



Synthesis and Single Crystal X-Ray Structure Determination of 3,3',5,5'-tetramethyl-4,4'-bipyrazolium tetrachloromanganate(II) monohydrate ([H₂Me₄bpz]₂[MnCl₄]Cl₂·H₂O)

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ABSTRACT

The title compound was synthesized mechanochemically by grinding MnCl₂·4H₂O and the protonated organic ligand [H₂Me₄bpz] resulting in the formation of [H₂Me₄bpz][MnCl₄]. Suitable single crystal of this compound was analysed through X-ray diffraction technique to ascertain its composition and internal structure. Single crystal structure determination at 100 K revealed needle-like crystals in an orthorhombic crystal system. The asymmetric unit of the cell consists of an isolated chloride ion, one half of a tetrahedral [MnCl₄]²⁻ anion, a [H₂Me₄bpz]²⁺ dication and one half of a molecule of water.

Keywords: Crystal Engineering, Hydrogen Bond, X-ray Crystallography

INTRODUCTION

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 intermolecular 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.

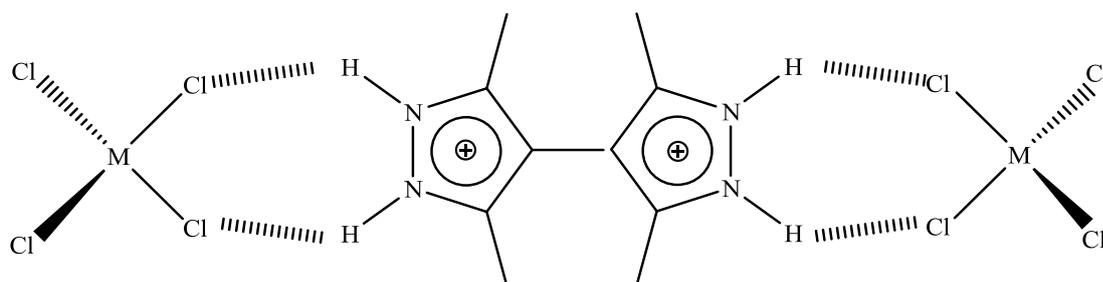


Fig. 1: N—H...Cl hydrogen-bonding synthon

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

MATERIALS AND METHODS

Analar 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 ml of concentrated aqueous hydrochloric acid and 40 ml and deionised water. The solution was reduced to 25 ml by boiling and 50 ml 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: $[\text{H}_2\text{Me}_4\text{bpz}][\text{MnCl}_4]\cdot\text{H}_2\text{O}$:

$[\text{H}_2\text{Me}_4\text{bpz}]\text{Cl}_2$ (263 mg, 1 mmol) and 198 mg (1 mmol) of $\text{MnCl}_2\cdot\text{H}_2\text{O}$ were ground in agate mortar resulting in the formation of a colourless polycrystalline compound.

Crystal Growth:

Suitable single crystals of the title compound were obtained by dissolving 5 mg amount of the synthesized compound in a 5 ml of concentrated hydrochloric acid solution. This was allowed to evaporate slowly at room temperature and after two weeks suitable single crystals were obtained.

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.

RESULTS AND DISCUSSION

Mechanochemical grinding of the reactants resulted in the formation white solid which dissolved in concentrated HCl solution yielding a colourless solution. Slow evaporation of this solution led to the re-crystallization of the title compound as colourless needle-like crystals. The compound was dissolved in concentrated hydrochloric acid in order to enforce the protonation of the pyrazole nitrogen atoms. Single crystal structure determination at 100 K revealed an

orthorhombic crystal in the $Pnma$ space group. The asymmetric unit of the cell consists of an isolated chloride ion, one half of a tetrahedral $[\text{MnCl}_4]^{2-}$ anion, a $[\text{H}_2\text{Me}_4\text{bpz}]^{2+}$ dication and one half of a molecule of water indicating both molecules are sitting on a crystallographic inversion centres. In the crystal structure, the water molecule contributes to the three-dimensional hydrogen-bonding, forming two $\text{O}\cdots\text{H}\cdots\text{Cl}$ hydrogen-bonds with tetrahedral $[\text{MnCl}_4]^{2-}$ anions, making a two-dimensional chain of hydrogen bond bridges along the crystallographic c -axis through $\{\text{O}\cdots\text{H}\cdots\text{Cl}\text{—}\text{Mn}\text{—}\text{Cl}\cdots\text{H}\text{—}\text{O}\}$ interactions (Fig. 2). It also

