FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 3 No. 4, December, 2019, pp 98 –104

MECHANOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF PYRAZOLE AND PYRAZOLATES COMPLEXES OF ZINC (II) IONS

***[1]Abubakar, T., [2]Kurawa, M. A. and [1]Isyaku, S.**

[1]Department of Chemistry, Faculty of Physical Sciences, Ahmadu Bello University, Zaria
[2] Department of Pure and Industrial Chemistry, Bayero University, Kano

*Corresponding Author's email: tukurabubakar19@gmail.com 08037457119.

ABSTRACT

Two synthetic routes were used to synthesized zinc (II) complexes of pyrazole mechanochemically.The first route involved direct reaction of the appropriate zinc (II) acetates with pyrazole and pyrazolium chloride to form bispyrazole zinc (II) salts, [(HPz)$_2$ZnCl$_2$]. This was ground further in the second route with a two equivalents of a base (KOH) to make polymeric zinc (II) pyrazolate [Zn(Pz)$_2$]. In all the synthesis above the ratio of ligand to zinc (II) acetate was 2:1. All the zinc (II) complexes were found to be of different colours and were characterized using solubility test, which showed that the complexes have poor solubility in most of the solvents used except in dimethylsulfoxide where they were soluble and the molar conductivity measurements of the complexes indicated low values (ranging from 2.10-2.23Ω^{-1}cm^{2}mol^{-1}) which showed that they are non-electrolytes. The decomposition temperature showed that all the complexes have relatively low decomposition temperatures (109˚C-110˚C). Characterization of the complexes via infrared analysis confirmed the coordination of metal with the ligand through pyridine-nitrogen and deprotonated-nitrogen in the range of 409.89cm^{-1}Zn-N 435.93cm^{-1} Zn-N bonds (for the route A and B respectively). The magnetic susceptibility measurements were carried out at room temperature and the effective magnetic moment values for all the complexes further confirmed complexation of the metal (II) ions with the ligand and also indicates that the zinc (II) complexes were diamagnetic.

Keywords: Mechanochemical, Pyrazole, Pyrazolium Chloride, Grinding, Mechanochemical Elimination.

INTRODUCTION

The term mechanochemistry is frequently used in a broad sense, covering any chemical reaction induced mechanically. This generates reactive centers (often radicals) which undergo further reactions.). IUPAC defines a mechano-chemical reaction as a Chemical reaction that is induced by the direct absorption of mechanical energy. Stretching and grinding are typical methods for the mechanochemical generation of reactive sites, usually macro radicals, in polymer chains that undergo mechano-chemical reactions (Balema *et al*., 2002).

Grinding is a general term describing mechanical action by hard surfaces on a material, normally to break up the material and reduce its particle size. It may therefore refer to manual methods (mortar and pestle) or non-manual methods such as ball milling. Very small amounts of added liquid can dramatically accelerate, and even enable mechanochemical reactions between solids (Halcrow 2009). Often the molar equivalents added are similar to those of the reactants themselves. Such reactions are therefore 'minimal solvent' rather than strictly 'solvent-free (Kuroda *et al.*, 2009). The term 'solvent-free' synthesis is often accurate in a practical sense and care must be taken when making mechanistic interpretations. In the same general context, while a reaction in itself may be described as 'solvent-free' (in the practical and/or mechanistic sense), purification may still be needed and this may require a solvent. Therefore, a solvent-free reaction does not necessarily correspond to a solvent-free process overall (Chen *et al.*, 1997 and Antesberger *et al.*, 2005,).

MATERIALS AND METHODS

All the chemicals and reagents were of analytical grade and used as received without further purifications.

