ISSN No:-2456-2165

Solvent Free Synthesis of Some Metal Complexes of Carboxylate and Nitrogen Donor Ligand

Abdulrahman, N.A., [1] Olowokere, 0.E [2]. , Adeyemi, K.A[2]
Department Of Science Technology,
Federal Polytechnic Ado Ekiti,
Ekiti State Nigeria

Abstract:- Metal-organic frameworks are a class of porous polymeric material, consisting of metal ions linked together by organic bridging ligands. They are recently emerging on the interface between molecular coordination chemistry and material science.The [Ca(PYR)$_2$], [Cu(ANTH)$_2$] and [Zn(MAL)(PYR)] complexes were synthesized by the solvent based and solvent free methods of synthesis using a combination of solvents.Physical and analytical data of the complexes formed shows the [Ca(PYR)] complex to be whitish powder with a melting point greater than 300°C while the [Cu(ANTH)] complex synthesized by refluxing method was observed to have a melting point >400. FTIR analysis of the complexes shows thebidentate mode of coordination of the [Zn(MAL)(PYR)] and the [Cu(ANTH)], observed in the absorption bands at 469 and 501 cm^{-1}attributed to the ʋ(M-N) and ʋ(M-O) in the [Zn(MAL)(PYR)], and at 495 and 521 cm^{-1} in the [Cu(ANTH)] synthesized by the solvent based method while the ʋ(M-N) and ʋ(M-O) bands for the [Cu(ANTH)] prepared by solvent free method of synthesis was observed at 484 and 515 cm^{-1}.

FTIR analysis results of the complexes synthesized by the solvent free method showed close similarity with the FTIR spectra of the complexes synthesized by the solvent based method. The complexes were observed to be stable up to a temperature of about 300°C.

I. INTRODUCTION

Coordination chemistry is undoubtedly the most active research area in inorganic chemistry. Several thousands of coordination complexes have been synthesized and investigated during the past few decades. Ever since the importance of coordination phenomenon in biological processes was realized, lot of metal containing macromolecules have been synthesized and studied to understand the role of these ligands in biological systems, and they also contribute to the development of new metal-based chemotherapeutic agents. These have resulted in the emergence of an important branch of inorganic chemistry viz. bioinorganic chemistry because in several cases, the metal chelates have been found to be more antimicrobial than the chelating agents themselves (Rowsell and Yaghi, 2004). The importance of pyrimidine derivatives arises from their biological, medicinal and agricultural applications. Metal complexes of pyrimidine have been extensively studied in recent years owing to their great variety of biological activity ranging from antimalarial, antibacterial, antitumor, antiviral activities etc.(Haus *et al.,*, 2009)

In the past century, coordination chemistry has lived through a renaissance with the discovery of highly porous, crystalline framework materials composed of metal ions or clusters joined by rigid, polytopic organic linkers.(Yaghi *et al*, 2003) The triumphant success and rapid growth of this class of hybrid materials, dubbed metal– organic frameworks (MOFs) or porous coordination polymers (PCPs), are largely based on their elegant yet simple synthesis and their versatility originating from the use of tailorable linkers and the resulting high surface areas and porosities.

The IUPAC Red Book of inorganic nomenclature from 2005 gives the following definition: A coordination compound is any compound that contains a coordination entity. A coordination entity is an ion or neutral molecule that is composed of a central atom, usually that of a metal, to which is attached a surrounding array of atoms or groups of atoms, each of which is called a ligand.’ ’ 8 We note that this is a very inclusive definition.

Although the validity of rational MOF synthesis is not universal and some doubt has been cast recently on the viability of true secondary building-block approaches. (Hauelorf *et al*, 2009) MOF chemistry continues to intrigue by offering modular and highly rational approaches to sophisticated network topologies, which is rarely seen in the synthesis of dense solid-state materials at elevated temperatures under zeeethermo dynamic control. The importance of the concepts ‘ ‘ surface’ ’ and porosity associated with MOFs, together with their inherent functionality hosted by both organic and inorganic building blocks, gives rise to a kaleidoscope of properties and, hence, applications.

The more traditional ones like adsorption (Kuppler *et al*, 2009), gas storage (Kensali *et al*, 2005) and separation [Venna, 2009] have been complemented in recent years by a host of emerging applications such as in sensor design, (Kensali *et al*, 2005) light harvesting, [Hatakayema *et al* 2011] bioimaging, [Nickerl *et al*] drug delivery,[Tella *et al*, 2014]) and selective heterogeneous catalysis. (Demessence *et al*, 2012) Such applications have been propelled by the ongoing down-sizing of MOFs to the nanoscale and the prospect of amplifying large internal surface areas by ever increasing external surface areas and of combining inherent functionality with high sensitivity. The miniaturization of MOFs has already become one of the most prosperous disciplines in current MOF chemistry as it bridges the gap between fundamental MOF science and prospective applications by imprinting MOFs with morphologies suitable for device fabrication[4]. It was as a result of these unique features as well as wide applicability therefore, that extensive work was done on more crystalline extended structures in which metal ions are joined by organic linkers containing Lewis base – multidentate binding atoms or sites such as nitriles and bipyridines, carboxylates, tetrazolates, sulfonates.

