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SYNTHESIS AND SINGLE CRYSTAL STRUCTURE ANALYSIS OF 3,3',5,5'-TETRAMETHYL-4,4'-BIPYRAZOLIUM TETRACHLOROCOBALTATE(II) MONOHYDRATE [H₂Me₄BPZ][CoCl₄] \cdot H₂O

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ABSTRACT

Slow evaporation of a solution of 3,3',5,5'-tetramethyl-4,4'-bipyrazolium chloride ([H₂Me₄bpz]Cl₂) with the cobalt chloride in concentrated aqueous HCl solution yielded block blue crystals and X-ray single crystal structure determination at 100K revealed that the molecule crystallized in the monoclinic system with a P2₁/n space group. The asymmetric units consist of tetrahedral [CoCl₄]²⁻ anions and tetramethyl bipyrazolium [H₂Me₄bpz]²⁺ dications and one water molecule which are connected through N—H \cdots Cl and N—H \cdots O hydrogen bond networks in the crystal lattice.

Keywords: Crystal structure, Hydrogen bond and crystal engineering

INTRODUCTION

Crystal engineering is "the design and synthesis of crystalline materials through the self-assembly of molecular building blocks", whose main aim is the development of new crystalline materials with a variety of properties, functions and applications (Brammer, 2004). While having older roots in organic solid-state photochemistry and solid-state reactions (Schmidt, 1971), the primary focus of contemporary crystal engineering is the identification or design of molecular level building blocks whose interactions with other building blocks (including self recognition) exhibit some degree of predictability. In this case we consider crystal engineering as the design and solid state synthesis of crystalline solids with desired properties through the exploitation of non-covalent intermolecular interactions. It can also be considered as a rapidly expanding *global* discipline with diverse interests in the modelling, synthesis, evaluation and utilization of crystalline solids", which overlaps considerably with supramolecular chemistry, X-ray crystallography and solid state chemistry (Desiraju, 2007).

X-ray crystallography is one of the most important and most powerful tools for investigation of the structures of chemical compounds. It plays a vital role in modern chemistry, organic as well as inorganic, and probably ranks alongside NMR and mass spectrometry as the three most important structural techniques, being less widely applicable than these other two in its requirement for a crystalline solid sample, but far more powerful in the richness of its detailed results when successful (Clegg, 2005). X-ray single crystal structure determination is undoubtedly the most important technique to characterize new compounds. No other analytical technique currently available can provide such complete and unambiguous information about internal structure, *i.e.* types of atoms, their spatial arrangement

and interactions. Single crystal structure determination yields the internal symmetry of crystals, coordinates and population of atoms (occupancies) and anisotropic thermal parameters. The results obtained by single crystal structure determination are vital for the study of compounds by various other techniques including molecular modelling, and for giving information about crystal packing, polymorphism, absolute structure configuration, intra- and inter-molecular contacts, hydrogen bonding, crystal phase transition (Harris, *et al.*, 2001; Evans and Evans 2004).

It has recently been established by a number of researchers that a range of hydrogen bonded complex metal salts and coordination compounds can be prepared without recourse to solution methods through the exploitation of crystal engineering (James *et al.*, 2012; Fernandez-Bertran, 1999; Fernandez-Bertran *et al.*, 1999; Kaupp *et al.*, 2001; Shan *et al.*, 2002; Braga and Grepioni, 2004; Sheldon, 2005; Kidwai, 2001; Garay *et al.*, 2007; Kurawa, 2012). This has provided access to new synthetic routes via solid state grinding of protonated ligands [H₂L]Cl (L = imidazole, pyrazole and 2,2'-biimidazole) with metal dichlorides MCl₂ (M = Co, Cu, Zn) which results in the formation of hydrogen bonded metal salts [H₂L]₂[MCl₄]. These salts ([H₂L]₂[MCl₄]) are designed to offer thermal reactivity towards dehydrochlorination to yield coordination compounds ([MCl₂(HL)₂]) with novel properties (Adams *et al.*, 2008; Christopher *et al.*, 2010; Kurawa, 2010). Having established that protonated pyrazole can be used as a building block in crystal engineering as it is capable of forming hydrogen bonds to tetrachlorometallate dianions and hence forming ([MCl₂(HL)₂] coordination compounds and ([ML₂] MOFs after dehydrochlorination, we attempted to use its derivative 3,3',5,5'-tetramethyl-4,4'-bipyrazole (Me₄bpz) in a similar fashion.

