

HYDROTHERMAL SYNTHESIS AND CHARACTERISATION OF BIS (4-HYDROXYBENZALDEHYDE) - P - PHENYLENEDIAMINE ZINC(II) PHOSPHATE

SAMUEL S. ETUK, JOSEPH G. ATAI AND AYI A. AYI

(Received 15 January 2014; Revision Accepted 14 March 2014)

ABSTRACT

The condensation of a para-phenylenediamine and two equivalent of para-hydroxybenzaldehyde in the presence of Zn^{2+} ions yielded a metallo-ligand of composition $[ZnL_2Ph(NH_3)_2(H_2O)_2]$ I. Compound I melts at $126^\circ C$ and is soluble in common organic solvents such as ethanol (C_2H_5OH), dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The scanning electron micrograph of compound I reveals a rectangular block crystals. The metalloligand synthesized was reacted with ortho-phosphoric acid under hydrothermal conditions at $105^\circ C$ to obtain colourless crystals of compound II with composition $[Zn_4L_2(HPO_4)_6(H_2O)_3]$. Compound II is insoluble in common organic solvents and melts above $300^\circ C$. The structure of compounds I and II have been studied with the help of Infrared and UV- visible spectroscopy. The complexes show broad band absorption in the region $3760 - 3765.71\text{ cm}^{-1}$ due to the symmetric stretching vibration of the co-ordinated water molecule.

KEYWORDS: Hydrothermal reaction, metalloligand, parahydroxybenzaldehyde, para-phenylenediamine, zinc phosphate.

INTRODUCTION

Metal organic framework (MOFs), also known as co-ordination polymers, are formed by the self assembly of metallic centres and binding organic linkers (Abu-Shandi, 2009; Dinca and Long, 2008; Halper, *et al.*, 2006). Owing to their permanent porosity, high surface area, large pore volume and adjustable size and shape, metal-organic framework (MOFs) have been extensively investigated in the past decades and have shown highly promising applications in heterogeneous catalysis, gas separation, gas storage, bio-sensing etc. (Wang *et al.*, 2009; Horike and Kitagawa, 2011).

The design of one, two or three dimensional crystalline network structure depends on choosing the right combination of metal ions (connectors) and the organic ligands (linkers) to form a network structure (Kitagawa, *et al.*, 2004; Li, *et al.*, 1999). In this work, we explore the use of 4-hydroxybenzaldehyde and paraphenylenediamine as ligands to isolate a novel metal organic framework with a potential application in gas storage, separation and catalysis.

Our aim is to offer beginners in the area of metal organic framework synthesis with the knowledge of using cheaper readily available alternative reagent to the costly 1,4- benzenedicarboxylic acid that is used as a house hold reagent in the isolation of metal-organic framework. We anticipate the isolation of crystalline solid by condensing 4-hydroxy benzaldehyde with paraphenylene diamine as ligand base on the basic chemistry that the carbonyl (C=O) group of the 4-

hydroxybenzaldehyde will condense with the amine groups of the paraphenylene diamine to give a new functional group, the azo-methine group (-C=N), while the hydroxyl groups of the 4-hydroxybenzaldehyde left are coordinated to the zinc metal ion.

EXPERIMENTAL

Synthesis of Bis(4-hydroxybenzaldehyde)-p-phenylenediamine Zinc(II) complex $[ZnL_2Ph(NH_3)_2(H_2O)_2]$ (I)

The resultant mixture with molar composition $ZnO + 2C_7H_6O_2 + C_6H_4(NH_2)_2 + 2HCl + 100H_2O + 200C_2H_5OH$

Procedure:

In the synthesis of compound I, 1.22g of Para-hydroxybenzaldehyde ($C_7H_6O_2$) was dispersed in aquoethanol solution made up of 55mL of ethanol and 7.2mL of water in a 250mL beaker. 0.43g of $C_6H_4(NH_2)_2$ (paraphenylenediamine) was added to the mixture and stirred vigorously with magnetic stirrer, followed by the addition of 0.324g of ZnO. 0.5mL of conc. HCl was added as a mineralizing agent. The resultant mixture was stirred for 15 minutes and then refluxed for 6 hours. The product was allowed to stand overnight before it was filtered. The filtrate was concentrated to half its original volume to ease crystal growth. The concentrated filtrate was covered with perforated aluminium foil and allowed to stand in a cupboard for two week. The crystals formed were filtered and dried at room temperature.

