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SOLID STATE SYNTHESIS AND CHARACTERIZATION OF PYRAZOLE AND PYRAZOLATES COMPLEXES OF COBALT (II) IONS

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ABSTRACT

There were two ways used to synthesized cobalt (II) complexes of pyrazole by solid state. The first route involved direct reaction of the appropriate cobalt (II) acetate with pyrazole and pyrazolium chloride to form bispyrazole cobalt(II) salts, $[(HPz)_2CoCl_2]$. This was further ground in the second route with a two equivalents of a base (KOH) to make polymeric cobalt (II) pyrazolate $[Co(Pz)_2]$. In all the synthesis above the ratio of ligand to cobalt (II) acetate was 2:1. All the cobalt (II) complexes were found to be of different colour from the starting materials 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 have low values (ranging from 6.44-6.45$\Omega^{-1}cm^2mol^{-1}$) which showed that they are non-electrolytes. The decomposition temperature showed that all the complexes have relatively low decomposition temperatures (93°C- 95°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 435.93cm^{-1} Co-N bonds and 406.99cm^{-1}Co –N (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 cobalt (II) complexes are paramagnetic. The plot of absorbance against mole fraction in each case gives a curve with maximum absorbance corresponding to the ligand mole fraction used in calculating the number of coordinated ligands and 1:2 metal-ligand ratios were obtained in all the complexes.

Keywords: Mechanochemical, Pyrazole, Pyrazolate, Grinding, Mechanochemical Elimination.

INTRODUCTION

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 (Chen *et al.,* 1997). Often the molar equivalents added are similar to those of the reactants themselves. Such reactions are therefore 'minimal solvent' rather than strictly 'solvent-free' (Halcrow 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 (Angelici 1971 and Antesberger *et al.,* 2005).

Pyrazole other name 1,2-Diazole is an organic compound with the formula $C_3H_3N_2H$. It is a heterocycle characterized by a 5-membered ring of three carbon atoms and two adjacent nitrogen atoms. Pyrazole is a weak base, with pK_b 11.5 (pK_a of the conjugated acid 2.49 at 25°C). Pyrazoles are also a class of compounds that have the ring C_3N_2 with adjacent nitrogen atoms (Balema *et al.*, 2002). A notable drug containing a pyrazole ring is celecoxib (Celebrex) (Retting *et al., 1991).*

Pyrazole (HPz) is a well-known monodentate ligand, coordinating via the pyridine nitrogen of the ring. Because HPz is a weak acid (pK = 14), it is also possible to obtain metal compounds with the pyrazolato ion (Pz^-) (Groeneveld *et al.,* 1976 and Sindhu *et al.,* 2013).

MATERIALS AND METHODS

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

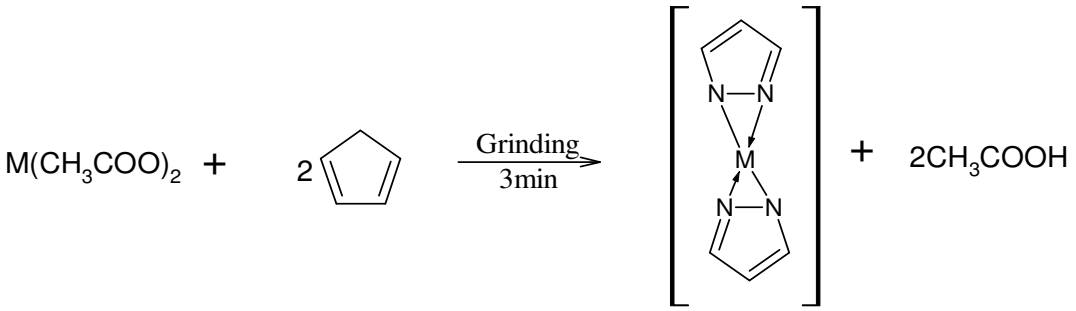
Synthesis

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.

The metal salts Co $(CH_3COO)_2$ and the ligands in each case were ground by hand using a mortar and pestle to give the desired products. The time required in grinding was mostly 3minutes 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

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



Coordination compound

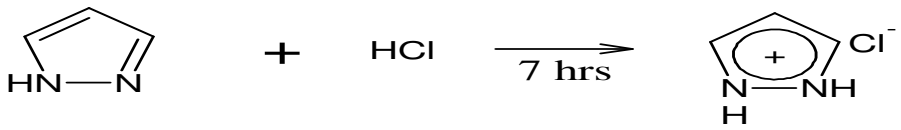
Scheme 1: Synthesis of coordination compound by direct grinding of pyrazole and metal (II) salts. [M = Co].