It was expected that this tecton (building block in crystal engineering) could form a hydrogen-bonding synthon as in Fig. 1 where the two NH donors bridge

an Cl-M-Cl pocket with a view of dehydrochlorination of 4 HCl molecules to generate a metal-organic framework.

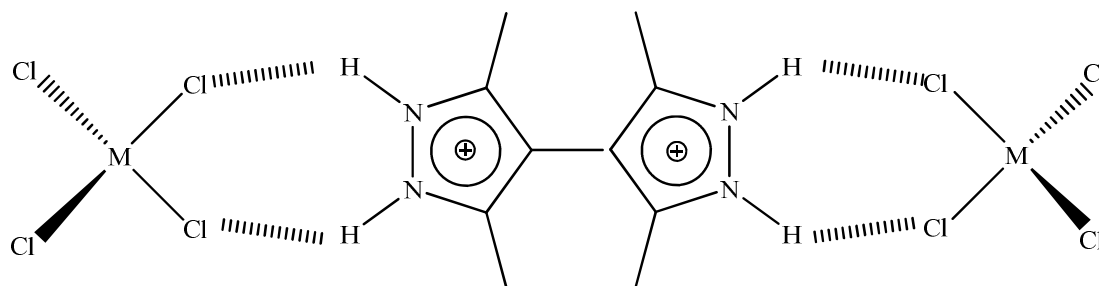


Figure 1: N—H···Cl hydrogen-bonding synthon

This paper reports the exploitation of the state of the art techniques in crystal engineering and solid state methods to synthesize $[\text{H}_2\text{Me}_4\text{bpz}][\text{ZnCl}_4]$ by reacting 3,3',5,5'-tetramethyl-4,4'-bipyrazolium dichloride ($[\text{H}_2\text{Me}_4\text{bpz}]\text{Cl}_2$) and zinc (II) chloride and the analysis of synthesized compound using X-ray single crystal structure determination.

Experimental

Anal grade reagents were purchased from Aldrich and Strem and used without further purification except where otherwise stated.

Preparation of the Ligand:

$[\text{H}_2\text{Me}_4\text{bpz}]\text{Cl}_2$

3,3',5,5'-tetramethyl-4,4'-bipyrazolium chloride $[\text{H}_2\text{Me}_4\text{bpz}]\text{Cl}_2$ was prepared by dissolving neutral 3,3',5,5'-tetramethyl-4,4'-bipyrazole (synthesized according to the literature) (Boldog *et al.*, 2001) in 15 cm^3 of concentrated aqueous hydrochloric acid and 40 cm^3 of deionised water. The solution was reduced to 25 cm^3 by boiling and 50 cm^3 of ethanol was added. The resulting mixture was put in the fridge to crystallize and white crystals were filtered out after five days. Microanalytical data (%), Calculated for $[\text{C}_{10}\text{H}_{16}\text{N}_4]\text{Cl}_2$: C, 45.64; H, 6.13; N, 21.29. Found C, 45.21; H, 6.54; N, 21.56.

Preparation of the Complex:

$[\text{H}_2\text{Me}_4\text{bpz}][\text{CoCl}_4] \cdot \text{H}_2\text{O}$ and Crystal growth:

1 mmol each of 3,3',5,5'-tetramethyl-4,4'-bipyrazolium chloride $[\text{H}_2\text{Me}_4\text{bpz}]\text{Cl}_2$ (263 mg) and anhydrous CoCl_2 (130 mg) were dissolved in 10 cm^3 of concentrated HCl. The solution was allowed to evaporate slowly at room temperature and blue crystals suitable for single crystal X-ray diffraction were obtained after 2 weeks.

X-ray Single Crystal analysis

Crystal suitable for X-ray structural analysis was mounted on a glass fibre and X-ray data was collected at 100 K on a Bruker APEX diffractometer using Mo-K α X-radiation. Data were corrected for absorption using empirical methods (SADABS) (Sheldrick, 1995) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. Crystal structures were solved and refined against all F^2 values using the SHELXTL suite of programs (Sheldrick, 2008).

Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

Thermogravimetric analysis

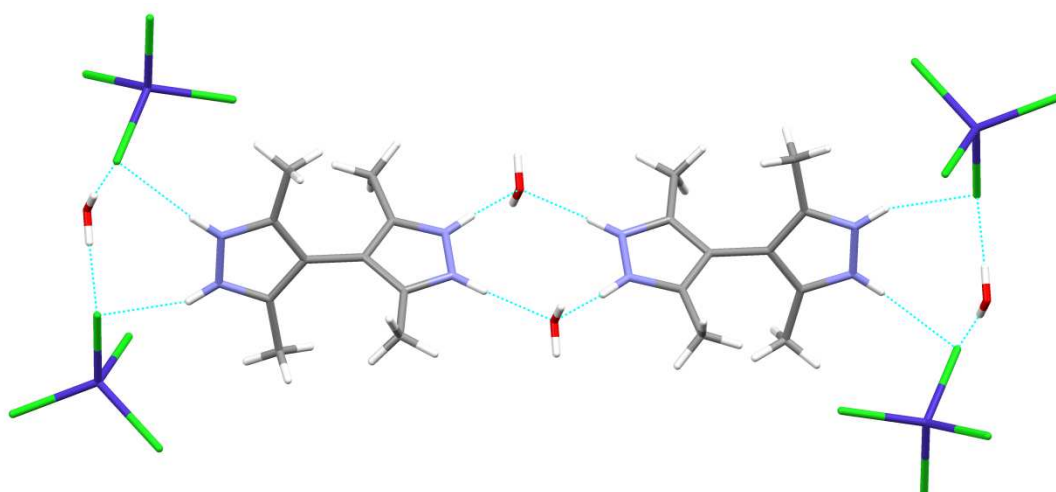
Thermal analysis of the sample of the compound was carried out on a TA Q500 V6.4 Build 193 instrument under N_2 flow over the temperature range 20 - 700°C at variable (high resolution mode) heating rate and analyzed by TA Universal analysis 2000 software.

Results and Discussion

Slow evaporation of a solution of $[\text{H}_2\text{Me}_4\text{bpz}]\text{Cl}_2$ with the metal dichloride in concentrated aqueous HCl solution yielded block blue crystals of the compound $[\text{H}_2\text{Me}_4\text{bpz}][\text{CoCl}_4]$. X-ray single crystal structure analyses revealed that the molecule crystallized in the monoclinic crystal system with a $P2_1/n$ space group. Detailed crystal and structure refinement data are presented in Table 1. The asymmetric unit of the cell consist of tetrahedral $[\text{CoCl}_4]^{2-}$ anions and tetramethylbipyrazolium $[\text{H}_2\text{Me}_4\text{bpz}]^{2+}$ dications and one water molecule which is adorned with various N-H···Cl, N-H···O and O-H···Cl interactions leading to the formation of a complex three-dimensional hydrogen bond network. The $[\text{H}_2\text{Me}_4\text{bpz}]^{2+}$ dication has two different pyrazolium hydrogen-bonding environments as shown in Figure 1. One pyrazolium ring hydrogen-bonds to two $[\text{CoCl}_4]^{2-}$ dianions, whilst the other forms NH···O contacts with two water molecules. The water molecules bond to another dication forming an $R_4(10)$ hydrogen-bonded dimer (Etter, 1990; Etter *et al.*, 1990). Furthermore, the two $[\text{CoCl}_4]^{2-}$ dianions are bridged by a water molecule *via* O-H···Cl bonds, leading to the formation of an $R_4(9)$ ring (Fig. 1). The hydrogen bond parameters for $[\text{H}_2\text{Me}_4\text{bpz}][\text{CoCl}_4]$ are reported in Table 2. Similar compound has been reported with $[\text{H}_2\text{Me}_4\text{bpz}]^{2+}$ dications and MnCl_4^{2-} dianions whose crystal structure displays revealed O—H···Cl—Mn—Cl···H—O hydrogen bond interactions (Kurawa and Orpen, 2015).

Table 1: Crystal Data and Structure Refinement for $[\text{H}_2\text{Me}_4\text{bpyz}][\text{CoCl}_4]$.

