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SYNTHESIS AND STRUCTURAL ANALYSES OF BIS(2-OXO-2,3-DIHYDROPYRIMIDIN-1-IUM) TETRACHLORO ZINCATE (II) [H_2pymo][$ZnCl_4$] AND BIS(PYRIMIDIN-2-OLATE) ZINC(II) [Zn(PYMO)$_2$]

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ABSTRACT

The preparation of [H_2pymo][$ZnCl_4$] by reacting [H_2pymo]Cl and $ZnCl_2$ in the solid state is reported using the state of the arts techniques in crystal engineering and solid state methods. Single crystal X-ray diffraction revealed an orthorhombic crystal in the *Pnma* space group The structures of complex metal salt was studied and analysed using X-ray single crystal structure determination and X-ray powder diffraction (XRD) methods and elemental analyses were used to further characterize and establish the composition of the crystalline salts. Solid state mechanochemical methods were then explored to synthesize Bis(pyrimidin-2-olate) zinc(II) [Zn(pymo)$_2$] (a metal-organic framework) between zinc metal and pyrimidine ligands.

Keywords: Mechanochemistry, crystal engineering, metal-organic framework, pyrimidine

Introduction

Solid-state synthesis has recently gained more attraction, possibly because the reactions are sometimes more convenient than using solvent-based synthesis, which are cost effective, and can reduce environmental contamination (Garay *et al*., 2007; Sheldon, 2005). In addition, safety may be increased and work-up is considerably simplified (Kidwai, 2001), and more importantly solid-state methods can provide much faster access to complexes which are inaccessible or usually take a long time to synthesize from solution or other methods (Kaupp *et al*., 2001). For example, the assembly of a hexa-palladium bowl-shaped cluster, which was obtained in quantitative yield at room temperature by simply grinding of [$Pd(NO_3)_2$en] and a tripodal ligand (2,4,6-(tripyridyl)-1,3,5-triazine), was achieved in only ten minutes while a similar reaction with platinum requires more than 4 weeks at 100 ºC in D_2O to be completed (Orita *et al*., 2002).

It has been established that solid state grinding of protonated ligands [H_2LCl] (L = imidazole or pyrazole) with metal dichlorides MCl_2 (M = Co, Cu, Zn) resulted in the formation of hydrogen bonded metal salts [H_2im]$_2$[MCl_4] (Adams *et al*., 2008) and [H_2pz]$_2$[MCl_4] (M = Co and Zn) (Christopher *et al*., 2010a). In addition salts of Palladium and Platinum with these ligands are also accessible through the solid state preparative methods to generate [H_2im]$_2$[MCl_4] (M = Pd, Pt) (Christopher *et al*., 2010b). Such complex metals salts are usually subjected to thermal or mechanochemical dehydrochlorination to afford discrete and network (polymeric) complexes [$MCl_2(HL)_2$] (M = Co, Zn, Pd and Pt). (Adams *et al*., 2007) The [$MCl_2(HL)_2$] coordination compounds can equally be prepared by direct mechanochemical grinding of MCl_2 and the ligands HL which upon exposure to HCl vapour (or dry HCl gas) results in the formation of the perchlorometallate salts. Remarkably these reactions proceed with (re)crystallisation at room temperature (at least in the mechanochemical cases) without use of bulk solvent (Gillon *et al*., 1999; Gillon *et al*., 2000; Lewis and Orpen, 1998; Adams *et al*., 2005; Adams et al., 2007; Adams et al., 2008; Angeloni *et al*., 2004; Podesta and Orpen, 2002; Podesta and Orpen, 2005; Garay *et al*., 2007; Christopher *et al*. 2010a, Christopher *et al*. 2010b; Christopher *et al*. 2010c).

Nð H···Cl interactions have been extensively exploited in crystal engineering to design and synthesize materials with the desired structures and properties.

The possibility of bonding through the heterocyclic N- atoms and the exocylic O- atom make the 2-hydroxypyrimidine (pymo) ligand very suitable for the design and syntheses of extended open metal-organic frameworks (MOFs) which mimic the properties of conventional porous solids. A number of coordination polymers of pymo have been prepared by conventional solution or solvothermal methods and fully characterized by chemical, spectroscopic, and thermal analyses (Masciocchi *et al*., 2000).