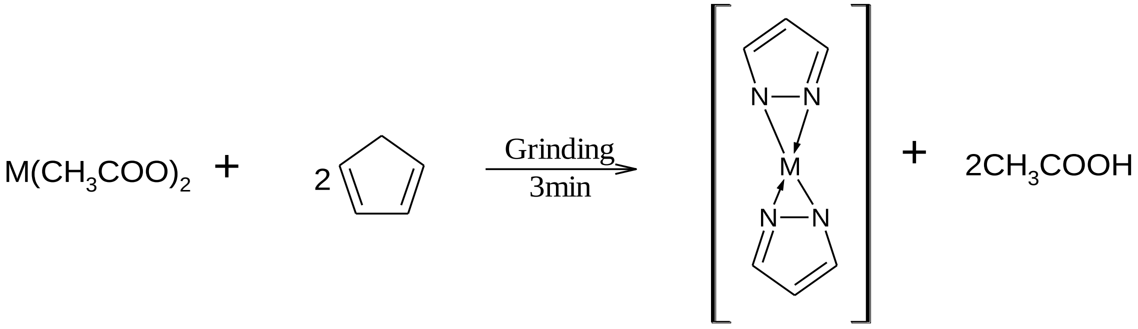
Synthesis

Two synthetic routes were used and carried out at room temperature using standard glassware. The glass wares were washed and dried in an oven before the start of each synthesis (Kumar and Pareek, 2013).

The metal salts Zn (CH$_3$COO)$_2$ and the ligands in each case were ground by hand using a mortar and pestle to give the desired products (Groeneveld *et al.,* 1976*)* . The time required in grinding was mostly 3 minutes which is typically only that necessary to be sure that all the reactants have been thoroughly mixed in each case. The reactants in each case were weighed using electric balance in the laboratory. In all the synthesis the ratio of the ligand to metal salts was 2:1. The Products were dried in oven at 50˚C (Adams *et al.,* 2008 and 2010).

A: synthesis using Pyrazole ($C_3H_4N_2$) as ligand

<u>Route A</u>: Direct grinding of $M(CH_3COO)_2$ with neutral pyrazole to form coordination compound $[M(Pz)_2]$.



Coordination compound

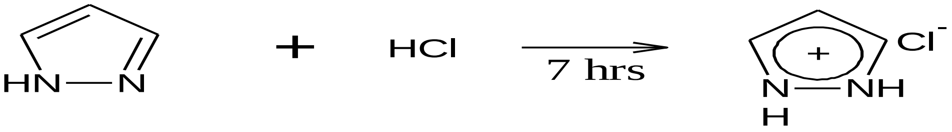
Scheme 1: Synthesis of coordination compound by direct grinding of pyrazole and metal (II) salts. [M = Zn].

Synthesis of Zinc pyrazolate Complex, $[Zn(Pz)_2]$:

220mg (1mmol) of $Zn(CH_3COO)_2.2H_2O$ was forcefully ground with 136mg (2mmol) of white crystalline pyrazole, a white crystalline powder was formed and the acetic acid was given off by drying the product in an oven at 50°C, (Adams *et al.,* 2010).

B: Synthesis Using Pyrazolium Chloride, $[H_2Pz]Cl$

Pyrazolium Chloride, $[H_2Pz]Cl$, a beaker containing some amount of pyrazole was placed in a sealed desiccators, containing some quantity of concentrated hydrochloric acid, HCl. The hydrogen chloride gas ($HCl_{(g)}$) produced from HCl acid was directly entered in to the beaker containing the white crystalline pyrazole continuously for 7hours. The white crystals instantaneously become a cream-coloured powder which is the pyrazolium chloride, $[H_2Pz]Cl$ (Adams *et al.,* 2008 and 2010).