Samuel S. Etuk, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State, Nigeria.

Joseph G. Atai, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State, Nigeria.

Ayi A. Ayi, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State, Nigeria.

Synthesis of Bis(4-hydroxybenzaldehyde)-p-phenylenediamine Zinc (II) phosphate $Zn_4L_2(HPO_4)_6(H_2O)_3$ (II)

The resultant mixture with molar composition:
 $[ZnL_2Ph(NH_3)_2(H_2O)_2] + 30DMF + H_3PO_4 + C_7H_7NO_2$

Procedure

$Zn_4L_2(HPO_4)_6(H_2O)_3$ was synthesized by interacting $[ZnL_2Ph(NH_3)_2(H_2O)_2]$ with phosphoric acid, para-amino benzoic acid and dimethyl formamide (DMF). 0.055g of compound I was dissolved in 2mL of DMF in a 50mL beaker. This was followed by the addition of 0.1mL of H_3PO_4 and 0.137g of p-amino benzoic acid under vigorous stirring. The stirring continued for 30 minutes for homogeneity. The pH of the mixture was noted to be 6. The resultant mixture was transferred into a 13mL Teflon-lined autoclave and heated at $105^\circ C$ for five days. The resulting colourless single crystals were filtered and dried at room temperature.

Characterization

Infrared spectroscopy (IR)

The Fourier Transform Infrared (FTIR) spectra of the compounds under investigation were recorded between $4000 - 350cm^{-1}$ on Perkin Elmer FTIR spectrophotometer. The compounds were prepared on KBr disc at the Multidisciplinary Central Research Laboratory, University of Ibadan.

UV-Visible spectroscopy

The UV-visible spectra were obtained at the range of $200 - 850nm$ on a UV-Visible spectrophotometer by Unicam at University of Uyo Chemistry Central Laboratory. The sample (compound I) was dissolved in ethanol then transferred into a cuvette before being placed in the spectrophotometer for the detection of the absorbance.

Melting point determination

The melting points of the compounds were measured using melting point apparatus (SMP₃ Biocote) and capillary tube. The capillary tube was sealed at one end and the sample was introduced through the open end of the tube. The samples in the tubes were inserted into the melting point instrument and the temperature at which the substances melted was noted.

pH determination

The pH of the reaction medium was measured using pH paper

Solubility determination

The solubility test of compound I and II were determined in water, ethanol, dimethylformamide (DMF) and dimethylsulphoxide (DMSO) at room temperature.

Elemental Composition

The elemental compositions of compounds I and II were obtained from the proposed structures by calculation. The percentage yields of the compounds were low, and as such, there were not enough samples for XRF analysis.

RESULT AND DISCUSSION

The SEM images of compound I and II (Fig.1 and Fig. 2) reveal rectangular block crystals for compound I and square plate for compound II. Compound I was insoluble in water but dissolves instantly in ethanol, DMF and DMSO while compound II was insoluble in all the solvents that dissolve compound I. This can be attributed to the differences in the amount of water molecules co-ordinated to the metal centre and the strengths of the metal- ligand bonds in the two compounds. The percentage yield and elemental compositions of the compounds calculated is presented in Table 1.

Thermal measurement of compound I show a low melting point of $126^\circ C$ while compound II was thermally stable up to $300^\circ C$. The low melting point of $126^\circ C$ for compound I is an indication of weak binding forces in the crystal lattice of the metal complex of compound I.