This paper reports the exploitation of the state of the art methods in crystal engineering and solid state methods to synthesize $[H_2pymo]_2[MCl_4]$ by reacting 2-hydroxypyrimidine hydrochloride, $[H_2pymo]Cl$ and metal dichloride in a 2:1 ratio and the analysis of synthesized materials using X-Ray diffraction methods. Furthermore, it also reports the application of mechanochemical methods in the synthesis of bis(pyrimidin-2-olate) zinc(II) $[zn(pymo)_2]$.

Materials and Methods

All reagents were purchased from Aldrich, Strem or Lancaster and used without further purification. Product samples were dried in *vacuo* or in the oven at 50 ºC.

X-ray Single Crystal Analysis

X-ray data were collected at 100 K on a Bruker APEX diffractometer using Mo-Kα 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.

X-ray Powder Diffraction Analysis:

All crystalline phases were analysed at room temperature by powder X-ray diffraction on a Bruker D8 diffractometer using Cu-Kα X-radiation. In all the cases the experimental pattern matches that calculated on the basis of the single crystal structure determination at room temperature.

Synthesis

Samples were ground by using an agate mortar and pestle in under ordinary atmospheric conditions to give solids with the expected elemental analysis and X-ray powder diffraction patterns. The time required in grinding (typically 20 seconds) is only that necessary to be sure that all the reagents have been thoroughly mixed.

$[H_2pymo][ZnCl_4]$

A millimole (136 mg) of $ZnCl_2$ and 265 mg (2 mmol) of $[H_2pymo]Cl$ were ground forcefully in an agate mortar resulting in the formation of a finely divided cream coloured powder. Microanalytical data (%), Calculated for $[C_4H_5N_2O]_2[ZnCl_4]$: C, 23.94; H, 2.51; N, 13.96. Found C, 23.98; H, 2.64; N, 13.72.

A small portion of this was dissolved in concentrated HCl forming a clear yellow solution which was allowed to evaporate at room temperature. Colourless crystals were obtained after a few weeks.

$[Zn(pymo)_2]_n$:

Mechanochemical elimination (internal base):

Five millimole (855 mg) of a mixture of Hpymo and KCl plus 0.5 mmol (275 mg) of $3Zn(OH)_2 \cdot 2ZnCO_3$ were ground in an agate mortar forming a cream coloured powder which was dried in *vacuo*. Microanalytical data (%), Calculated for $[(C_4H_3N_2O)_2Zn]$ + 2KCl: C, 23.75; H, 1.49; N, 13.85. Found C, 23.62; H, 1.83; N, 14.16.

Mechanochemical elimination (external base (KOH)):

A millimole (328 mg) of $[ZnCl_2(Hpymo)_2]$ was ground with 2 mmol (112 mg) of KOH in an agate mortar. An off-white coloured powder was formed and then dried in *vacuo*. Microanalytical data (%), Calculated for $[(C_4H_3N_2O)_2Zn]$ + 2KCl: C, 23.75; H, 1.49; N, 13.85. Found C, 23.46; H, 1.69; N, 13.70.

Mechanochemical elimination (external base (K_2CO_3)):

A millimole (401 mg) of $[H_2pymo]_2[ZnCl_4]$ and 2 mmol (276 mg) of K_2CO_3 were ground in an agate mortar. The reaction proceeded with no visible effervescence and no distinct colour change, forming a beige powder which was dried in *vacuo*. Microanalytical data (%), Calculated for $[(C_4H_3N_2O)_2Zn]$ + 4KCl: C, 17.35; H, 1.09; N, 10.12. Found C, 17.40; H, 1.12; N, 10.34.

Results and Discussion

The slow evaporation of a solution of zinc(II) chloride and 2-hydroxypyrimidine in concentrated HCl led to the formation of colourless block crystals. Single crystal X-ray diffraction revealed an orthorhombic crystal in the *Pnma* space group. The asymmetric unit of the cell consists of one half of a $[ZnCl_4]^{2-}$ anion and one $[H_2pymo]^+$ cation. The $[ZnCl_4]^{2-}$ anion lies on an inversion centre