Pyrazole Pyrazolium Chloride

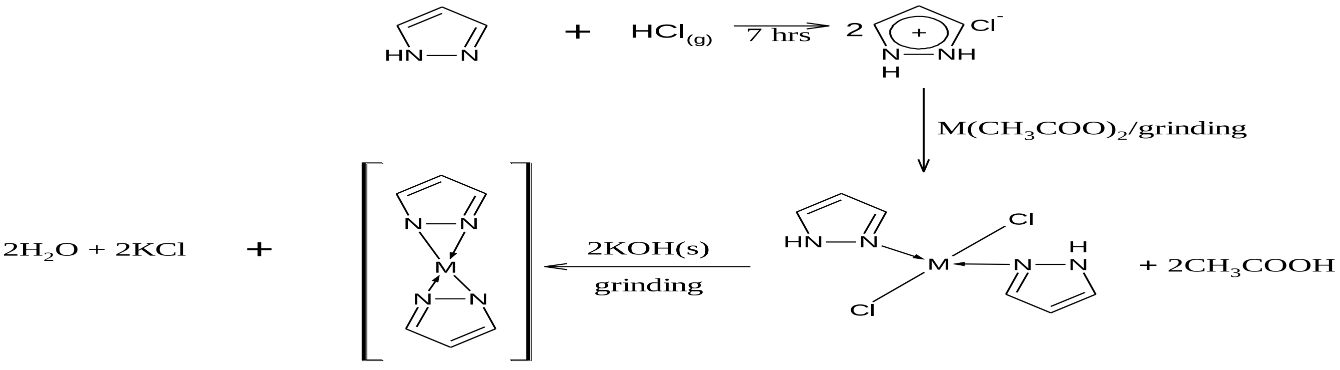
Scheme 2: Synthesis of pyrazolium chloride

209mg (2mmol) of pyrazolium chloride, $[H_2Pz]Cl$ was grinded with 1mmol of the zinc (II) acetates, $Zn(CH_3COO)_2.2H_2O$. In all the ratio of the ligand to metal salts was 2:1 to give a general form as $[ZnCl_2(HPz)_2]$ + acetic acid given off on drying in an oven at 50°C (Adams *et al.,* 2008 and Alan, 2009).

$$Zn(CH_3COO)_2 + 2[H_2Pz]Cl \rightarrow [ZnCl_2(HPz)_2] + 2CH_3COOH\uparrow$$

Mechanochemical Elimination:

This method was used to eliminate the chloride in $[MCl_2(HPz)_2]$ using $KOH_{(s)}$ and metal pyrazolates, $[M(Pz)_2]$ + 2KCl + $2H_2O$ were obtained.



Coordination compound intermediate coordination compound

Scheme 3: Synthesis of coordination compound using pyrazolium chloride, [M=Zn].

Synthesis of Zinc pyrazolate Complex, [Zn(Pz)$_2$]

220mg (1mmol) of Zn(CH_3COO)$_2$. 2H_2O was forcefully ground with 209mg (2mmol) of cream-coloured powder pyrazolium chloride, a white crystalline powder [ZnCl_2(HPz)$_2$] was formed and the acetic acid was given off by drying the product in an oven at 50˚C, (Adams *et al.*, 2008 and 2010). 272mg (1mmol) of white powder [ZnCl_2(HPz)$_2$] obtained above and 112mg (2mmol) of KOH were mixed and grinded in a mortar and pestle, resulting in the formation of white powder of [Zn(Pz)$_2$] + 2KCl which was dried in oven at 50˚C, (Adams *et al.*, 2008 and 2010).

RESULTS AND DISCUSSION

Results

The results of the mechanochemical synthesis carried out above are shown in the tables below.

Table1a: Solubility test of the Ligand and Zn (II) Complex obtained by Route A in some Common Solvents:

Solvents/L /Complexes	**Dist. H_2O**	**Ethanol**	**Methanol**	**CCl_4**	**$CHCl_3$**	**Ether**	**C_6H_6**	**n-Hexane**	**Acetone**	**DMSO**
[HPz]	S	S	S	S	S	S	S	S	S	S
[Zn(Pz)$_2$]	IS	IS	SS	SS	SS	IS	SS	SS	IS	S

Table1b: Solubility test of the Ligand and Zn (II) Complex obtained by Route B in some Common Solvents:

Solvents/L /Complexes	**Dist. H_2O**	**Ethanol**	**Methanol**	**CCl_4**	**$CHCl_3$**	**Ether**	**C_6H_6**	**n-Hexane**	**Acetones**	**DMSO**
[H_2Pz]Cl	S	S	S	S	S	S	S	S	S	S
[Zn(Pz)$_2$]	SS	IS	IS	SS	SS	IS	SS	IS	SS	S

S = SOLUBLE, SS = SLIGHTLY SOLUBLE AND IS = INSOLUBLE

Table2a: Molecular mass, melting point/decomposition temperature, colours of the ligand (pyrazole) and the synthesized complex obtained by Route A.

Ligand/complexes	Molecular mass (g/mol)	Melting point (˚C)	Decomposition Temp.(˚C)	Colour
$C_3H_4N_2$	68.08	70	-	White crystals
[Zn($C_3H_3N_2$)$_2$]	199.00	-	110	White

Table2b: Molecular mass, melting point/decomposition temperature, colours of the ligand (Pyrazolium Chloride) and the synthesized complex obtained by Route B.

Ligand/complexes	Molecular mass (g/mol)	Melting point (˚C)	Decomposition Temp(˚C)	Colour
[$C_3H_5N_2$]Cl	104.58	75	-	Cream Powder
[Zn($C_3H_3N_2$)$_2$]	199.00	-	109	White

Table 3a: Conductivity Measurement for the Zn (II) Complex obtained by Route A

Complex	Specific Conductance ($\Omega^{-1}cm^{-1}$)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)
[Zn(Pz)$_2$]	2.23×10^{-6}	2.23

Table 3b: Conductivity Measurement for the Zn (II) Complex obtained by Route B

Complex	Specific Conductance ($\Omega^{-1}cm^{-1}$)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)
Zn(Pz)$_2$]	2.01×10^{-6}	2.01

Table 4a: Magnetic Susceptibility Measurement for Zn (II) acetates

Metal(II) acetates	Gram Magnetic Susceptibility x_g	Molar magnetic Susceptibility x_m	µeffective in Bohr Magnetons,(B.M)	Properties
$(CH_3COO)_2Zn$	-4.58×10^{-7}	-1.01×10^{-4}	Dia.	Diamagnetic

Table 4b: Magnetic Susceptibility Measurement for Zn (II) Complexes obtained by Route A

Complexes	Gram Magnetic Susceptibility x_g	Molar magnetic Susceptibility x_m	µeffective in Bohr Magnetons, (B.M)	Properties
$[Zn(C_3H_3N_2)_2]$	$-2.51x10^{-7}$	$-5.00x10^{-5}$	Dia.	Diamagnetic

Table 4c: Magnetic Susceptibility Measurement for Zn (II) Complexes obtained by Route B.

Complexes	Gram Magnetic Susceptibility x_g	Molar magnetic Susceptibility x_m	µeffective in Bohr Magnetons, (B.M)	Properties
$[Zn(C_3H_3N_2)_2]$	$-3.59x10^{-7}$	$-7.14x10^{-5}$	Dia.	Diamagnetic

Table 5a: Selected characteristic IR bands for Ligand and the Zn (II) Complexes obtained by Route A.

Complex	v(C-N) cm^{-1}	v(M-N) cm^{-1}
$C_3H_4N_2$	1646.30	-
$[Zn(C_3H_3N_2)_2]$	1587.47	409.89

Table 5b: Selected characteristic IR bands for Ligand and the Zn (II) Complexes obtained by Route B.