makes two $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds with $[\text{H}_2\text{Me}_4\text{bpz}]^{2+}$ dications. The $[\text{H}_2\text{Me}_4\text{bpz}]^{2+}$ dication has two different pyrazolium hydrogen-bonding environments as shown in Figure 3, one pyrazolium hydrogen-bonding to two $[\text{MnCl}_4]^{2-}$ anions and a water through $\text{N}\cdots\text{H}\cdots\text{Cl}$ and $\text{N}\cdots\text{H}\cdots\text{O}$ bonds respectively, whilst the other forms $\text{NH}\cdots\text{Cl}$ contacts with two isolated chlorine atoms. Detailed hydrogen bond geometry is presented in table 1. The presence of the water of crystallization in the molecule rendered it unsuitable for designed synthetic route of synthesizing MOFs from hydrogen bonded complex $[\text{H}_2\text{Me}_4\text{bpz}][\text{MnCl}_4]$.

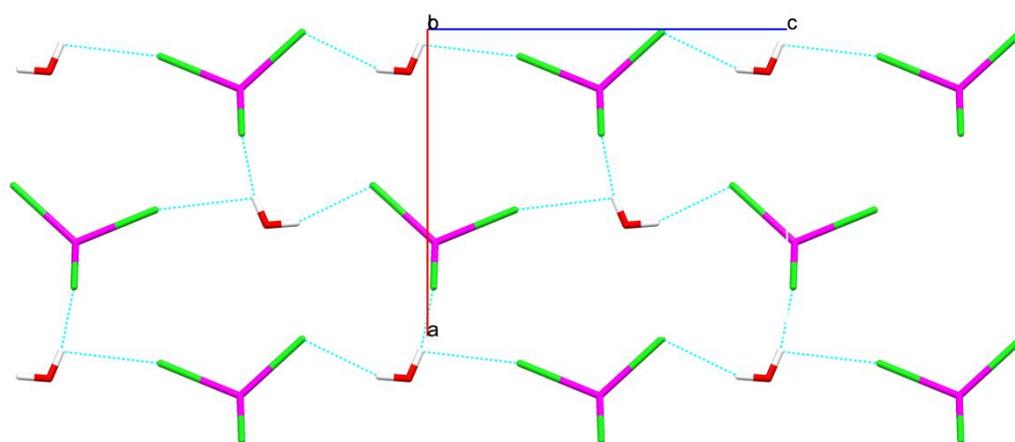


Fig. 2: Two dimensional $\text{MnCl}_4\text{—H}_2\text{O}$ hydrogen-bonded chains in $[\text{H}_2\text{Me}_4\text{bpz}][\text{MnCl}_4]$ viewed along the c -axis.

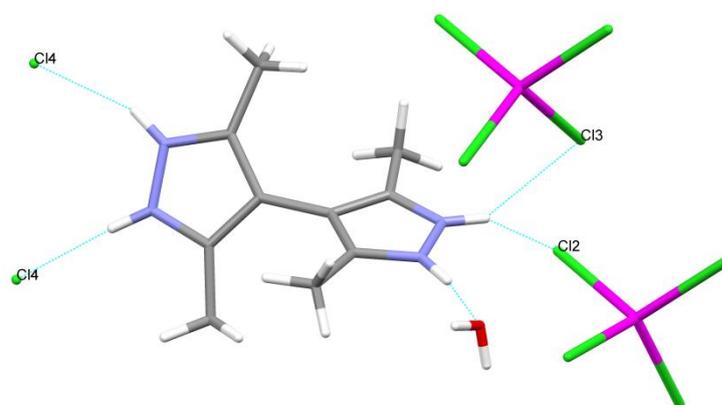


Fig. 3: The cation environment seen in the structure of $[\text{H}_2\text{Me}_4\text{bpz}][\text{MnCl}_4]$.

The overall packing in the crystal structure consists of a central layer of the $[\text{MnCl}_4]^{2-}\text{-H}_2\text{O}$ chain sandwiched between two layers of the

$[\text{H}_2\text{Me}_4\text{bpz}]^{2+}$ dications, which in turn are packed between layers of the isolated chloride ions (Fig. 4).