In the crystal structure the $[H_2pymo]^+$ cations form dimeric intramolecular eight-membered $R_2^2(8)$ hydrogen-bonded motif (Fig. 1) through N−H⋯O interactions, while with the anions they form a C(4) chain motif (Fig. 2). Combination of the two motifs generates a hydrogen-bonded ribbon running parallel to the crystallographic *b*ï axis (Fig. 3)

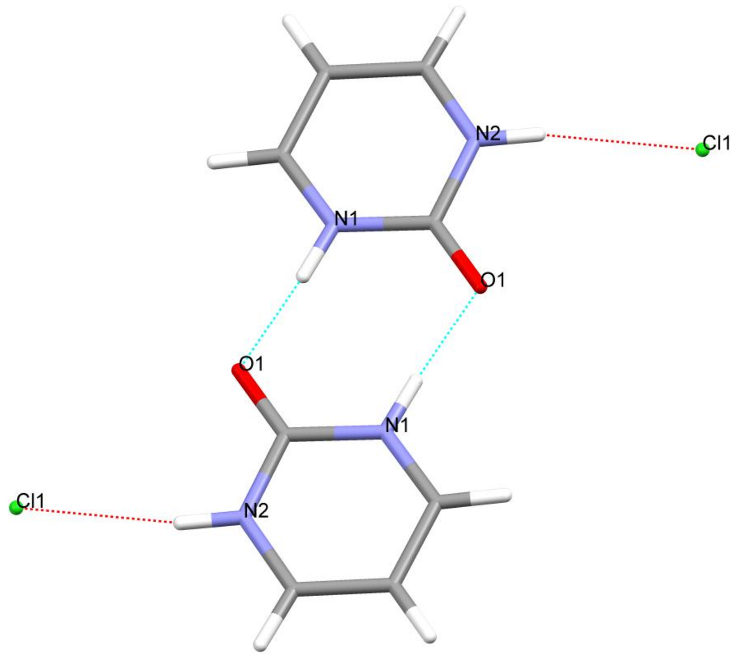

Figure 1: The $R_2^2(8)$ motif in $[H_2pymo]_2[ZnCl_4]$.

Two types of hydrogen bond interactions were observed in the internal geometry of the molecule. Short Nð H···O interaction and a slightly longer Nð H···Cl interaction (Table 1). The difference in length between the two interactions is attributed to the difference in the Electronegativity value of the acceptor atoms i.e O and Cl.

Table 1 shows the hydrogen bond geometry in the title compound while table 2 presents detailed crystal and structure refinement data.

Table 1: Hydrogen bond geometry for $[H_2pymo]_2[ZnCl_4]$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)^A	0.88	1.95	2.812(2)	164.6
N(2)-H(2A)...Cl(1)^B	0.88	2.40	3.2245(16)	156.3

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

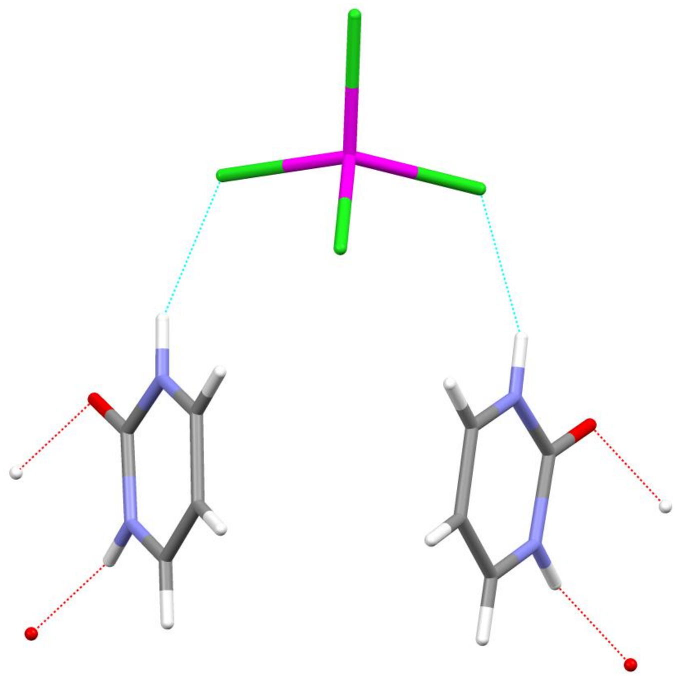

Figure 2: The anion environment in the structure of $[H_2pymo]_2[ZnCl_4]$.