Synthesis of Cobalt pyrazolate Complex, $[Co(Pz)_2]$:

249mg (1mmol) of $(CH_3COO)_2Co.4H_2O$ and 136mg (2mmol) of white crystalline pyrazole were mixed and grinded, resulting in the formation of a green powder and dried in an oven at 50°C to evaporate the acetic acid, (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

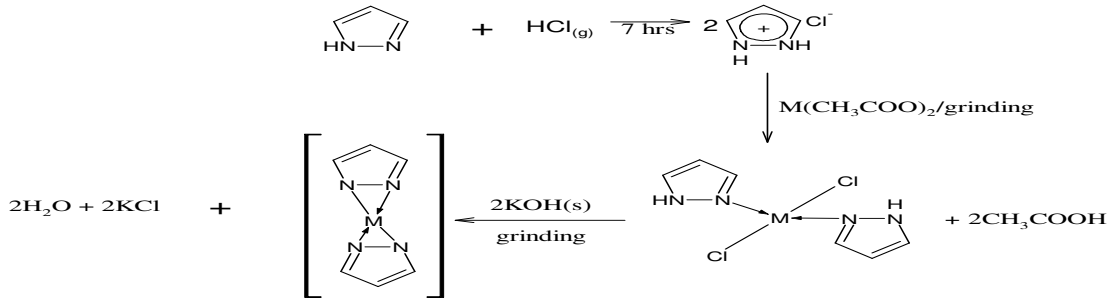
209mg (2mmol) of pyrazolium chloride, $[H_2Pz]Cl$ was grinded with 1mmol of the metal acetates, $Co(CH_3COO)_2 .4H_2O$. In all the ratio of the ligand to metal salts was 2:1 to give a general form as $[CoCl_2(HPz)_2]$ + acetic acid given off on drying in an oven at 50°C, (Adams *et al.,* 2008 and 2010).

$$Co(CH_3COO)_2 + 2[H_2Pz]Cl \rightarrow [CoCl_2(HPz)_2] + 2CH_3COOH \uparrow$$

1 : 2

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=Co].

3.3.3.3 Synthesis of Cobalt pyrazolate Complex, $[Co(Pz)_2]$

249mg (1mmol) of $(CH_3COO)_2$ $Co.4H_2O$ and 209mg (2mmol) of cream-coloured pyrazolium chloride were mixed and grinded, resulting in the formation of a dark green polycrystalline powder $[CoCl_2(HPz)_2]$ and dried in an oven to evaporate the acetic acid, (Adams *et al.,* 2008 and 2010).

266mg (1mmol) of dark green crystalline powder $[CoCl_2(HPz)_2]$ obtained above was forcefully ground in a mortar and pestle with 112mg (2mmol) of KOH. An immediate colour change from dark green to pale brown of $[Co(Pz)_2]$ + 2KCl was observed and the crystalline powder was dried in an oven at 50°C, (Adams *et al.,* 2008 and 2010).

RESULTS AND DISCUSSION

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

Table1a: Solubility test of the Ligand and Co(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
$[Co(Pz)_2]$	SS	SS	SS	IS	IS	IS	IS	IS	IS	S

Table1b: Solubility test of the Ligand and Co (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
$[Co(Pz)_2]$	SS	IS	IS	SS	SS	IS	IS	IS	IS	S

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

Table2a: Molecular mass, melting point/decomposition temperature, colours of the ligand (pyrazole) and the synthesized complexobtained 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
$[Co(C_3H_3N_2)_2]$	193.00	-	93	Dark Green

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
$[Co(C_3H_3N_2)_2]$	193.00	-	95	Pale –Brown

Table 3a: Conductivity Measurement for the Co (II) Complexobtained by Route A

Complex	Specific Conductance ($\Omega^{-1}cm^{-1}$)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)
$Co(Pz)_2]$	6.44×10^{-6}	6.44

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

Complex	Specific Conductance ($\Omega^{-1}cm^{-1}$)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)
$[Co(Pz)_2]$	6.45×10^{-6}	6.45

Table4a: Magnetic Susceptibility Measurement for Co (II) acetates

Metal(II) acetates	Gram Magnetic Susceptibility x_g	Molar magnetic Susceptibility x_m	μeffective in Bohr Magnetons, (B.M)	Properties
$(CH_3COO)_2Co$	2.24×10^{-5}	5.58×10^{-3}	3.65	Paramagnetic

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

Complexes	Gram Magnetic Susceptibility x_g	Molar magnetic Susceptibility x_m	μeffective in Bohr Magnetons, (B.M)	Properties
$[Co(C_3H_3N_2)_2]$	$1.88x10^{-5}$	$3.62x10^{-3}$	2.94	Paramagnetic

Table4c: Magnetic Susceptibility Measurement for Co (II) Complexes obtained by Route B.