The metal ions which serve as the centre connector are usually chosen from Cu, Zn, Mn, Ni, and Co. The connectors-linkers form continuous porous network structures that can be classified by porous structure as dots (0D cavity), channels (1D space), layers (2D space), and intersecting channels (3D space). MOFs was popularized by Yaghi et al., (2003)especially after MOF-5 was reported. Until now, MOF-5 and Cu-BTC (HKUST-1) were still among the most studied MOFs mainly due to their robust porosity. From 2002, a series of Zn- dicarboxylate MOFs were synthesized and thereby form the concept of isoreticular structure MOFs (IRMOF, $Zn_4O(BDC\text{-}X)_3$, X=Br, NH_2, C_3H_7O), which were prepared by using a variety of 1,4-benzenedicarboxylate acid (BDC) and other elongated dicarboxylate acids with functional groups such as phenols, alkylamines and thiols.

II. METHODOLOGY

A. *APPARATUS*

The apparatus used for this research were obtained from Department of Chemistry, University of Ilorin, these include: beakers, capillary tubes, conical flasks, desiccators, flat-bottomed flask, funnel, gallen-kamp melting point apparatus, oven, magnetic stirrer hotplate, measuring cylinder, mortar and pestle, retort stand with clamp, round-bottomed flask, spatula and filter paper.

B. *MATERIALS AND SOLVENTS*

Ligands and solvents used in this research work were of analytical grade and were used as obtained from Aldrich Co. Ltd. The metal salts used were obtained from the Department of Chemistry, University of Ilorin. These include: calcuim hydroxide [$Ca(OH)_2$] copper (II) acetate monohydrate [$Cu(CH_3CO_2)_2.H_2O$], zinc(II) nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$], and zinc(II) acetate dihydrate [$Zn(CH_3CO_2)_2.2H_2O$] and copper nitrate trihydrate $Cu(NO_3)_2.\ 3H_2O$.

The solvents included dimethyl formamide (DMF), triethylamine (TEA), methanol, ethanol, and distilled water. The ligands used include: malonic acid, pyrazole and N-phenylanthralinic acid.

C. *SYNTHESIS OF MALONIC ACID COMPLEXES*

a) Room temperature synthesis of Zinc – malonate [Zn(Mal)(Pyr)] Complex

The mixture of methanolic solutions of 1 mmol of Malonic acid (0.104g), 1 mmol of Zinc trioxonitrate (V) hexahydrate [$Zn\ (NO_3)_2\ .6H_2O$] (0.297g), and 1 mmol of 3,5-dimethylpyrazole, DMP, (0.096g) was stirred for an hour at room temperature using magnetic stirrer. A white crystalline solid was obtained after 12 days. The crystals were filtered and washed thrice using methanol.

The equation of the reaction is shown in the Scheme 2.1:

$$Zn(NO_3)_2\ .6H_2O + \text{Malonic acid} + \text{Pyr} \xrightarrow[\text{RT, 1 hr}]{\text{Methanol}} [Zn(Mal)(H_2O)_2]_{(s)}$$

Scheme 2.1: Equation of reaction for synthesis of [Zn(Mal)(Pyr)]

Yield: 81 %, M. pt. >300 °C, IR (KBr,cm^{-1}): ʋ(O-H) 3553; ʋ(C-O) 1153; ʋ(M-O) 501; ʋ(M-N) 469

D. *SYNTHESIS OF METAL – PYRAZOLE COMPLEX*

a) Solvent based synthesis of Calcium – pyrazole [Ca(PYR)2]

0.5 mmol, 0.037g of Calcuim hydroxide was dissolved in 10ml of ethanol, then 20 ml of ethanol was also added to pyrazole, DMP, (0.096g) in a beaker and triethylamine TEA (3ml). The TEA was added to the mixture for deprotonation. The resulting solution was refluxed for an hour at a temperature of 60°C. A white powder residue was obtained after refluxing which was filtered, washed with ethanol and dried inside the desiccator.

The equation of the reaction is shown in the Scheme 2.2:

$$Ca(OH)_2\ + 2\ PYR \xrightarrow[60°C,\ 1\ hr]{\text{Ethanol, TEA}} Ca(PYR)_2\ .H_2O)_2$$

Scheme 2.2: Equation of reaction for synthesis of [$Ca(PYR)_2$]

Yield: 89 %, M. pt. >300°C, IR (KBr,cm^{-1}): ʋ(M-N) 485; ʋ(C=N) 1689; ʋ(C-N) 1409

b) Mechano chemical synthesis of Calcium – pyrazole [Ca(Pyr)2]
0.5 mmol of Calcium hydroxide $Ca(OH)_2$ (0.037g) and 1 mmol of pyrazole (0.096g) were weighed into a mortar and pestle that has been previously washed and dried. The reactants were ground for 15 minutes to a fine white powder at a room temperature. The white powder was washed with methanol to remove unreacted starting materials and dried at room temperature. The product was kept in a vial.