The IR spectra provide valuable information regarding the nature of functional groups present in the compounds. The important IR vibrational frequencies for the compounds Fig.4 and Fig.5 were recorded in the region of $400 - 4000cm^{-1}$ on a KBr pellet as presented in Table 2. The complexes show broad band absorption in the region $3760 - 3765.71 cm^{-1}$ due to the symmetric stretching vibration of the water molecule co-ordinated to the metal atom (Chaplin, 2012). The band at $3438cm^{-1}$ in complex II can be attributed to symmetric vibration of $\nu(N-H)$. The absorption bands in the region $1592.78 - 1615cm^{-1}$ indicates the formation of the azomethine group $\nu(-C=N)$. It also indicates the reduction of the double bond character of carbon-nitrogen bond of the azomethine group (Usharani, Akila and Rajavel, 2012). The bands in the region $2885.71 - 3000cm^{-1}$ can be assigned to the $\nu(-C-H)$ symmetric stretching vibration of aromatic ring. The absorption band at $2371.14cm^{-1}$ indicates the disappearance of the primary amine of paraphenylene diamine as the azomethine group was formed. (Badawi *et al.*,2007). The absorption bands in the region $1905cm^{-1} - 2028cm^{-1}$ can be assigned to *in-plane* bending mode of the aromatic (-C-H) group of compound I (Coates, 2000). The absorption bands at $1450cm^{-1}$ for compound I can be attributed to the symmetric vibration mode of $\nu(-C-N)$ unit. The bands in the region $1663cm^{-1} - 1669cm^{-1}$ is assigned to (-C=C-) symmetric vibration of the aromatic ring. The band at $1039cm^{-1}$ is due to symmetric stretching of the PO_4 group in complex II, while the band at $937cm^{-1}$ indicates the P-O bending vibrational mode. The metal-oxygen (Zn-O) vibrational mode is observed in the region $501 - 591cm^{-1}$ and that of metal -nitrogen (Zn-N) is at $367cm^{-1} - 466cm^{-1}$.

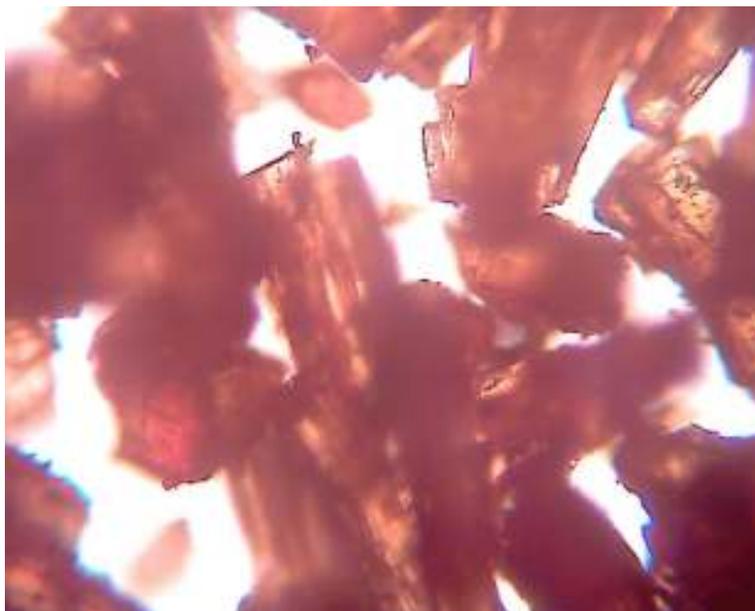
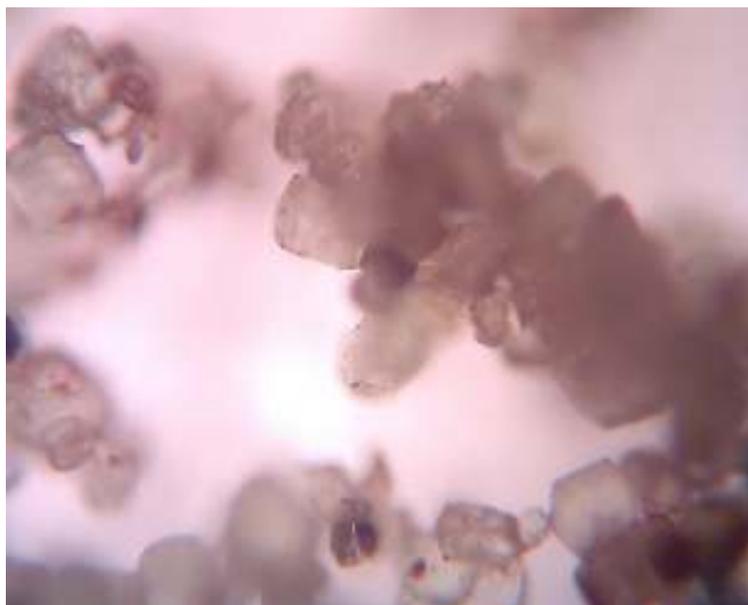
The formation of the Zinc (II) complexes was further confirmed by UV-Visible absorption spectra. The absorption spectrum of the diamagnetic Zinc (II) complex was recorded as C_2H_5OH solution in the range of $200-850nm$ using quartz cuvette of 1 cm path length shows that the absorption band observed between $250-350nm$ is attributed to $n-\pi^*$ electronic transition of the azomethine (-C=N-) group involving the whole conjugation.