Complex	v(C-N) cm^{-1}	v(M-N) cm^{-1}
$C_3H_4N_2$	1646.30	-
$[Zn(C_3H_3N_2)_2]$	1457.27	435.93

Table 6: **Mole fraction of the ligand and absorbance values for Zn^{2+} ion: λ_{max}= 540nm**

Zn : L	**L mole fraction**	**Absorbance**
15:01	0.0625	0.0624
13:03	0.1875	0.0676
11:05	0.3125	0.0685
09:07	0.4375	0.0994
07:09	0.5625	0.1553
05:11	0.6875	0.1985
03:13	0.8125	0.1654
01:15	0.9375	0.1121
00:16	1.0000	0.1123

DISCUSSION

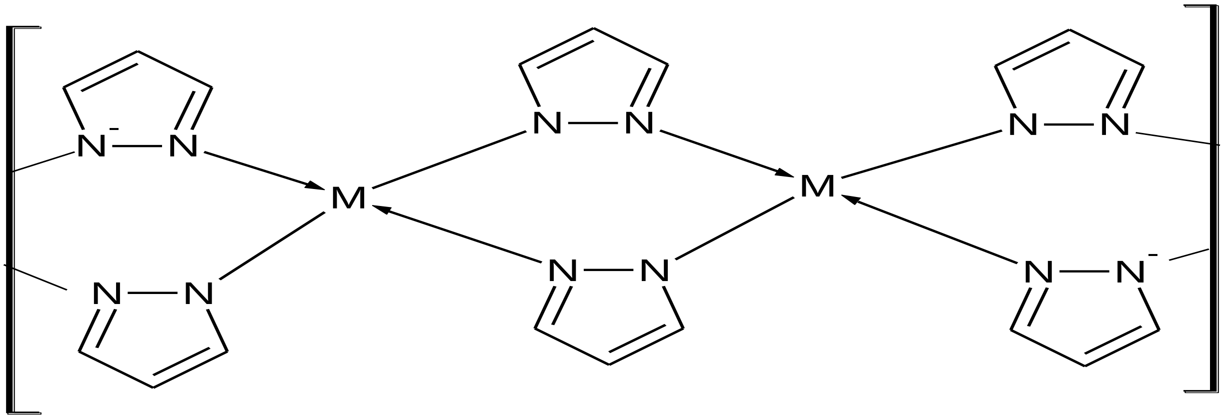
Pyrazole was deprotonated to give pyrazolate anion (Pz^-) which function as a ligand and reacted with metal ion (Zn^{2+}) to form coordination compounds [$Zn(Pz)_2$]. The proton combined with acetate ion (OAC^-) and give acetic acid (HOAC) (Bahl and Bahl, 2007).

Zinc (II) pyrazolate complex was found to be insoluble in ethanol, ether, distilled water, and acetone, slightly soluble in methanol, carbon tetrachloride, chloroform, benzene and n-hexane and soluble in DMSO solvents, (Tables1a and 1b). The melting point of pyrazole and the decomposition temperature of metal complexes were determined using microprocessor melting point apparatus (WRS-IB) and Gallen kamp melting point apparatus. The results obtained showed that the complex which is white with pyrazole and pyrazolium salt has decomposition temperatures of 110˚C and 109˚C (Tables 2a and 2b). (Aliyu and Zayyan, 2013).

The molar conductivity measurements revealed that the complex have low values (2.01 - 2.232 $\Omega^{-1}cm^2mol^{-1}$) which showed that they are non-electrolytes.

The magnetic susceptibility measurements were carried out at room temperature (Tables 4a, 4b and 4c) and the effective magnetic moment values for Zn (II) acetate and Zn (II) complexes showed diamagnetic which was a characteristic of Zn (II) (d^{10}) paired electron system (Seel *et al.*, 1968 and Lancashire, 2015).