Complexes	Gram Magnetic Susceptibility x_g	Molar magnetic Susceptibility x_m	μeffective in Bohr Magnetons, (B.M)	Properties
$[Co(C_3H_3N_2)_2]$	$1.91x10^{-5}$	$3.69x10^{-3}$	2.96	Paramagnetic

Table5a: Selected characteristic IR bands for Ligand and the Co(II) Complexes obtained by Route A.

Complex	v(C-N) cm^{-1}	v(M-N) cm^{-1}
$C_3H_4N_2$	1646.30	-
$[Co(C_3H_3N_2)_2]$	1619.29	435.93

Table5b: Selected characteristic IR bands for Ligand and the Co(II) Complexes obtained by Route B.

Complex	v(C-N) cm^{-1}	v(M-N) cm^{-1}
$C_3H_4N_2$	1646.30	-
$[Co(C_3H_3N_2)_2]$	1596.15	406.99

Table 6: Mole fraction of the ligand and absorbance values for Co^{2+} ion: λ_{max}= 400nm

Co : L	L mole fraction	Absorbance
15:01	0.0625	0.1908
13:03	0.1875	0.1864
11:05	0.3125	0.3012
09:07	0.4375	0.3112
07:09	0.5625	0.3401
05:11	0.6875	0.3861
03:13	0.8125	0.3543
01:15	0.9375	0.2343
00:16	1.0000	0.2132

DISCUSSION

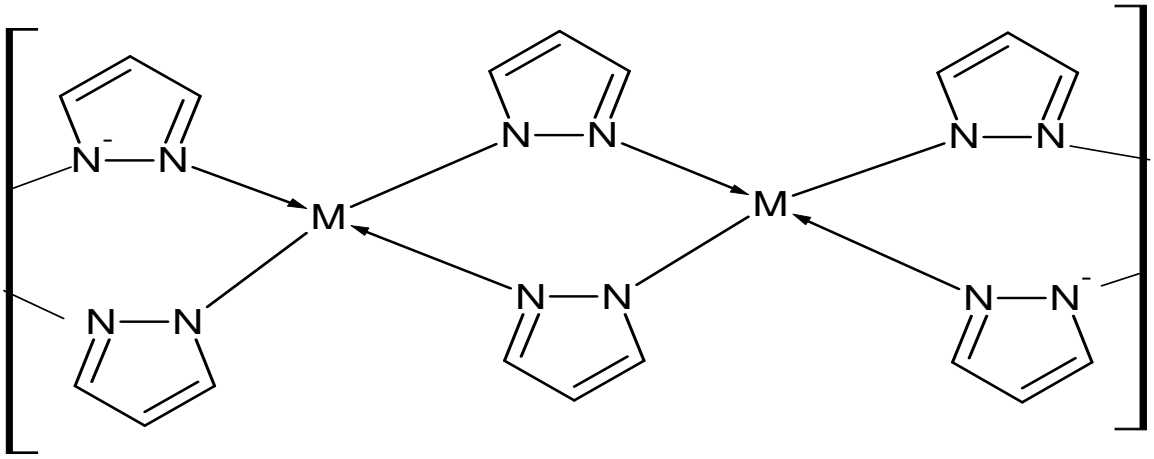
Pyrazole was deprotonated to give pyrazolate anion (Pz^-) which function as a ligand and reacted with metal ion (Co^{2+}) to form coordination compounds $[Co(Pz)_2]$. The proton combined with acetate ion (OAC^-) and give acetic acid (HOAC) (Mamatha *et al.,* 2006).

Cobalt (II) pyrazolate complex was found to be insoluble in ethanol, carbon tetrachloride, chloroform, ether, benzene, n-hexane, distilled water, and acetone, slightly soluble in methanol and soluble in DMSO solvents (Flook *et al.,* 1973) (Tables 1a and 1b). The melting point of pyrazole and the decomposition temperature of metal complexes were determined using microprocessor melting point apparatus (WRS-IB) and Gallenkamp melting point apparatus. The results obtained showed that the complex which is dark-green with pyrazole and pale-brown with pyrazolium salt has decomposition temperatures of 93°C and 95°C (Tables 2a and 2b). (Kumar and Pareek, 2013).

The molar conductivity measurements revealed that the complex have low values (6.44-6.45$\Omega^{-1}cm^2mol^{-1}$) which showed that they are non-electrolytes.

The magnetic susceptibility measurements were carried out at room temperature and the effective magnetic moment values for Co (II) complexes obtained are within characteristic of mononuclear, Co (II) (d^7) indicating paramagnetic nature (Seel and Sperber 1968; 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 cobalt (II) acetate[17]. These bands assigned to v(M–N) vibrations observed at 435.93cm^{-1} and 406.99cm^{-1} for Cobalt, (Maurya 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 (Alan 2009 and Bahl, 2007) (Table 6).