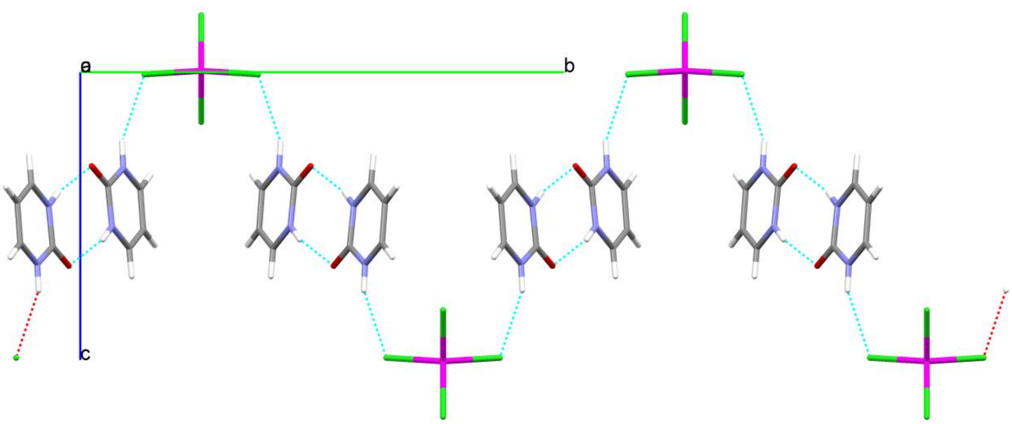

Figure 3: A hydrogen-bonded ribbon in $[H_2pymo]_2[ZnCl_4]$.

Table 2: Crystal data and structure refinement for [H_2pymo][$ZnCl_4$].

Identification code	mak338a	
Empirical formula	$C_8H_{10}Cl_4N_4O_2Zn$	
Formula weight	401.37	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 9.1446(6) Å	α= 90°.
	b = 16.2553(9) Å	β= 90°.
	c = 9.6349(6) Å	γ = 90°.
Volume	1432.21(15) $Å^3$	
Z	4	
Density (calculated)	1.861 mg/m^3	
Absorption coefficient	2.462 mm^{-1}	
F(000)	800	
Crystal size	0.499 x 0.299 x 0.124 mm^3	
Theta range for data collection	2.46 to 27.45°.	
Index ranges	-11<=h<=11, -21<=k<=20, -11<=l<=12	
Reflections collected	13654	
Independent reflections	1692 [R(int) = 0.0407]	
Completeness to theta = 27.45°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. Transmission	0.7456 and 0.3930	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1692 / 0 / 91	
Goodness-of-fit on F^2	1.264	
Final R indices [I>2sigma(I)]	R1 = 0.0199, wR2 = 0.0698	
R indices (all data)	R1 = 0.0238, wR2 = 0.0980	
Largest diff. peak and hole	0.465 and -0.719 e.$Å^{-3}$	

On the other hand mechanochemical treatment of $3Zn(OH)_2{\cdot}2ZnCO_3$ with 10 molar equivalents of Hpymo (+ KCl) in an agate mortar led to the formation of [Zn(pymo)$_2$] in high yields, with the elimination of water (removed *in vacuo*) and CO_2. Equally, grinding of [$ZnCl_2$(Hpymo)$_2$] with KOH or K_2CO_3 affords the title compound and KCl in quantitative yields after the elimination of H_2O and CO_2 (in the latter). Bis(pyrimidin-2-olate) zinc(II) was originally synthesized from solution by the reaction of 2-hydroxy-pyrimidine and $ZnCl_2$ in water in the presence of a deprotonating agent and its structure, determined via *ab initio* XRPD methodology and its crystal structure showed a tetrahedrally coordinated Zn (II) ions which are linked to four nitrogen atoms of distinct pymo ligands (Masciocchi *et al*., 2000).

The one-step solid state synthetic method by simply grinding [$ZnCl_2$(Hpymo)$_2$] with KOH (or K_2CO_3 in some cases) or by grinding the basic metal salt here $3Zn(OH)_2{\cdot}2ZnCO_3$ with the corresponding neutral ligands (Hpymo) provided a much easier and direct route for synthesizing metal-organic frameworks as compared to the long and laborious solvothermal methods which involves the application of heat and deprotonating agents to obtain the pyrimidinolate (Masciocchi *et al*., 2000).