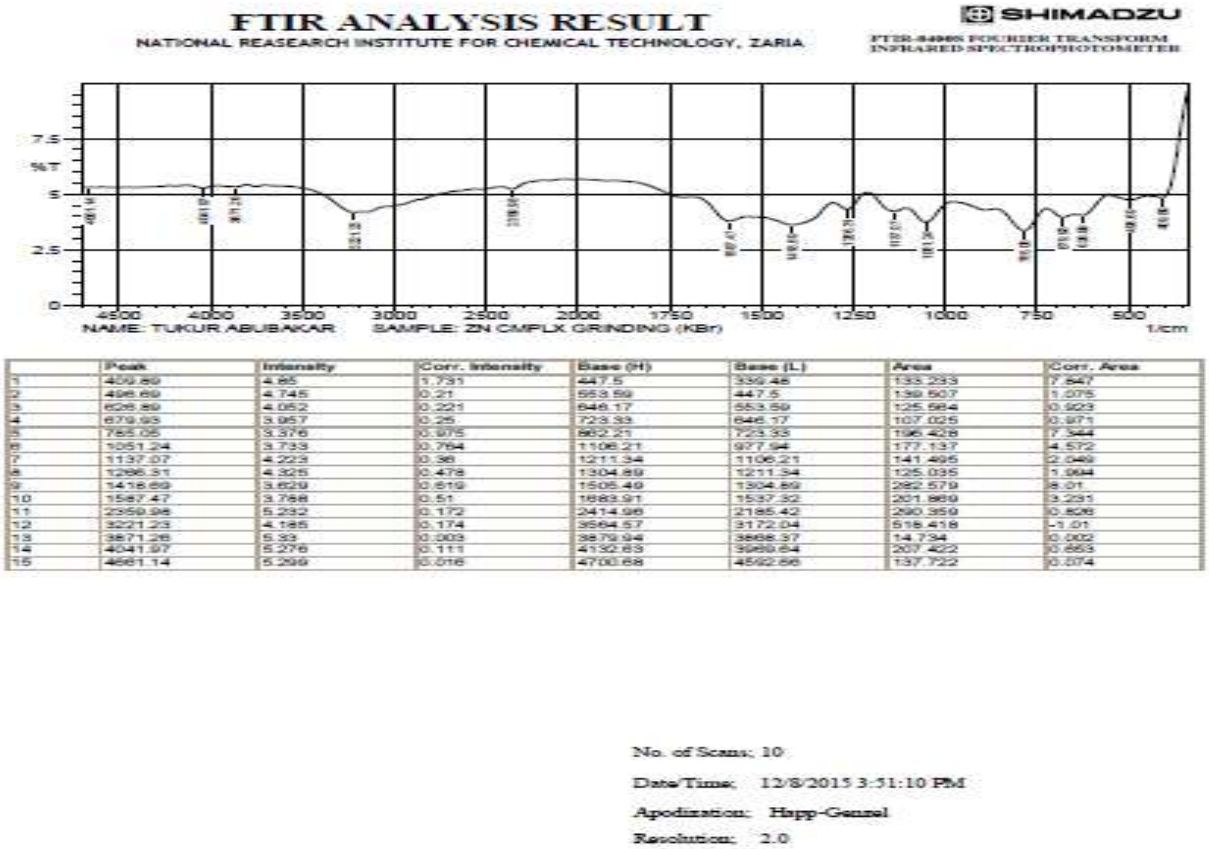
In the low-frequency region, the spectra of the metal complexes exhibited new bands which are not present in the spectrum of the ligand and zinc (II) acetate (Sindhu *et al.*, 2013). These bands assigned to ν(M−N) vibrations observed at 409.89cm^{-1} and 435.93cm^{-1} for Zinc (Maurya *et al.*, 2004 and Raman *et al.*, 2010) (Tables 5a and 5b) . The plot of absorbance against mole fraction gives a curve with maximum absorbance corresponding to the ligand mole fraction used in calculating the number of coordinated ligand and 1:2 metal-ligand ratios was obtained in all the complexes (Angelici 1971) (Table 6).



PROPOSED STRUCTURE OF THE COMPLEX (M = Zn)

CONCLUSION

It is clear that mechanochemistry offers some advantages as an alternative approach to synthesis. These advantages include environmentally friendly low cost and greater efficiency with regard to time, materials and energy usage, as well as the discovery of new or improved reactivity and products. Its usage therefore looks likely to continue to grow. Mechanochemical synthesis in the field of coordination polymers and metal organic frame works is attractively fast and convenient, does not require additional heating.