PROPOSED STRUCTURE OF THE COMPLEX (M = Co)

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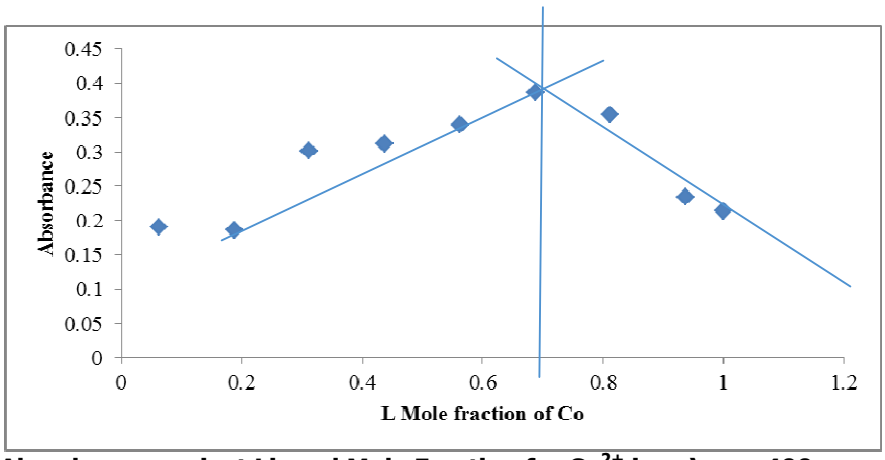

Plot of Absorbance against Ligand Mole Fraction for Co^{2+} ion: λ_{max}= 400nm

FTIR ANALYSIS RESULT

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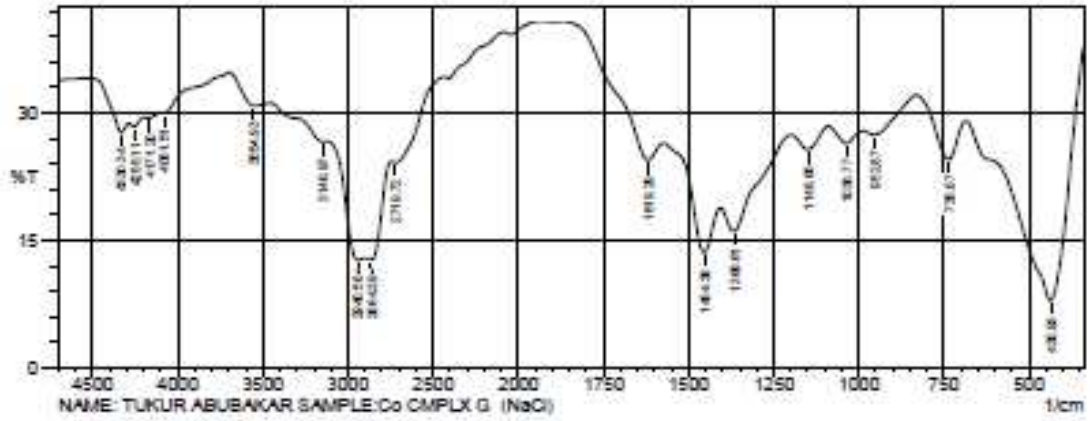
SHIMADZU

FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	435.93	7.85	27.41	684.75	339.46	253.15	87.23
2	795.87	24.49	5.57	829.42	685.72	79.77	5.62
3	952.87	27.4	1.36	987.59	830.38	84.12	1.71
4	1036.77	26.4	1.73	1087.89	988.55	96.08	1.36
5	1148.65	25.68	2.18	1198.8	1088.85	82.91	1.97
6	1386.61	16.02	4.49	1406.15	1199.78	139.57	6.89
7	1454.38	13.45	7.52	1572.04	1407.12	116.03	9.19
8	1619.29	24.42	4.25	1664.28	1573	143.31	4.04
9	2719.72	24.11	0.92	2742.67	2440.03	164.37	2.64
10	2864.39	12.7	2.59	2897.18	2743.83	119.72	5.3
11	2940.58	12.63	2.67	3119	2898.14	163.18	5.46
12	3146.97	28.58	0.41	3456.55	3119.96	181.82	0.6
13	3554.93	30.8	1.89	3694.77	3457.52	117.59	3.05
14	4081.51	29.96	0.17	4095.01	3695.73	195.67	0.13
15	4171.2	29.38	0.22	4196.28	4095.98	53.01	0.15
16	4255.11	28.37	0.58	4284.04	4197.24	46.91	0.35
17	4330.34	27.85	2.11	4516.47	4285.01	117.97	1.98

No. of Scans: 10

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Resolution: 2.0