The equation of the reaction is shown in the Scheme 2.3:

$$Ca(OH)_{2(s)} + 2\,PYR_{(S)} \xrightarrow[\text{No solvent, 15 minutes}]{\text{Grinding}} Ca(PYR)_{2(s)}$$

Scheme 2.3: Equation of reaction for synthesis of $[Cu(Mal)(H_2O)_2]$

Yield: 89 %, M. pt. >300°C, IR (KBr,cm^{-1}): υ(M-N) 491; υ(C=N) 1670; υ(C-N) 1417

c) Solvent based synthesis of Copper N- phenyl anthralinate [Cu(ANTH)2]
1 mmol of N- phenyl anthralinic acid (0.213 g) was dissolved in 15 ml ethanol and 1 ml of triethylamine (TEA) was added for deprotonation. 0.5 mmol of Copper nitrate trihydrate $Cu(NO_3)_2.\ 3H_2O$ (0.063 g) was dissolved in 5ml DMF. The resulting solutions were mixed and stirred using a magnetic stirrer for 10 minutes giving a dirty green coloration. The mixture was refluxed at 70°C for 2 hours 15 minutes and a brown solution was observed. The precipitate formed was filtered, washed, dried and stored in a sample bottle.

The equation of the reaction is shown in the Scheme 2.4:

$$Cu(NO_3)_2.3H_2O_{(aq)} + 2\,ANTH_{(aq)} \xrightarrow[\text{DMF, Ethanol, TEA}]{\text{Reflux, 70°C, 2hrs 15mins}}$$
$$Cu(ANTH)_{2(s)}$$

Scheme 2.4: Equation of reaction for synthesis of $[Cu(ANTH)_2]$

Yield: 86 %, M. pt. >400°C,IR (KBr,cm^{-1}): υ(O-H) 3355; υ(C-O) 1171; υ(M-O) 521; υ(M-N) 495

d) Mechanochemical synthesis of Copper N- phenyl anthralinate [Cu(ANTH)2] 8b
0.5 mmol of Copper acetate monohydrate (0.199 g) and 1 mmol of N- phenyl anthralinic acid (0.213 g) were ground for 25 minutes. A dark green powder was obtained and was washed with methanol to remove unreacted starting materials. Thereafter, it was oven dried at a temperature of 50°C for 3 hours

The equation of the reaction is shown in the Scheme 2.5:

$$Cu(OAc)_2.H_2O_{(aq)} + 2\,ANTH_{(aq)} \xrightarrow{\text{Grinding, 25 mins}} Cu(ANTH)_{2(s)}$$

Scheme 2.5: Equation of reaction for synthesis of $[Cu(ANTH)_2]$

Yield: 90%, M. pt. = >300 °C, IR (KBr,cm^{-1}): υ(O-H) 3341; υ(C-O) 1158; υ(M-O) 515; υ(M-N) 484

III. RESULTS AND DISCUSSION

A. PHYSICAL AND ANALYTICAL DATE OF THE COMPLEXES

Physical and analytical data of the complexes are shown in Table 3.1. The [Ca(PYR)] complex was observed to be whitish powder with a melting point greater than 300 ^{o}C while the [Cu(ANTH)] complex synthesized by refluxing method was observed to have a melting point >400.

Ligand/MOFs	Appearance	Yield (%)	Molecular Weight (g/mol)	Melting Point (^{o}C)
Pyrazole	White powder	-	68.079	66 – 70
N-Phenyl Anthralinic acid	White powder	-	213.23	124-128
Malonic Acid	White powder White Crystal	-	104.061	135 - 137
[Ca(PYR)] sb	White powder	85	-	>300
[Ca(PYR)] sf	White powder	89	-	>300
[Cu(ANTH)] sf	Dark Green powder	90	-	>300
[Cu(ANTH)] sb	Dark blue	86	-	>400
[Zn(MAL)(PYR)]	White powder	81	-	>300

Table 1: Physical and Analytical Data of the complexes and ligands (n-phenylanthralinic , malonic acid and pyrazole)

B. FT-IR SPECTROSCOPIC RESULT OF THE COMPLEXES

FTIR spectra of the metal complexes showed bands within the range of 3553 - 3341 cm^{-1} which for the [Zn(MAL)(PYR)] and [Cu(ANTH)$_2$] metal complexes and assigned to the υ(OH) absorption bands. The bidentate mode of coordination of the [Zn(MAL)(PYR)] and [Cu(ANTH)$_2$] was observed in the absorption bands at 469 and 501 cm^{-1} attributed to the υ(M-N) and υ(M-O), in the [Zn(MAL)(PYR)], and at 495 and 521 cm^{-1} in the [Cu(ANTH)$_2$] synthesized by the solvent based method of synthesis while the υ(M-N) and υ(M-O) bands for the [Cu(ANTH)$_2$] prepared by solvent free method of synthesis was observed at 484 and 515 cm^{-1}. The relevant absorption bands for the Schiff base and its complexes are presented in Table 3.2 while the spectra are shown in Figures 3.1 – 3.5.