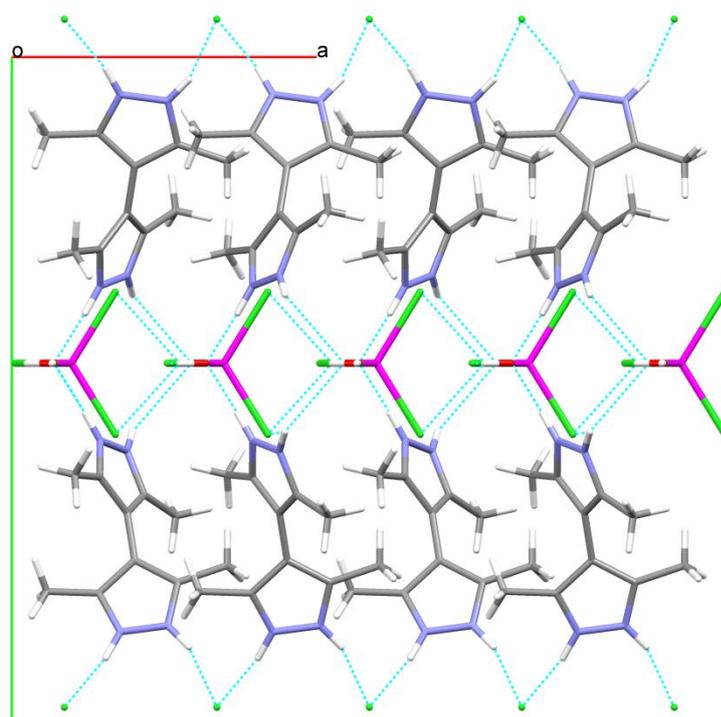


Fig. 4: Crystal packing of $[\text{H}_2\text{Me}_4\text{bpz}][\text{MnCl}_4]$.

Table 1 shows the hydrogen-bond geometry of the $[\text{H}_2\text{Me}_4\text{bpz}][\text{MnCl}_4]$ molecule,

while table 2 presents its detailed crystal and structure refinement data.

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

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1A)...O(1) ^A	0.88	1.86	2.713(3)	162.4
N(2)-H(2A)...Cl(3) ^B	0.88	2.57	3.221(2)	131.0
N(4)-H(4A)...Cl(4) ^A	0.88	2.19	3.022(2)	157.2
O(1)-H(1)...Cl(2) ^C	0.833(19)	2.734(15)	3.342(2)	131.2(8)
O(1)-H(1)...Cl(2) ^D	0.833(19)	2.734(15)	3.342(2)	131.2(8)
O(1)-H(2)...Cl(1) ^E	0.834(19)	2.38(2)	3.166(3)	158(4)

Symmetry transformations used to generate equivalent atoms: ^A $x+1/2, y, -z+3/2$ ^B $x+1/2, y, -z+1/2$

^C $x-1, -y+1/2, z+1$ ^D $x-1, y, z+1$ ^E $x-1/2, y, -z+1/2$.

Table 2. Crystal data and structure refinement for [H₂Me₄bpz][MnCl₄]

Identification code	mak058a	
Empirical formula	C ₁₀ H ₁₇ Cl ₃ Mn _{0.50} N ₄ O _{0.50}	
Formula weight	335.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 8.5855(17) Å	α = 90°.
	b = 34.715(7) Å	β = 90°.
	c = 9.997(2) Å	γ = 90°.
Volume	2979.6(10) Å ³	
Z	8	
Density (calculated)	1.494 Mg/m ³	
Absorption coefficient	1.011 mm ⁻¹	
F(000)	1380	
Crystal size	0.25 x 0.15 x 0.10 mm ³	
Theta range for data collection	1.17 to 27.48°.	
Index ranges	-10 ≤ h ≤ 11, - 45 ≤ k ≤ 45, - 12 ≤ l ≤ 12	
Reflections collected	32148	
Independent reflections	3465 [R(int) = 0.0784]	
Completeness to theta = 27.48°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.885950	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3465 / 0 / 177	
Goodness-of-fit on F ²	1.106	
Final R indices [I > 2σ(I)]	R1 = 0.0390, wR2 = 0.1015	
R indices (all data)	R1 = 0.0593, wR2 = 0.1199	
Largest diff. peak and hole	0.535 and -0.484 e.Å ⁻³	

CONCLUSION:

In conclusion, it has been shown X-ray single crystal structure determination revealed that despite the presence of water molecules in their lattice, the crystal structure of title compound displayed great potential as NH donors that could be used to synthesize crystalline solids which are explicitly planned to have thermal or other 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 [MCl₄]²⁻ and the [H₂Me₄bpz]²⁺ cations stacked into sheets and layers. Furthermore, it has been shown that mechanochemistry can be exploited in the synthesis of hydrogen bonded

metal complex which can serve as a precursor for the synthesis of coordination compounds.

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