FTIR ANALYSIS RESULT

NATIONAL REASEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA

SHIMADZU

FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER

NAME: TUKUR ABUBAKAR　　SAMPLE: ZN CMPLX GRINDING (KBr)

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	409.89	4.85	1.731	447.5	339.48	133.233	7.847
2	496.69	4.745	0.21	553.59	447.5	139.507	1.075
3	626.89	4.052	0.221	646.17	553.59	125.984	0.923
4	679.93	3.957	0.25	723.33	646.17	107.025	0.971
5	765.05	3.376	0.975	862.21	723.33	196.428	7.344
6	1051.24	3.733	0.794	1106.21	977.94	177.137	4.572
7	1137.07	4.223	0.38	1211.34	1106.21	141.495	2.049
8	1266.31	4.325	0.478	1304.89	1211.34	125.035	1.994
9	1418.69	3.629	0.619	1505.49	1304.89	282.579	8.01
10	1587.47	3.768	0.51	1683.91	1537.32	201.869	3.231
11	2359.96	5.232	0.172	2414.96	2185.42	290.359	0.808
12	3221.23	4.185	0.174	3564.57	3172.04	518.418	-1.01
13	3871.26	5.33	0.003	3879.94	3868.37	14.734	0.002
14	4041.97	5.276	0.111	4132.63	3989.64	207.422	0.863
15	4661.14	5.299	0.016	4700.68	4592.66	137.722	0.074

No. of Scans: 10

Date/Time: 12/8/2015 3:51:10 PM

Apodization: Happ-Genzel

Resolution: 2.0

Fig. 1: IR Spectra for Zinc (II) Complexes

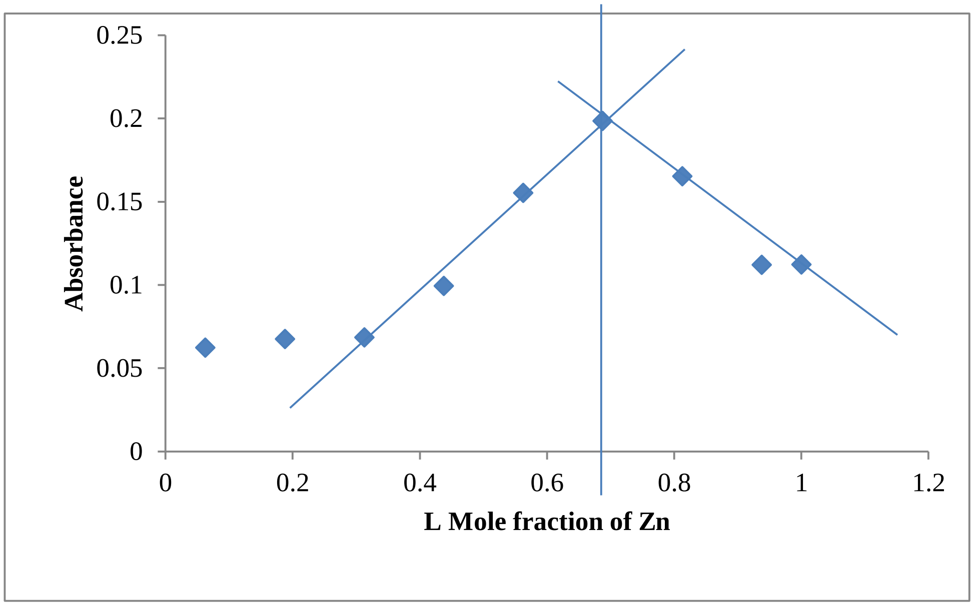


Fig. 2: Plot of Absorbance against Ligand Mole Fraction for Zn^{2+} ion: λ_{max}= 540nm

REFERENCES

Adams C. J., Kurawa M. A. and Orpen A. G., (2010). Coordination chemistry in the solid state: synthesis and interconversion of pyrazolium salts, pyrazole complexes, and pyrazolate MOFs. J. Royal Society of Chemistry. *Dalton Trans*., 39:6974–6984.