The υ(C-N) absorption band observed in the pyrazole ligand at 1419 cm^{-1} was shifted to lower values of 1409 and 1417 cm^{-1} in the [Ca(PYR)$_2$] complexes prepared by the solvent based and solvent free methods respectively, while the υ(M-N) for the [Ca(PYR)$_2$] complexes was observed at 485 and 491 cm^{-1} for the solvent based and solvent free methods respectively.

Ligand/complexes	υ(O-H) cm^{-1}	υ(C-O) cm^{-1}	υ(M-O) cm^{-1}	υ(M-N) cm^{-1}	υ(C=O) cm^{-1}	υ(C=N) cm^{-1}	υ(C-N) cm^{-1}
Pyrazole	-	-	-	-	-	1676	1419
Malonic acid	3480	1194	-	-	1703	-	-
Anthranilic acid	3370	1185	-	-	1710	-	1425
[Ca(PYR)$_2$]	-	-	-	485	-	1659	1409
[Ca(PYR)$_2$] grinding	-	-	-	491	-	1670	1417
[Cu(ANTH)$_2$]	3355	1171	521	495	1700	-	1415
[Cu(ANTH)$_2$] grinding	3341	1158	515	484	1701	-	1422
[Zn(MAL)(PYR)]	3553	1153	501	469	1707	1682	1403

Table 2: FTIR absorption bands of the complexes and ligands

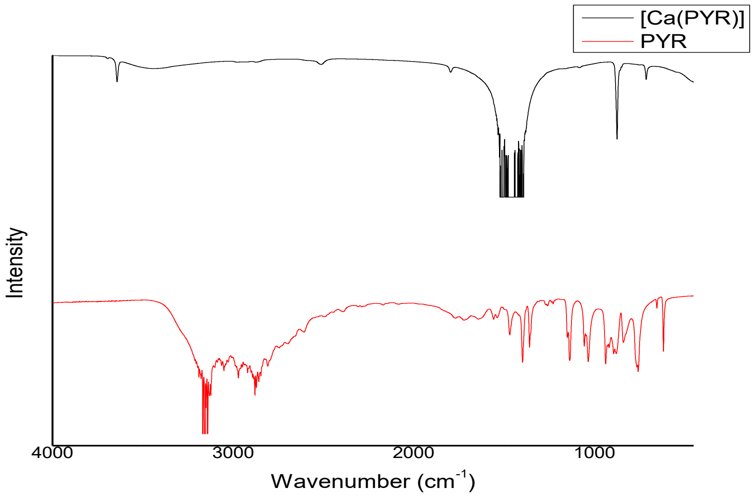

Fig. 1: FTIR spectra of [Ca(PYR)$_2$] prepared by solvent based method

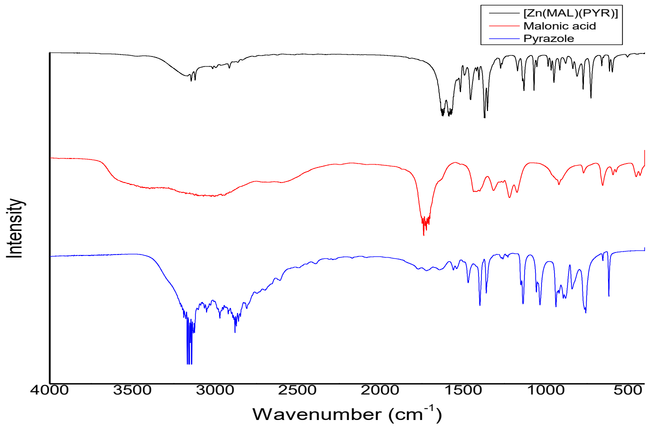

Fig. 2: FTIR spectra of the [Zn(MAL)(PYR)]