Table 1: Percentage Yield and Elemental Compositions of compounds

Compound	Formula	% Yield	Elemental compositions (%)				
			Zn	C	H	N	O
I	$\text{ZnL}_2\text{Ph}(\text{NH}_3)_2(\text{H}_2\text{O})_2$	13.50	7.79	65.76	5.00	10.00	11.44
II	$\text{Zn}_4\text{L}_2(\text{HPO}_4)_6(\text{H}_2\text{O})_3$	85.45	17.35	31.84	2.92	3.71	31.84

Table 2: Infrared Vibrational Frequencies for Compounds I and II(All measurements are in cm^{-1})

Complexes	$\nu(\text{H}_2\text{O})$	$\nu(-\text{C}=\text{N})$	$\nu(-\text{N}-\text{H})$	$\nu(-\text{C}=\text{C}-)$	$\nu(-\text{C}-\text{H})$	$\nu(\text{P}-\text{O})$	$\delta(\text{P}-\text{O})$	$\nu(\text{Zn}-\text{O})$	$\nu(\text{Zn}-\text{N})$
I	3765.71	1592.78	-	1669.15	2885.71	-	-	591.81	444.04
II	3760	1615.28	3438	1663.73	2931.42	1039	937	612.17	466.83

**Fig.1:** SEM Image of $[\text{ZnL}_2\text{Ph}(\text{NH}_3)_2(\text{H}_2\text{O})_2]$ **Fig 2:** SEM Image of $[\text{Zn}_4\text{L}_2(\text{HPO}_4)_6(\text{H}_2\text{O})_3]$