Identification code	mak080a	
Empirical formula	$\text{C}_{10} \text{H}_{18} \text{Cl}_4 \text{Co N}_4 \text{O}$	
Formula weight	411.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 11.762(2)$ Å	$\bullet = 90^\circ$.
	$b = 12.490(3)$ Å	$\bullet = 103.49(3)^\circ$.
	$c = 12.117(2)$ Å	$\bullet = 90^\circ$.
Volume	$1731.0(6)$ Å ³	
Z	4	
Density (calculated)	1.577 Mg/m^3	
Absorption coefficient	1.608 mm^{-1}	
F(000)	836	
Crystal size	$0.30 \times 0.20 \times 0.10 \text{ mm}^3$	
Theta range for data collection	2.38 to 27.48° .	
Index ranges	$-15 \leq h \leq 15$, $-9 \leq k \leq 16$, $-15 \leq l \leq 15$	
Reflections collected	11759	
Independent reflections	3964 [R(int) = 0.0166]	
Completeness to theta = 27.48°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.676959	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3964 / 0 / 187	
Goodness-of-fit on F^2	1.048	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0255$, $wR_2 = 0.0717$	
R indices (all data)	$R_1 = 0.0271$, $wR_2 = 0.0728$	
Largest diff. peak and hole	0.671 and -0.669 e.Å^{-3}	

**Figure 1:** The cation environment in $[\text{H}_2\text{Me}_4\text{bpyz}][\text{CoCl}_4] \cdot \text{H}_2\text{O}$

The hydrogen-bonding environment of the anion shows two single $\text{O-H} \cdots \text{Cl}$ hydrogen-bonds to two water molecules and two single $\text{N-H} \cdots \text{Cl}$ hydrogen-bonds to two cations. The adjacent pyrazolium NH donors in conjunction with water molecules and chlorine atoms

from neighbouring anions are involved in the formation of an $R_4^2(9)$ hydrogen-bond motif (Fig. 2).

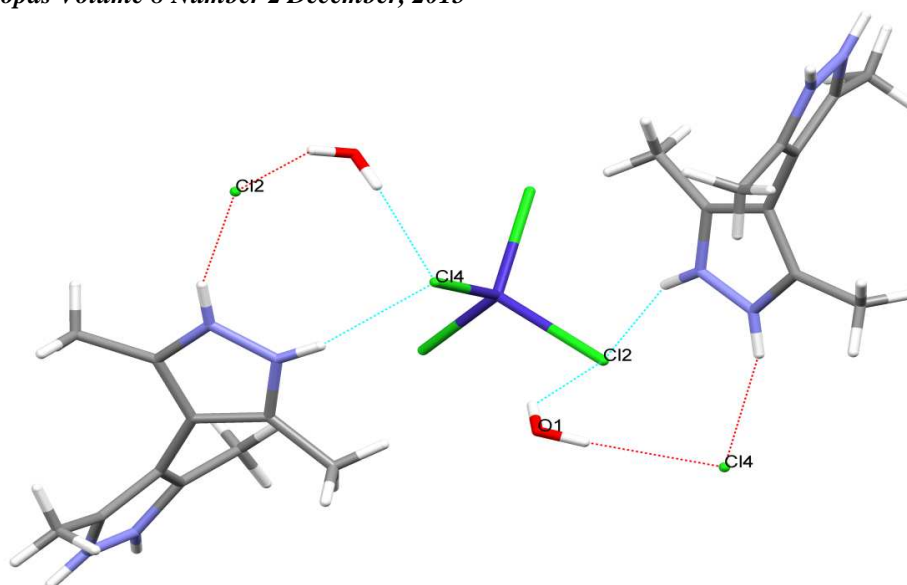


Figure 2: The anion environment in the structure of $[\text{H}_2\text{Me}_4\text{bpyz}][\text{CoCl}_4]\cdot\text{H}_2\text{O}$

Table 1: Hydrogen bond geometry for $[\text{H}_2\text{Me}_4\text{bpyz}][\text{CoCl}_4]$ [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1A)...Cl(4) ^B	0.88	2.35	3.1615(12)	153.8
N(2)-H(2A)...Cl(2) ^C	0.88	2.28	3.1046(13)	155.6
N(3)-H(3A)...O(1) ^D	0.88	2.00	2.8504(16)	162.3
N(4)-H(4A)...O(1) ^A	0.88	1.92	2.7966(15)	177.5
O(1)-H(1)...Cl(2) ^E	0.803(16)	2.55(2)	3.2264(14)	142(2)
O(1)-H(2)...Cl(4) ^F	0.824(17)	2.449(17)	3.2707(13)	176(3)

Symmetry transformations used to generate equivalent atoms: ^A x, y, z ^B $-x+1, -y+1, -z+2$ ^C $x+1/2, -y+1/2, z+1/2$ ^D $-x+2, -y+1, -z+1$ ^E $x+1/2, -y+1/2, z-1/2$ ^F $-x+1, -y+1, -z+1$.

