied Sciences* 7(5): 628 – 633.
3. Raman, N., Kulandaisamy A. & Jeyasubbramanian, K. (2002) Synthesis, structural characterization, redox and antimicrobial studies of Schiff base Copper(II), Nickel(II), Cobalt(II) Manganese(II), Zinc(II) and Oxovanadium(II) complexes derived from Benzil and 2-Aminobenzyl alcohol. *Polish Journal Chemica* 76: 1085-1094.
4. Bottcher, A., Toshihiko, T. K., Thomas, I. H. & Gary, H. B. (1997) Spectroscopy and Electrochemistry of Cobalt(III) Schiff base complexes. *Inorganica Chemica* 36: 2498-2504.
5. Radecka-Paryzek, W., Kaczmarek, M. T. & Luks, E. (2002) Metal-Ion-Directed Synthesis of Homo- and Heteronuclear Dimetallic Schiff Base Podates. *Polish Journal Chemica* 75: 35-42.
6. Venkatesh, P. (2011) Synthesis Characterization and Antimicrobial Activity of Various Schiff Base Complexes of Zinc(II) and Copper(II). *Asian Journal of Pharmacology and Health Sciences* 1(1): 1 – 9.
7. Aytac, A., Ozmen, U. & Kabasakaloglu, M. (2005) Investigation of Some Schiff Base as Acidic Corrosion of Alloy AA3102. *Materials Chemistry and Physics* 89: 176 – 181.
8. Jean Pierre Costes, Jean Francois Lamere, Chritine Lepetit, Paschal G. Lacroix and Francoise

- Dahan (2005) Synthesis, crystal Structures and Nonlinear Optical (NLO) Properties of New Schiff-Base Nickel(II) Complexes. Towards a New Type of Molecular Switch. *Inorganic Chemistry* 44: 1973 – 1982.
9. Emara, Adel A. A. & Adyl, Omima M. I. (2007) Synthesis and Spectroscopic Studies of New Binuclear transition metal complexes of Schiff bases derived from 4,6-diacetylresocinol. *Transition Metal Chemistry* 32:889 – 901.
 10. Sastry, P. S. S. J., Lonibala, R. K. & Rao, T. R. (1995) Synthesis and Structural Studies on 3d Metal Complexes of Furfurlisonictinoylhydrazone. *Synthesis Reaction Inorganica Met-Organica Chemica* 25(S): 1261 – 1278.
 11. Raman, N. R., Pitchaikani, Y. & Kulandaisamy, A. (2001) Synthesis and characterization of Cu(II), Ni(II) Mn(II) Zn(II) and V(II) Schiff base derived from o-phenylenediamine and acetoacetanilide. *Indian Academy Science (Chemica Science)* 113(3): 183 – 189.
 12. Sarika, R. Yaul, Amit, R. Yaul, Gaurav, B. Pethe & Anand, S. Aswar (2009) Synthesis and Characterization of Transition Metal Complexes with N-, O-Chelating Hydrazone Schiff Base Ligand. *American-Eurasian Journal of Scientific Research* 4 (4): 229 – 234.
 13. Grace E. Iniama, Ayi, Ayi, Peter C. Okafor, Chris A. Edem & Emmanuel E. O. Duke (2014) Copper (II) mixed ligands: Synthesis characterization and antimicrobial activity. *International Journal of Applied Chemistry* 10 (1): 67 – 76.