



Synthesis and Single Crystal X-Ray Crystallographic Analysis of 2-oxo-2,3-dihydropyrimidin-1-ium{trichloridopyrimidin-2(1H)-one} Cobaltate (II) [H₂pymo][CoCl₃(Hpymo)]

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ABSTRACT

Mechanochemical synthetic method was employed to synthesise *bis*(2-oxo-2,3-dihydropyrimidin-1-ium) tetrachlorocobaltate(II) [H₂pymo]₂[CoCl₄]. The compound was re-crystallized in diethyl ether to obtain a suitable single crystal for X-ray diffraction analysis which revealed a molecule crystallizes in the orthorhombic crystal system with the chiral space group *P*2₁2₁2₁ and a Flack parameter value of 0.514 (13). The asymmetric unit of the cell contains one discrete [H₂pymo]⁺ cation and a [CoCl₃(Hpymo)]⁻ anion which are bonded to each other through N—H···O and N—H···Cl interactions.

Keywords: Crystal Engineering, Mechanochemical, Single Crystal X-ray Diffraction

INTRODUCTION

Development of new materials for solid state science and technology depends on access to new synthetic methods; hence the need for the exploration of new frontiers in the science of synthesis without the use of solvents. Recently a number of researchers have shown that a range of hydrogen bonded complex metal salts and coordination compounds can be prepared without recourse to solution methods (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; Kidway, 2001; Garay *et al.*, 2007).

Solid state grinding of protonated ligands [H₂L]Cl (L = imidazole or pyrazole) with metal dichlorides MCl₂ (M = Co, Cu, Zn) resulting in the formation of hydrogen bonded metal salts [H₂im]₂[MCl₄] has been established (Adams *et al.*, 2008) and [H₂pz]₂[MCl₄] (M = Co and Zn) (Christopher *et al.*, 2010). In addition salts of Palladium and Platinum with these ligands are also accessible through the solid state preparative methods to generate [H₂im]₂[MCl₄] (M = Pd, Pt) (Christopher *et al.*, 2010). Such complex metals salts are usually subjected to thermal or mechanochemical dehydrochlorination to afford discrete and network (polymeric) complexes [MCl₂(HL)₂] (M = Co, Zn, Pd and Pt). (Adams *et al.*, 2007).

Access to coordination (or polymeric) compounds by coordination through the heterocyclic N- atoms and the exocyclic 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, solvothermal or solid state methods and fully characterized by chemical, spectroscopic, and thermal analyses (Masciocchi *et al.*, 2000; Kurawa, 2012).

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. (Evans and Evans 2004; Harris *et al.*, 2001)

This paper reports the exploitation of the state of the art methods in crystal engineering and mechanochemical methods to synthesize [H₂pymo]₂[CoCl₄] by reacting 2-hydroxypyrimidine hydrochloride, [H₂pymo]Cl and Cobalt (II) chloride and the analysis of synthesized

materials 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 Complex: $[\text{H}_2\text{pymo}][\text{CoCl}_4(\text{Hpymo})]$:

130 mg (1 mmol) of anhydrous CoCl_2 and 265 mg (2 mmol) of $[\text{H}_2\text{pymo}]\text{Cl}$ were ground in an agate mortar forming a blue-green polycrystalline powder which was stored in a sealed vial. Microanalytical data (%), Calculated for $[\text{C}_4\text{H}_5\text{N}_2\text{O}]_2[\text{CoCl}_4]$: C, 24.33; H, 2.55; N, 14.19. Found C, 24.38; H, 2.68; N, 14.00.

Crystal Growth:

Suitable single crystals of the title compound were obtained by vapour diffusion re-crystallization technique in ethanol and diethyl ether. 10 mg of product obtained from grinding was dissolved in 15 ml of ethanol in a small vial. The vial was immersed in a bigger one containing a 20 ml of diethyl ether and the cap of the bigger vial is screwed tightly. A few hours diffusion of the diethyl ether vapours in to the ethanol solution initiated the crystallization of suitable single crystals of the title compound.