A view of the crystal packing down the c -axis reveals layers of $[\text{H}_2\text{Me}_4\text{bpyz}]^{2+}$ dications and water molecules

packed between layers of $[\text{CoCl}_4]^{2-}$ anions (Fig. 3) whilst a view down the b -axis revealed channels formed by $[\text{CoCl}_4]^{2-}$ anions occupied by the $[\text{H}_2\text{Me}_4\text{bpyz}]^{2+}$ dications and water molecules (Fig. 4).

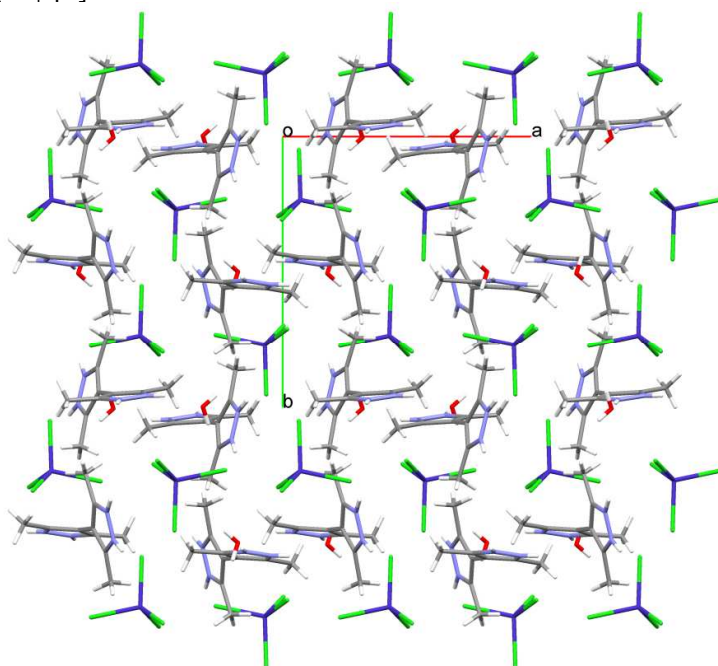


Figure 3: Crystal packing in $[\text{H}_2\text{Me}_4\text{bpyz}][\text{CoCl}_4]$ viewed down the crystallographic c -axis.