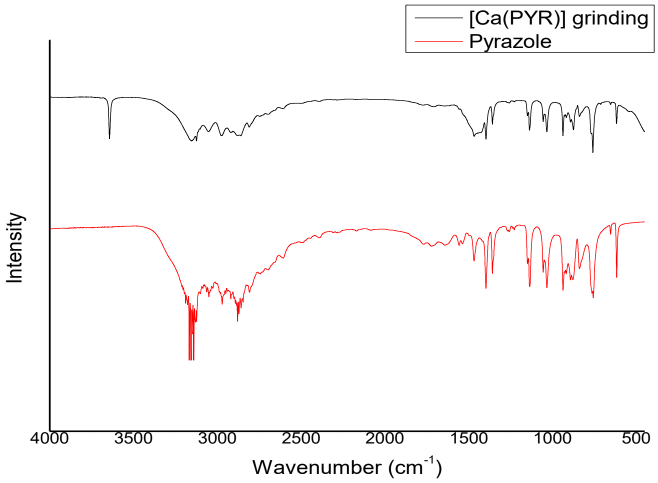

Fig. 3: FTIR spectra of [Ca(PYR)$_2$] prepared by solvent free method

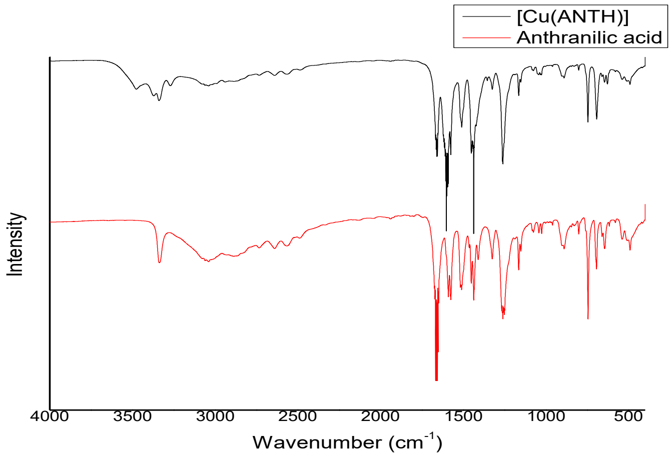

Fig. 4: FTIR spectra of [Cu(ANTH)$_2$] prepared by Solvent free method

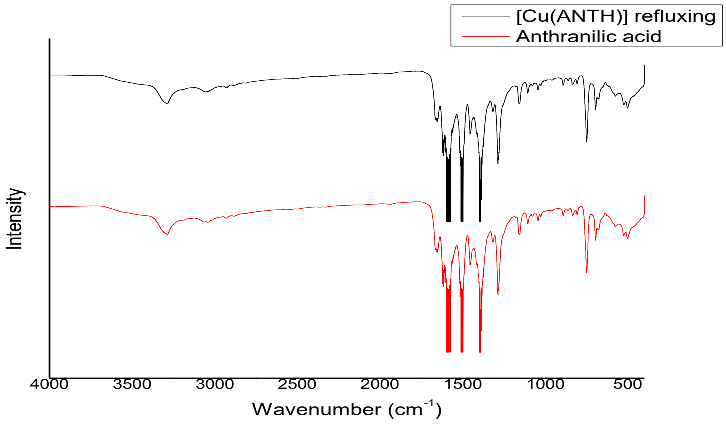

Fig. 5: FTIR spectra of [Cu(ANTH)$_2$] prepared by solvent based method of refluxing

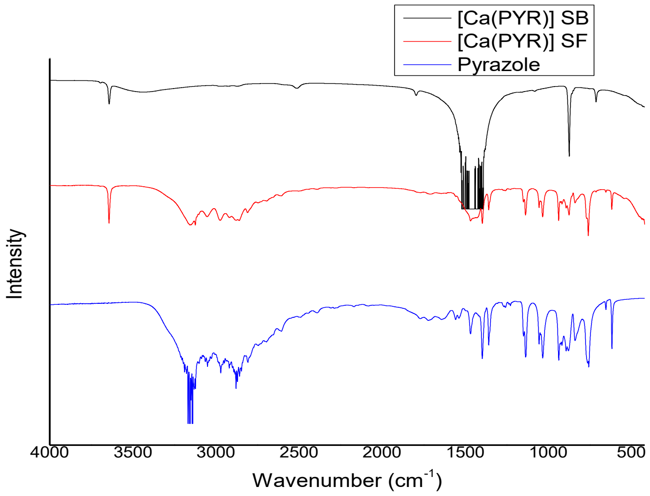

Fig. 6: FTIR spectra of the [Ca(PYR)$_2$] complexes prepared by solvent based and solvent free methods

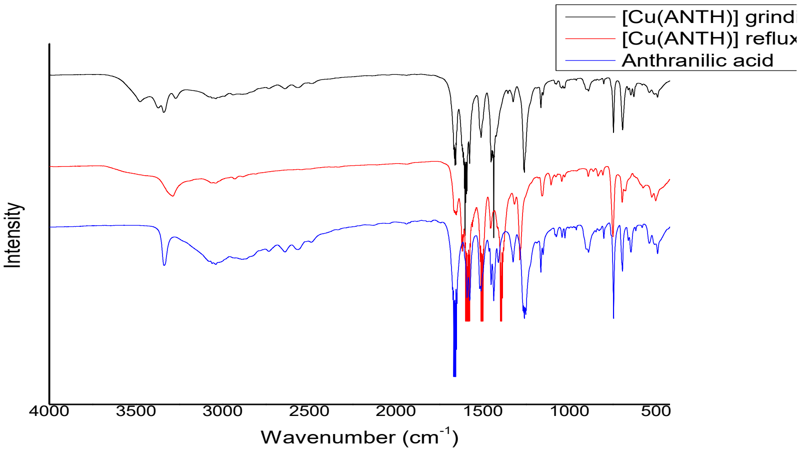

Fig. 7: FTIR spectra of the $[Cu(ANTH)_2]$ complexes prepared by solvent based and solvent free methods