Adams C. J., Kurawa M. A., Lusi M. and Orpen A. G.,(2008). Solid State synthesis of coordination compounds from basic metal salts. *Cryst. Eng Comm.*, 10:1790–1795

Alan L. Balch, (2009). Solid state synthesis of coordination compounds from basic metal salt. *J. Angew. Chem., Int. Ed.*, 48:2641–2644.

Angelici, R.J. (1971). "Synthesis and Techniques in Inorganic Chemistry", W. B. Savders Company, Dalton Trans. 2nd Edition, pp 115-125.

Antesberger J., G. W. V. Cave, M. C. Ferrarelli, M. W. Heaven, C. L. Raston and J. L. Atwood, (2005). Solvent-free, direct synthesis of supramolecular nano-capsules. *Chem*. *Commun*., 892–894.

Bahl A. and Bahl B. S. (2007). *Advanced Organic Chemistry,* S. C and and Company Ltd, Ram Nagar, New Delhi, 20th edition, pp 490 – 497.

Balema V. P., J. W. Wiench, M. Pruski and V. K. Pecharsky,(2002). Mechanochemically induced solid state generation of phosphorus ylides and the solvent-free witting reaction. *Chem. Commun.* Cambridge, Pp 45-47.

Chen T., B. Liang and X. Xin, (1997). Studies on Solid-Solid Reactions between 4-Methylbenzenamine and Copper (II)Chloridedihydrate, Cobalt (II)Chloridehexahydrate and

Groeneveld W.L, Okkersen H., and Reedijk J., (1976). Pyrazolato and related anions, salt of 4-nitropyrazole. *Rec. Trav. Chim*., 92:947.

Halcrow M. A., (2009). Pyrazole and pyrazolides-flexible synthons in self. In Heterocyclic chemistry. J. *Dalton Trans.*,2059 – 2073.

Kumar N. Sharma and Pareek A. (2013), synthesis of new Schiff base complexes and their applications. *International Journal of Applied Research and Studies* II (2):307-315.

Kuroda R., Yoshida J., Nakamura A. and Nishikiori S.I., (2009). Annealing assisted mechanochemical synthesis of transition-metal coordination compounds and co-crystal formation. J. *Cryst. Eng. Comm.,* 11:427 – 432.

Lancashire R.J., (2015), Coordination Chemistry. Kingston, Jamaica. Available on www.chem.uwimona.edu.jm/spectra/Mag Mon.html.

Maurya R. C. and Rajput S., (2004), Oxovanadium (IV) complexes of bioinorganic and medicinal relevance: synthesis, characterization and 3D molecular modeling and analysis of some oxovanadium (IV) complexes involving O, O-donor environment*, J. Mol. Struct* . 687(1): 35–44.

Raman N., Jeyamurugan R., Rajkapoor, B. and Mitu, L. (2010). Novel metal- based pharmacologically dynamic agents of transition metal (II) complexes: Designing, synthesis, structural elucidation, DNA binding and photo-induced DNA cleavage: activity*, Spectro chim. Acta, Part A* 75(1):88-97.

See1 F., and Sperber V., (1968). Interpretation of NMR chemical shifts and magnetic susceptibilities. *J. Angew. Chem.*, 80:38.

Sindhu Y., Athira C.J., Sujamol M. S., Selwin R.J. and Mohanan K., (2013). Synthesis, characterization, DNA cleavage, and antimicrobial studies of some transition metal complexes with a novel Schiff base derived from 2-aminopyrimidine, Synth. React. *Inorg. Met-Org. Nano-Met. Chem.* 43(3):226-23