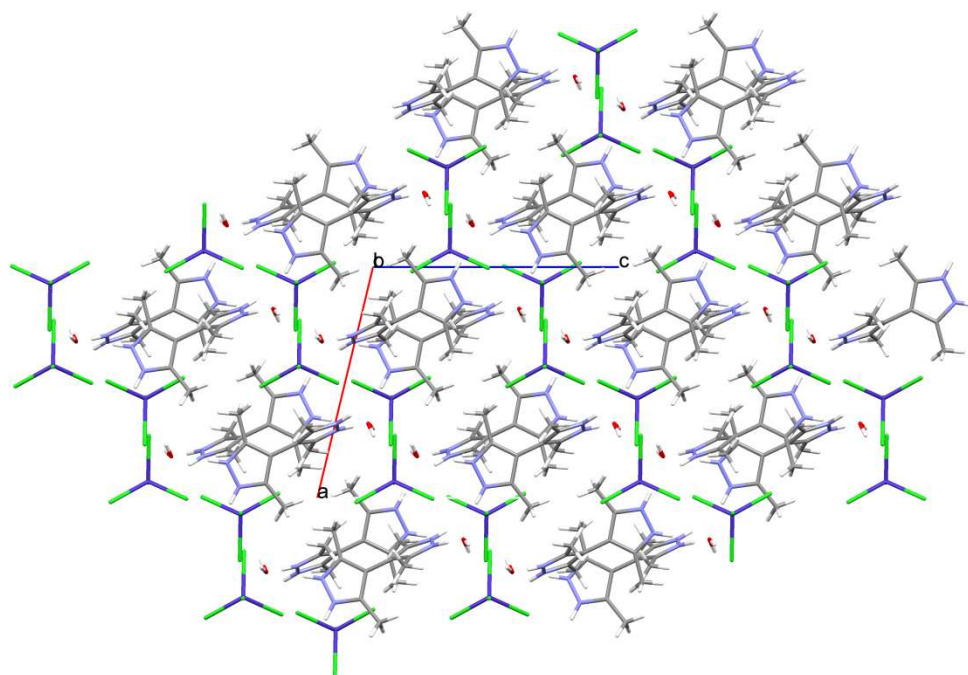


Figure 4: Crystal packing in $[H_2Me_4bpz][CoCl_4]$ viewed down the crystallographic b -axis.

Thermogravimetric analysis of a sample of the compound did not show any distinct mass loss which corresponds to water molecule or HCl molecule (see figure 5). Similar behaviour was displayed by the

pyrazole predecessors of the compound which showed no clear mass loss corresponding to HCl molecules (Christopher *et al.*, 2010).

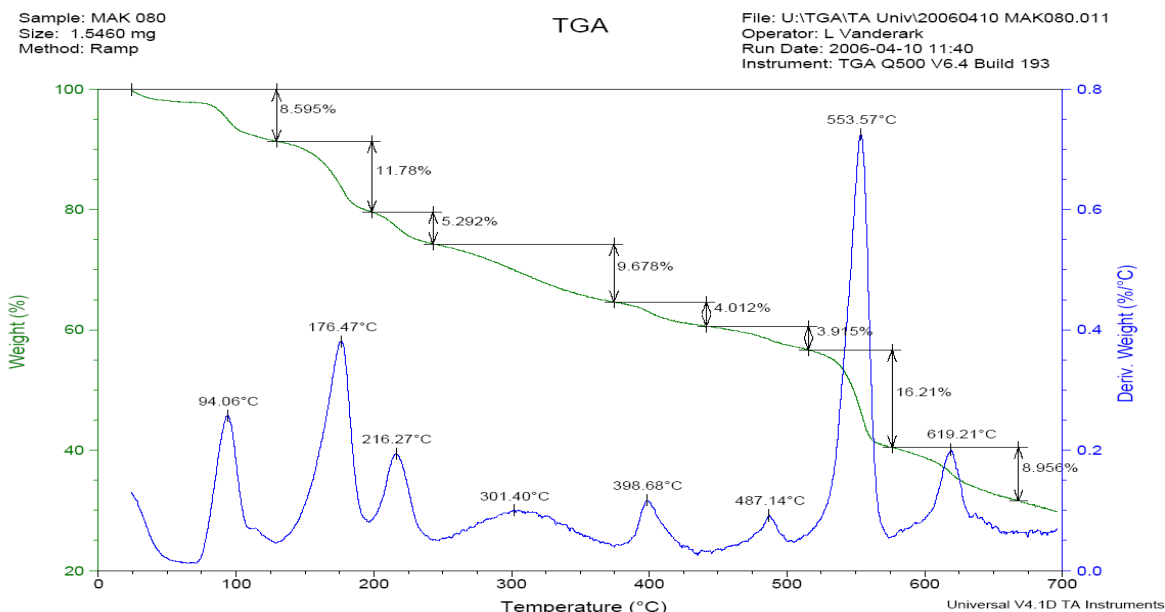


Figure 5: TGA Diagram for $[H_2Me_4bpz][CoCl_4]$

Conclusion:

In conclusion, we note that X-ray crystallographic analysis of the single crystal of the title compound revealed that despite the presence of water molecules in their lattice, the crystal structure displayed great potential as NH donors that could be exploited to synthesize crystalline solids which are explicitly planned to have thermal or mechanochemical reactivity, and to yield coordination compounds with novel properties. The structures display robust hydrogen-bonded networks which give rise to well-defined arrangements with the tetrachlorometallate anions $[CoCl_4]^{2-}$ and the

$[H_2Me_4bpz]^{2+}$ cations stacked into sheets and layers. The thermogravimetric analysis of the compound did not show any distinct mass loss corresponding to either water molecule or HCl molecule an indication that it does not have any definite thermal behaviour that could be explored in the generation of MOFs via thermal elimination method.

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