C. ULTRAVIOLET – VISIBLE SPECTRA ANALYSIS

UV-vis spectroscopic analysis of the complexes showed a shift from the n-π* transition values observed in the ligands. This may be attributed to the presence of the metal ion in the complexes. The n-π* transition for $[Cu(ANTH)_2]$ observed at 251 and 262 nm showed a shift from the 214 nm observed in the anthranilic acid ligand used while the band at 576 nm shows the e_g - T_{2g} transition. The $[Ca(PYR)_2]$ showed a at 560 and 584 nm which is attributed to the coordination of the metal atom to the ligand. The [Zn(MAL)(PYR)] complex showed peaks at 265 nm and 295 nm attributed to the n-π* electronic transitions.

Ligand/complex	Wavelength (nm)	Transitions
Pyrazole	225	n-π*
	269	n-π*
Anthranilic acid	214	n-π*
	264	n-π*
Malonic acid	224	n-π*
	266	n-π*
[Cu(ANTH)]	251	n-π*
	262	
	576	e_g - T_{2g}
[Ca(PYR)]	227	n-π*
	271	n-π*
[Zn(MAL)(PYR)]	273	n-π*
	304	π-π*

Table 3: Ultraviolet –Visible Spectra Data of the complexes and ligands

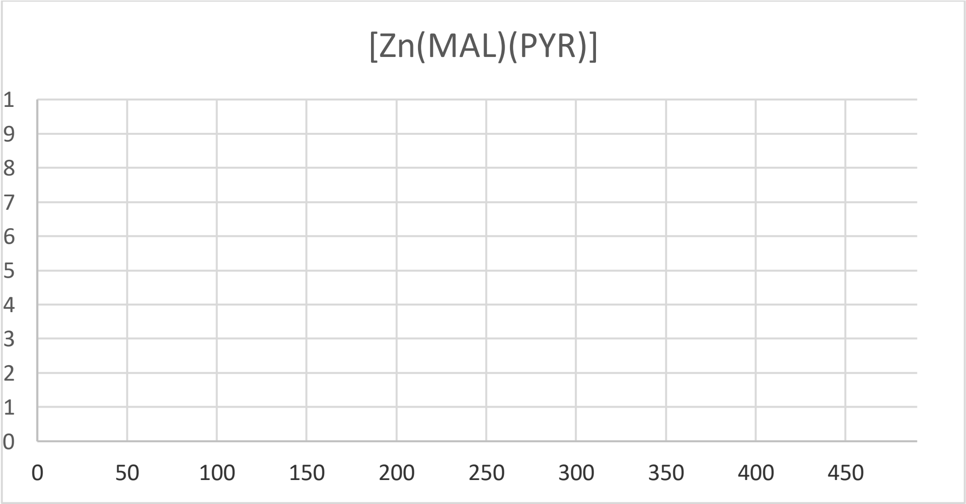

Fig. 8: UV-Vis spectra of the [Zn(MAL)(PYR)] complex

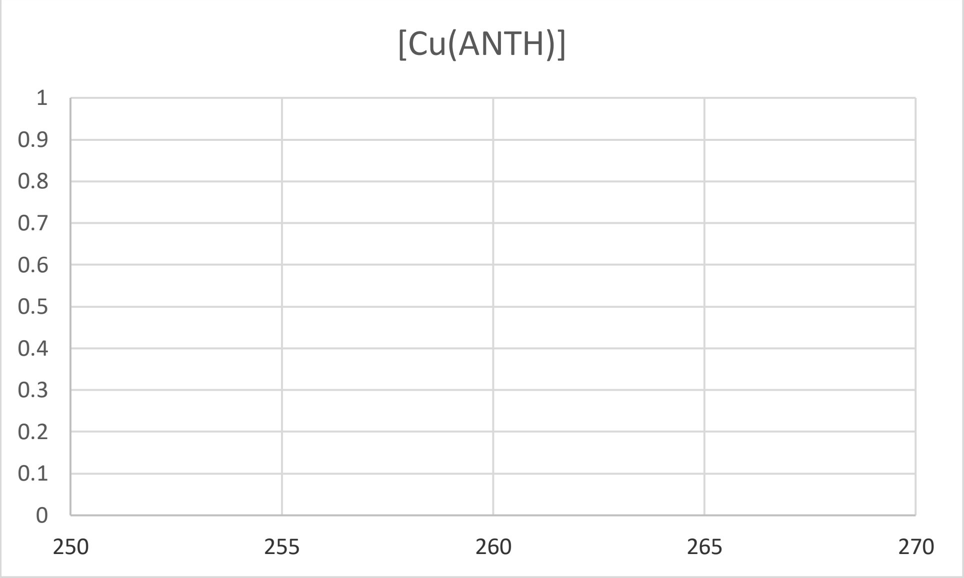

Fig. 9: UV-Vis spectra of the [Cu(ANTH)$_2$] complex

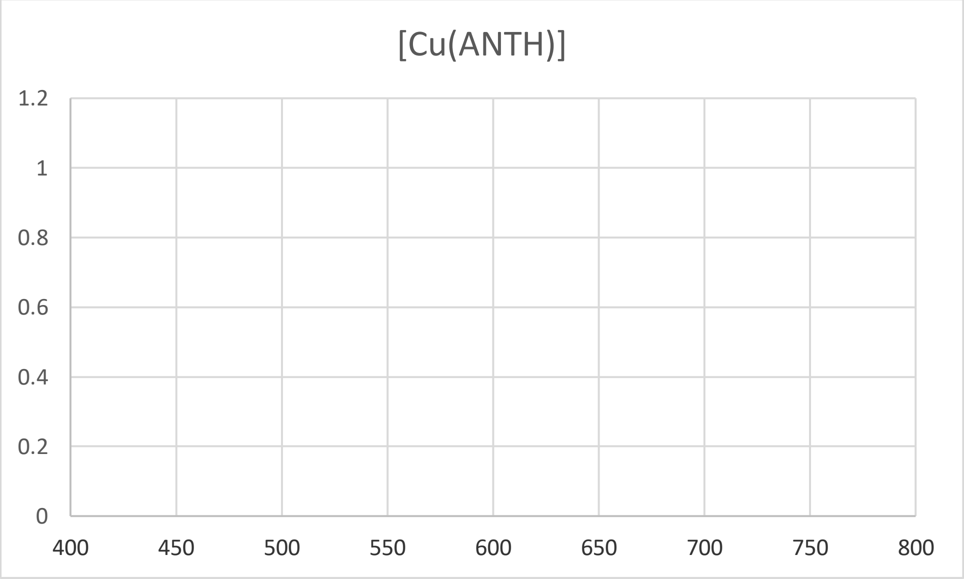

Fig. 10: UV-Vis spectra of the [Cu(ANTH)$_2$] complex

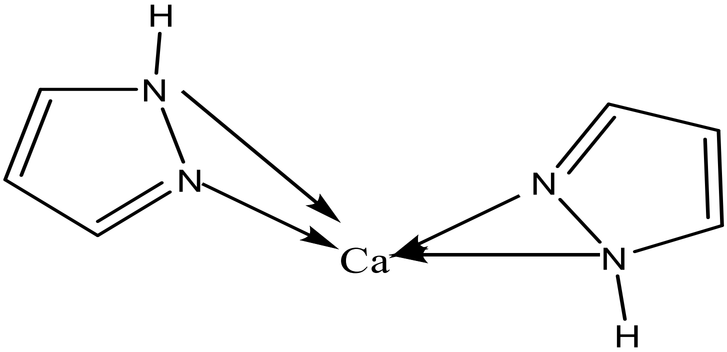

Fig. 11: Proposed structure of the [Ca(PYR)$_2$] complex

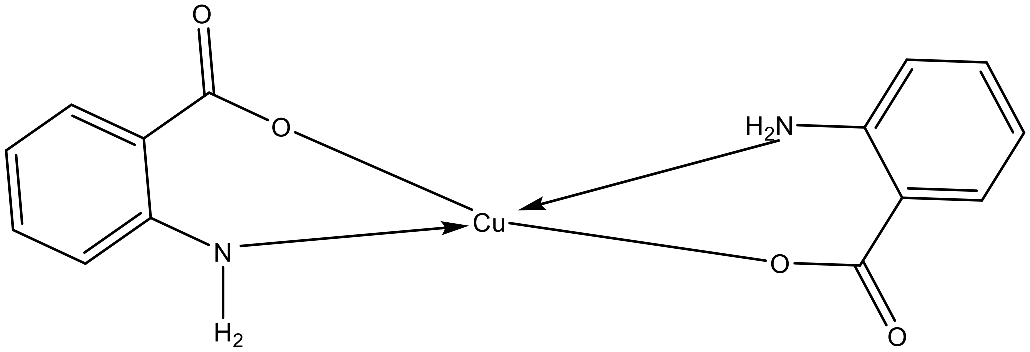

Fig. 12: Proposed structure of the [Cu(ANTH)$_2$] complex

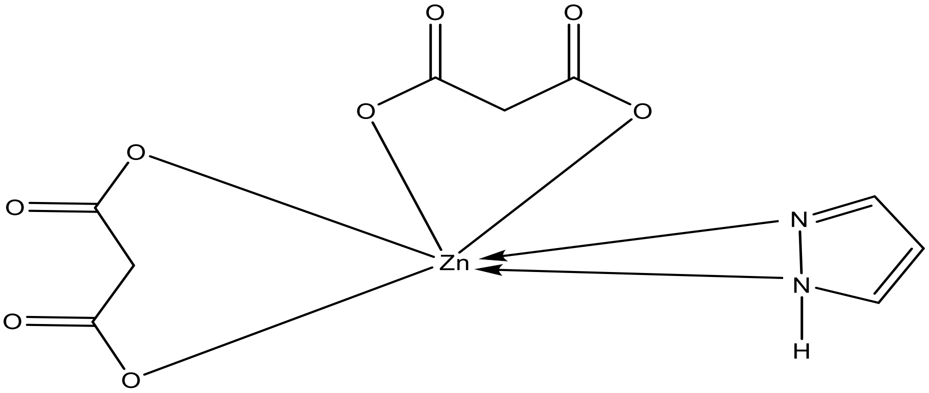

Fig. 13: Proposed structure of the [Zn(MAL)(PYR)] complex

IV. CONCLUSION