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 2 moles of pyrimidinium chloride ($[\text{H}_2\text{pymo}]\text{Cl}$) and one mole of CoCl_2 resulted in the formation blue-green polycrystalline powder of *Bis*-(2-Oxo-2,3-Dihydropyrimidin-1-ium) Tetrachloro cobaltate (II) ($[\text{H}_2\text{pymo}]_2[\text{CoCl}_4]$) as deduced by the elemental analysis result. However, attempt to re-crystallize $[\text{H}_2\text{pymo}]_2[\text{CoCl}_4]$ via diethyl ether vapour diffusion into an ethanol solution of $[\text{H}_2\text{pymo}]_2[\text{CoCl}_4]$ resulted in the crystallization of the title compound whose asymmetric unit of the cell contains one discrete $[\text{H}_2\text{pymo}]^+$ cation and a $[\text{CoCl}_3(\text{Hpymo})]^-$ anion (Fig. 1).

Single crystal structure analysis of the compound showed that the molecule crystallizes in the orthorhombic crystal system with the chiral space group $P2_12_12_1$, with a Flack parameter value of 0.514 (13) indicating nearly 50:50 inversion twinning. Detailed crystal and structure refinement data are presented in Table 1.

The anion consists of a cobalt (II) ion tetrahedrally bonded to one nitrogen from the 2-oxo-2,3-pyrimidin-2(1H)-one ligand and three chloride ions, two of which form hydrogen-bonds to the $[\text{H}_2\text{pymo}]^+$ cations. The coordinated ligand forms an $\text{N}-\text{H}\cdots\text{O}$ contact with another cation (Fig.2). The planar $[\text{H}_2\text{pymo}]^+$ cation, with both nitrogen atoms protonated and the oxygen atom unprotonated, forms one $\text{N}-\text{H}\cdots\text{Cl}$ and one $\text{N}-\text{H}\cdots\text{O}$ interactions with two anions (Fig. 3). Similar interactions have been reported with the same cations and and a complex trinuclear $[\text{Cd}_3\text{Cl}_{11}]^{5-}$ anion of approximately D_{3h} symmetry (Kurawa *et al.*, 2008).



Figure 1: The asymmetric unit of $[\text{H}_2\text{pymo}][\text{CoCl}_3]$ with atom labels and 50% probability displacement ellipsoids for non-H atoms.

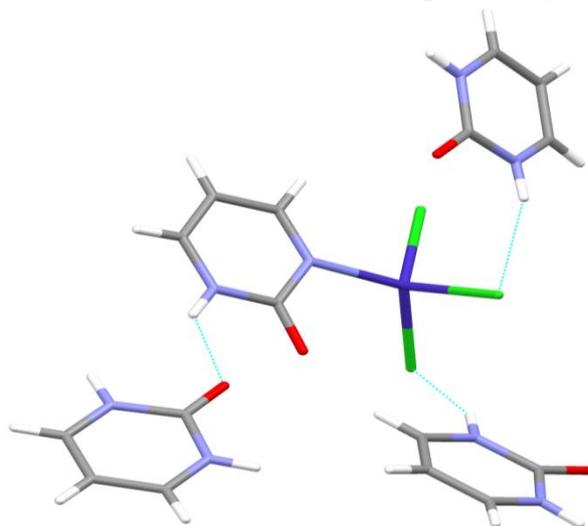


Figure 2: The anion environment in the structure of $[\text{H}_2\text{pymo}][\text{CoCl}_3]$.