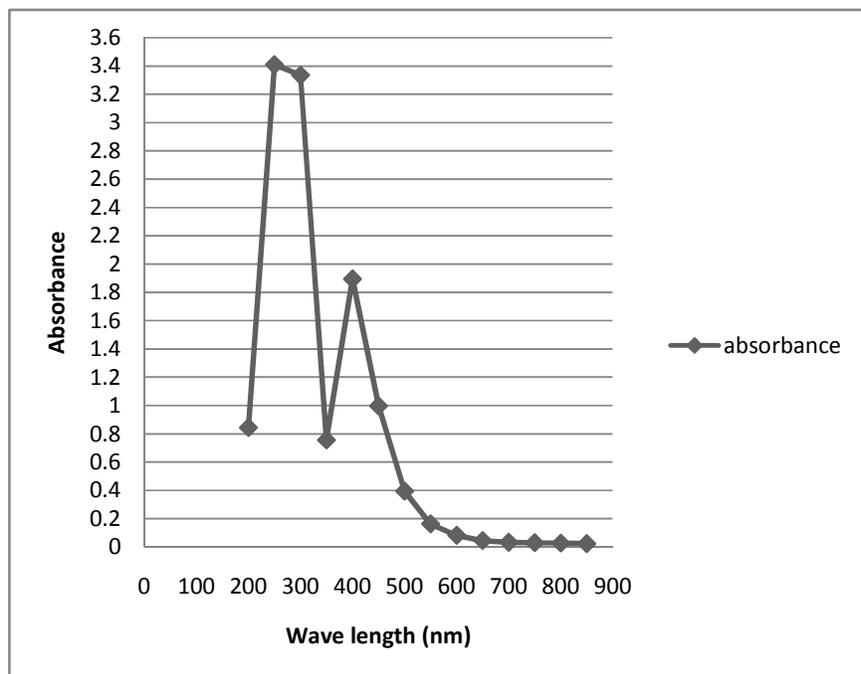


FIG 3: UV Visible Spectrum of $[ZnL_2Ph(NH_3)_2(H_2O)_2]$

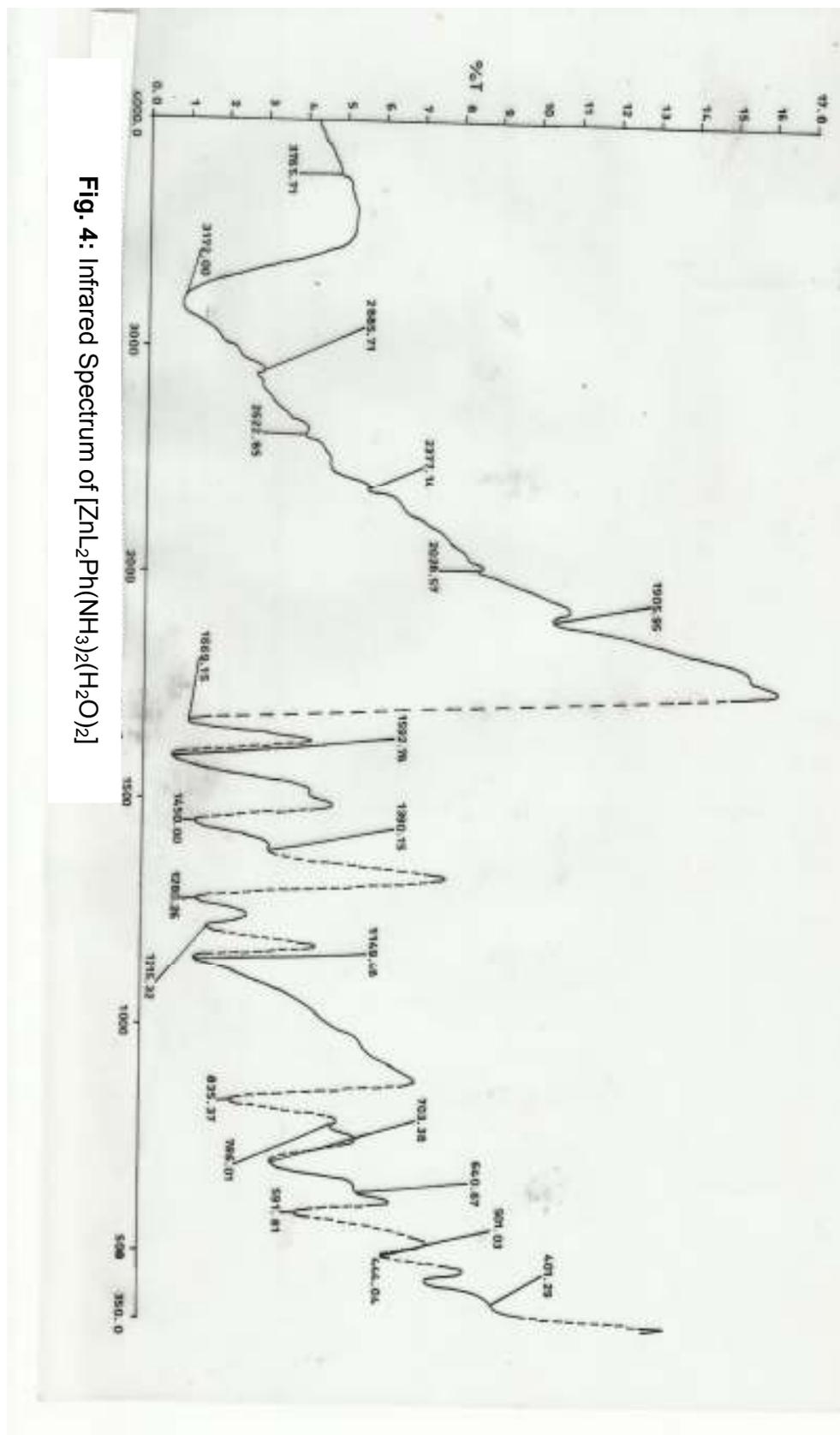


Fig. 4: Infrared Spectrum of $[ZnL_2Ph(NH_3)_2(H_2O)_2]$

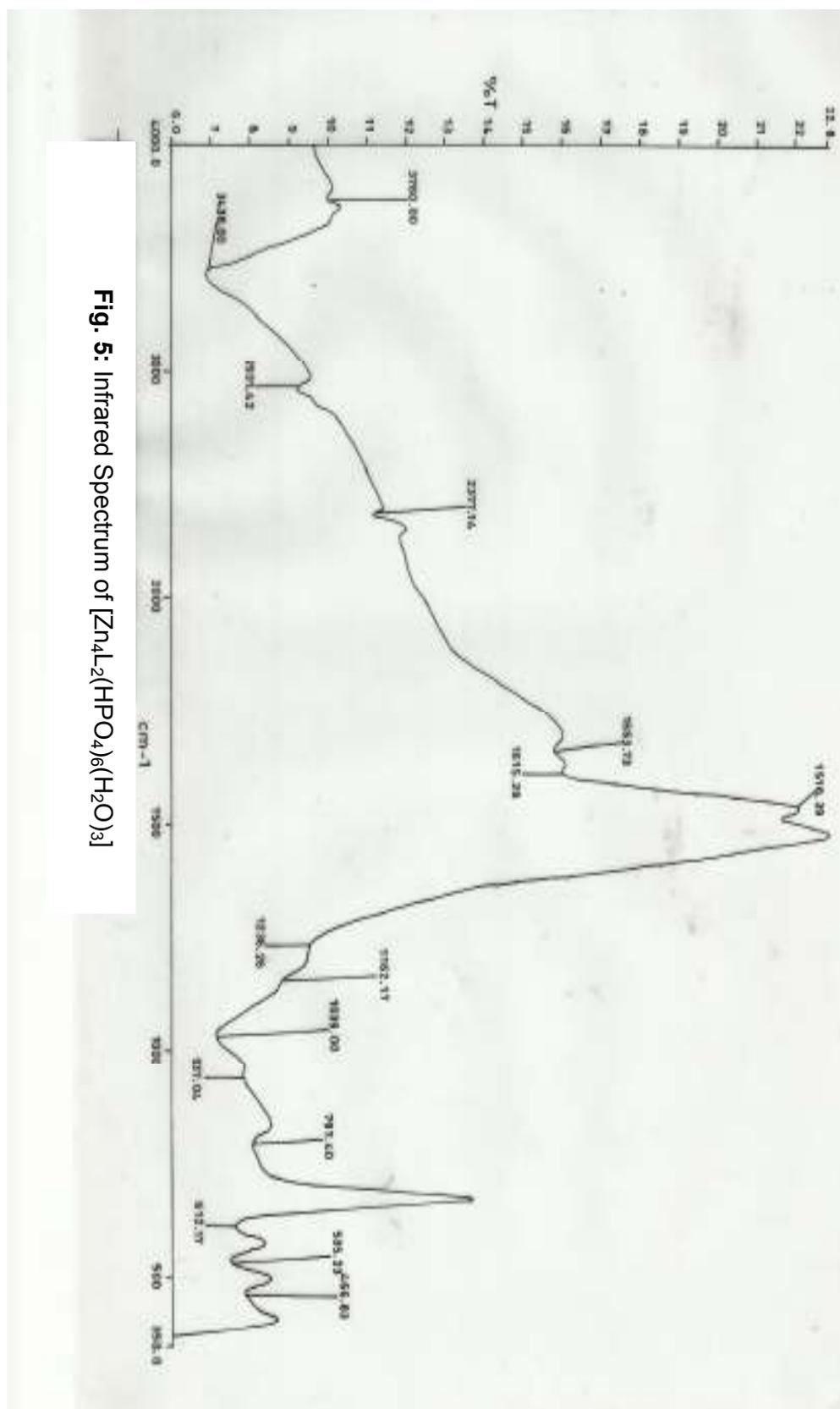