Five MOFs have been successfully prepared using solvent-based and solvent-free synthesis. The products obtained in the two methods exhibit excellent chemical and physical properties. These MOFs were constructed from Zn(II), Cu(II), Ca(II); The compounds obtained from both methods were characterized FT-IR spectroscopy and Uv Analysis. Out of the total five MOFs synthesized, one was a crystal with FTIR which were observed to be stable up to a temperature of about 300^{o}c.

V. RECOMMENDATION

It is recommended that further structural characterization should be done such as BET, TGA, NMR and X-ray crystallography to completely elucidate and establish the structure of the MOF. Also, it is recommended that further analytical methods such as SEM, BET and TGA analysis should be carried out on the mechanochemically synthesized MOFs to determine the morphology of the adsorbent most especially their pore sizes and surface areas respectively; and subject them to various applications. More researches should be done on other applications of MOFs, such as in the area of drug loading and delivery, catalysis and most especially in military and security sector on how they can be used for detecting explosives chemicals/compounds.

REFERENCES

[1.] Demessence, A.; Boissiere, C.; Grosso, D.; Horcajada, P.; Serre, C.; Ferey, G.; Soler-Illia, G. J. A. A. and Sanchez, C. (2010): “ Adsorption properties in high optical quality nanoZIF-8 thin films with tunable thickness” *J. Mater. Chem.*; **20**, 7676– 7681.

[2.] Han, S. S. and Goddard, W. A. (2007): “ Lithium-Doped Metal-Organic Frameworks forReversible H_2 Storage at Ambient Storage” *J. Am. Chem. Soc.***129**, 8423-8422.