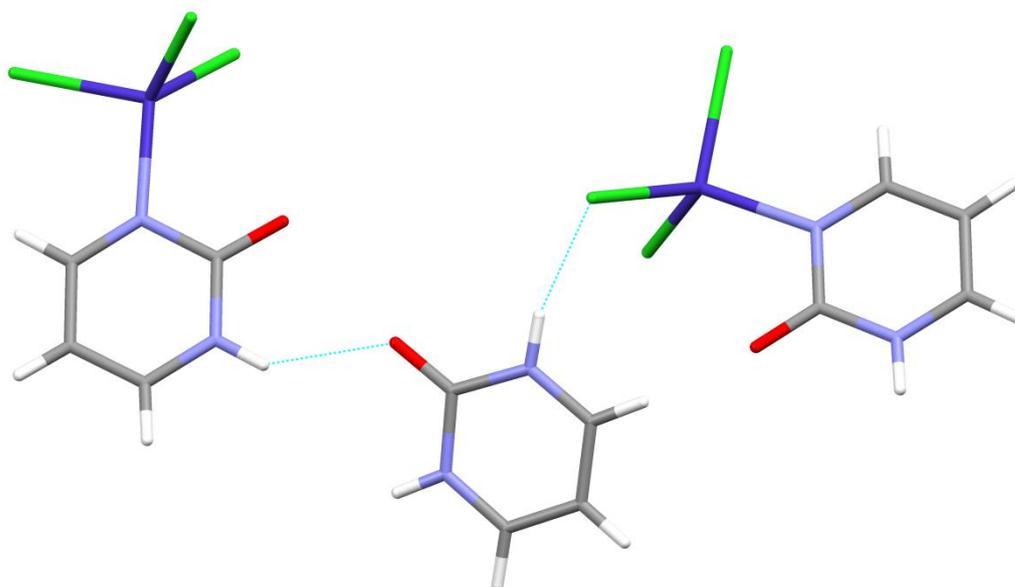


Figure 3: The cation environment in the structure of $[\text{H}_2\text{pymo}][\text{CoCl}_3]$.

The ability of the anion and the cation to interact through hydrogen bonding informed the decision to exploit this molecule in the synthesis of coordination compounds through the mechanochemical or thermal dehydrochlorination of 2 molecules of HCl from the designed and synthesized $[\text{H}_2\text{pymo}]_2[\text{CoCl}_4]$ molecule to obtain $[\text{CoCl}_2(\text{Hpymo})_2]$. This would have allowed for

further dehydrochlorination of two more molecules of HCl leading to the formation of a metal-organic framework $[\text{M}(\text{pymo})_2]$.

Table 2 shows the hydrogen bond geometry for $[\text{H}_2\text{pymo}][\text{CoCl}_3]$, which are obtained from $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{O}$ interactions in the molecule.

Table 1: Crystal Data and Structure Refinement for [H₂pymo][CoCl₃(Hpymo)].

| | | |
|-----------------------------------|---|----------|
| Empirical formula | C ₈ H ₉ Cl ₃ CoN ₄ O ₂ | |
| Formula weight | 358.47 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | <i>P</i> 2 ₁ 2 ₁ | |
| Unit cell dimensions | a = 7.07840(10) Å | α = 90°. |
| | b = 13.2991(3) Å | β = 90°. |
| | c = 14.1769(3) Å | γ = 90°. |
| Volume | 1334.56(5) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.784 Mg/m ³ | |
| Absorption coefficient | 1.884 mm ⁻¹ | |
| F(000) | 716 | |
| Crystal size | 0.348 x 0.149 x 0.109 mm ³ | |
| Theta range for data collection | 3.22 to 27.49°. | |
| Index ranges | -9 ≤ h ≤ 9, -17 ≤ k ≤ 16, -16 ≤ l ≤ 18 | |
| Reflections collected | 7998 | |
| Independent reflections | 3057 [R(int) = 0.0182] | |
| Completeness to theta = 27.49° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.816 and 0.720 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 3057 / 0 / 164 | |
| Goodness-of-fit on F ² | 1.041 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0216, wR2 = 0.0541 | |
| R indices (all data) | R1 = 0.0222, wR2 = 0.0545 | |
| Absolute structure parameter | 0.514(13) | |
| Largest diff. peak and hole | 0.798 and -0.310 e.Å ⁻³ | |

Table 2: Hydrogen Bond Geometry for [H₂pymo][CoCl₃(Hpymo)] [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------------------|--------|----------|------------|--------|
| N(3)-H(3A)...Cl(3) ^A | 0.88 | 2.33 | 3.1407(19) | 153.7 |
| N(4)-H(4A)...Cl(1) ^B | 0.88 | 2.35 | 3.1894(18) | 158.8 |
| N(2)-H(2A)...O(2) ^C | 0.88 | 2.40 | 3.131(3) | 141.3 |
| N(2)-H(2A)...Cl(3) ^D | 0.88 | 2.82 | 3.3877(19) | 123.7 |

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

CONCLUSION:

In conclusion, it has been shown that the use mechanochemistry can be exploited in the synthesis of complex metal salts where complex anion and the organic cation are bonded through hydrogen bond. Furthermore, X-ray single crystal study of the complex revealed the deprotonation of one of the cations and its subsequent coordination on the cobalt (II) metal centre. The solved crystal structure ultimately confirms the composition of the molecule which was earlier predicted through elemental analysis.

Despite the presence of the exocyclic oxygen atom, no coordination through the O-atom has been observed in the compound all metal-ligand coordination bonds were through one or both heterocyclic N-atoms. In addition, the loss of one of protons rendered the synthesized compound unsuitable for the designed reaction routes.

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