The calculated and the observed X-ray diffraction powder patterns for the various routes followed to synthesize the title compound bis(pyrimidin-2-olate) [Zn(pymo)$_2$] are consistent as can be seen in Figure 4. The blue (top) pattern is the calculated pattern obtained from the single crystal structure (Masciocchi *et al*., 2000); while the green (below) pattern was obtained when $3Zn(OH)_2{\cdot}2ZnCO_3$ was ground with the neutral ligand (Hpymo) in a ratio of one metal to two ligands; the pink (middle) pattern was obtained when $[ZnCl_2(Hpymo)_2]$ was ground with 2moles of KOH; whereas the turquoise pattern was obtained when $[ZnCl_2(Hpymo)_2]$ was ground with K_2CO_3.

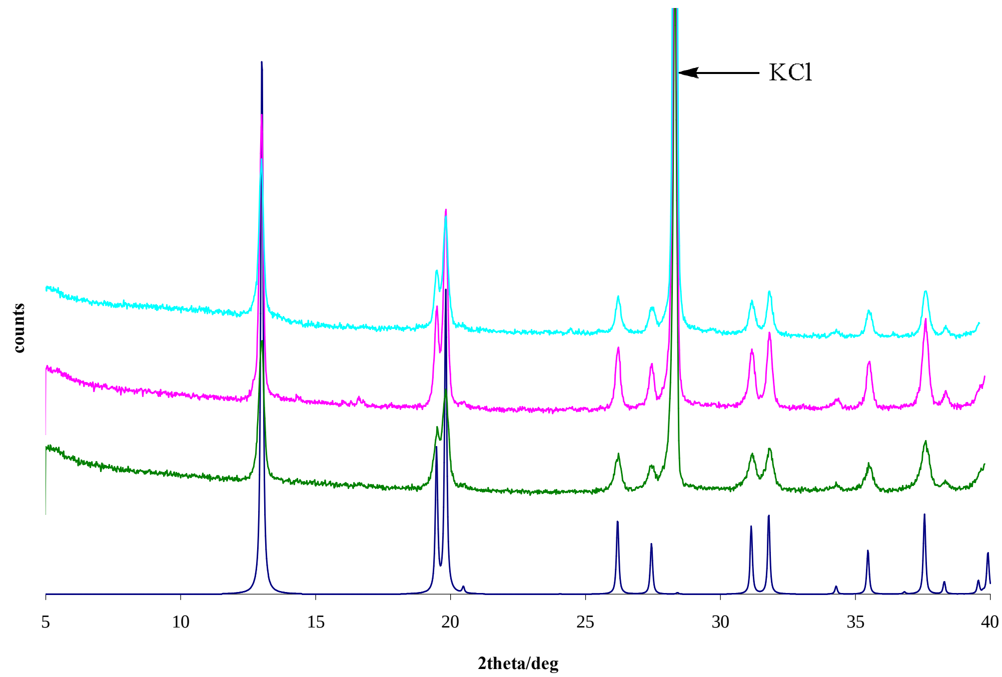

Figure 4: *XRPD* patterns for $[Zn(pymo)_2]_n$. Blue = calculated from the crystal structure; green = $3Zn(OH)_2{\cdot}2ZnCO_3$ + 2Hpymo + KCl; pink = $[ZnCl_2(Hpymo)_2]$ + 2KOH; turquoise = $[ZnCl_2(Hpymo)_2]$ + K_2CO_3.

Conclusion:

In conclusion, it has been shown that the use of ñinternalò or ñexternalò bases to afford crystalline coordination compounds $[MCl_2(HL)_2]$ (L = imidazole or pyrazole) can be now extended to the synthesis of polymeric metal-organic frameworks such as the zinc(II) pyrimdin-2-olate $[\{Zn(pymo)_2\}_n]$ species. Furthermore, the crystal structure of the complex metal salt $[H_2pymo]_2[ZnCl_4]$ revealed that the tetrahedral $[ZnCl_4]^{2-}$ anions and the pyrimin-1-ium cations are held together through Nð H···Cl interactions in addition to an intra-molecular interaction between the cations through Nð H···O interactions.

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