[3.] Hatakeyama, W.; Sanchez, T. J.; Rowe, M. D.; Serkova, N. J.; Liberatore, M. W. and Boyes, S. G. (2011): “Synthesis of Gadolinium Nanoscale Metal À Organic Framework with Hydrotropes : Manipulation of Particle Size and Magnetic Resonance Imaging Capability”ACS Appl. Mater. Interfaces, **3**, 1502– 1510.

[4.] Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C. and Lin, W. (2005): “ Highly Interpenetrated Metal– Organic Frameworks for Hydrogen Storage” *Angew. Chem.*; Int. Ed.;**44**, 72– 75.

[5.] Rowsell, J. L. C. and Yaghi, O. M. (2004): “Metal – organic frameworks : a new class of porous materials”. *Microppoorous M esoporous Mater.*; **73,** 3–14.

[6.] Tella, A. C.; Owalude, S. O.; Ojekanmi, C. a. and Oluwafemi, O. S.(2014):“ Synthesis of copper Sonicotinate metal– organic frameworks simply by mi xing solid reactants and investigation of their adsorptive properties for the removal of the fluorescein dye. *New J. Chem.***38,** 4494.

[7.] Venna, S. R. and Carreon, M. A. (2009). Highly permeable zeolite Imidazolate framework Membranes for CO_2/CH_4 Separation” *J. Am. Chem. Soc.*; 132, 76– 78.

[8.] Yaghi, O. M. and Li, Q. (2009): “ Reticular chemistry and metal-organic frameworks for cleanenergy” . *Mrs Bulletin*, **34,** 682-690.

[9.] Yaghi, O. M.; Keeffe, M. O.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M. and Kim, J. (2003): “ Reticular synthesis and the design of new materials” *Nature*, **423**, 705-714..

[10.] Yuan, W. (2010): "Study of the mechanochemical formation and resulting properties of an archetypal MOF: $Cu_3(BTC)_2$ (BTC=1,3,5-benzenetricarboxylate).” *Cryst. Eng. Comm.***12**(12), 4063-4065.