Fig. 5: Infrared Spectrum of $[Zn_4L_2(HPO_4)_6(H_2O)_3]$

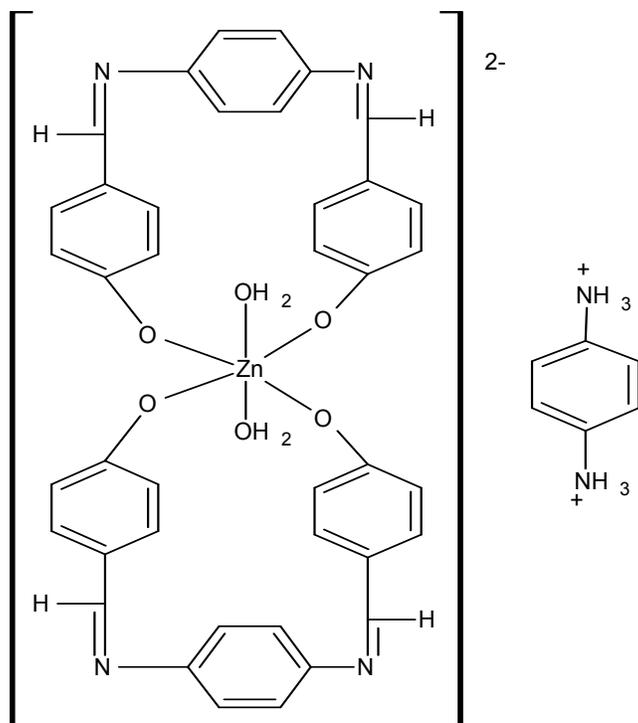


Fig.6: Proposed structure for [ZnL₂Ph(NH₃)₂(H₂O)₂]

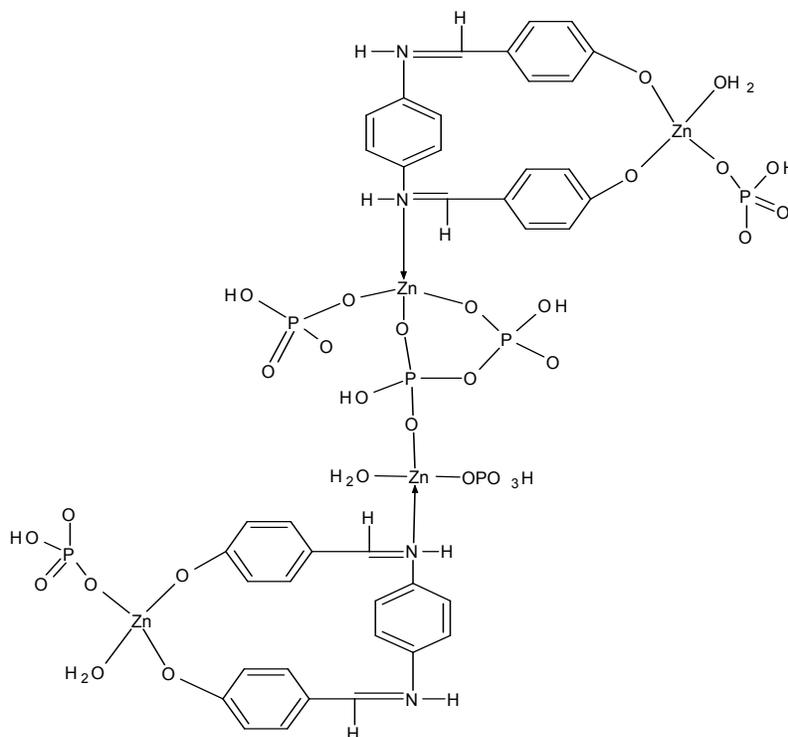


Fig 7: Proposed Structure for [Zn₄L₂(HPO₄)₆(H₂O)₃]

CONCLUSION

We have been able to isolate a novel metal organic framework compound with relatively cheap organic reagents based on basic chemistry as its underlying principle of formation for new scholars in the field of metal organic framework synthesis to start their laboratory work.

The compounds isolated reveals prominent functional groups with their infrared vibrational frequencies between $1592.78 - 1615\text{cm}^{-1}$ for $\nu(-\text{C}=\text{N})$, $1663 - 1669\text{cm}^{-1}$ for $\nu(-\text{C}=\text{C}-)$ and the metal-oxygen (Zn-O) vibration mode between $501 - 591\text{cm}^{-1}$ which can be easily observed in the infrared spectrum of the compounds.

ACKNOWLEDGEMENT

We are grateful to the University of Uyo for allowing us access into their Chemistry Central Laboratory to use their UV-Visible Spectrophotometer to analysis our products and University of Ibadan for granting us access to their Multidisciplinary Central Research Laboratory to use their Fourier Transform Infrared (FTIR) Spectrophotometer for Infrared characterization of our sample. We sincerely appreciate all the authors that their papers were cited in this work.

REFERENCES

- Abu-Shandi, K. H., 2009. Metal phosphate: From synthesis and structures to application in sorption, catalysis and teeth erosion protection. Ph.D., Dissertation, Faculty of Chemistry and Pharmacy, Albert-Ludwigs University, Freiburg. pp 20 – 40.
- Badawi, A. M., Mohamed-Mekawis, A. S., Mohamed, M. Z and Khowdiary, M. M., 2007. Surface and antitumor activity of some novel metal-based cationic surfactants. *Journal of Cancer Research and Therapeutics*, (3): 198 – 206.
- Chaplin, M., 2012. Water Absorption Spectrum. *Water Structure and Science*, p 1.
- Coates, J., 2000. Interpretation of Infrared Spectra, A Practical Approach. Chichester: John Wiley and Sons Ltd. pp 10815 – 10837.
- Dinca, M and Long, J. R., 2008. Hydrogen storage in microporous metal-organic frameworks with exposed metal sites. *Angewandte Chemie International Edition*, (47): 6766 – 6779.

- Halper, S. R., Do, L., Stork, J. R and Cohen, S. M., 2006. Topological Control in Heterometallic Metal-organic frameworks by Anion Templetting and Metalloligand Design. *Journal of American Chemical Society*, (128): 15255 – 15268.
- Horike, S and Kitagawa, S., 2011. *Metal Organic Frameworks: Applications from Catalysis to Gas Storage (First Edition)*. Weinheim: Wiley-VCH Verlag GmbH & Company. pp 209 – 300.
- Housecroft, C. E and Sharpe, A. G., 2008. *Inorganic Chemistry (3rd Edition)*. Edinbrush Gate: Pearson Educational Ltd. pp 89 – 97.
- Kitagawa, S., Kitaura, R and Noro, S., 2004. Functional Porous Coordination Polymers. *Angewandte Chemie International Edition*, (4): 2334 – 2375.
- Li, H., Eddarudi, M., O'Keeffe, M and Yaghi, O. M., 1999. Design and synthesis of an exceptional stable and highly porous metal-organic framework. *Nature*, (408): 275 – 279.
- Usharani, M., Akila, E and Rajavel, R., 2012. Mixed ligands Schiff base complexes: Synthesis, spectral characterisation and antimicrobial activity. *Journal of Chemical and Pharmaceutical Research*, (4): 726 – 731.
- Wang, X., Li, R., Chen, Y., Zhang, Q., Zhang, H., Chen, X. X., Ganguly, R., Li, Y., Jiang, J and Zhao, Y., 2013. A Rationally Designed Nitrogen-Rich metal Organic Framework and its Exceptionally High CO_2 and H_2 Uptake Capacity. *Scientific Reports*, (3): 1149.
- Zhang, Y., Yu, H., Zhou, Y., Hou, D and Kong, Li., 2010. Hydrothermal synthesis and structural characterisation of open framework Cobalt-Tungsten Phosphate. *Chemical Research of Chinese Universities*, (26): 862 – 865.
- Zhao, Y., 2009. Preparation and investigation of Group 13 Metal organo-phosphate hybrid framework materials. Department of Chemistry, Wake Forest University Graduate Schools of Arts and Science.