



## SOLID STATE SYNTHESSES AND INTERCONVERSION OF NEW METAL SALTS AND THEIR COORDINATION COMPOUNDS

**Mukhtar A. Kurawa**

Department of Pure and Industrial Chemistry, Bayero University, P. M. B. 3011 Kano Nigeria

kurawatik@hotmail.com

### ABSTRACT

**The state of the art in crystal engineering and solid state chemistry were exploited to prepare new crystalline solids  $[H_4biim][MCl_4]$  complexes ( $M = Co, 1; Cu, 2; Zn, 3$ ) and  $[MCl_2(H_2biim)]$  ( $M = Co, 4; Cu, 5; Zn, 6$ ) by solid state methods. The crystalline salts  $[H_4biim][MCl_4]$  ( $M = Co, Cu, Zn$ ) contain anionic metal complexes (perchlorometallate) which are hydrogen bonded to organic cations ( $H_2biim$ ) decorated with NH H-bond donor groups, are synthesized via various solid state methods and then dehydrochlorinated via thermal or mechanochemical methods to obtain the coordination compounds  $[MCl_2(H_2biim)]$ . X-ray single crystal structure determination, powder diffraction (XRPD), thermogravimetric and elemental analyses were used in the preliminary characterization of the new salts and the derived materials.**

**Keywords:** Mechanochemical, Complexes, Cations, Synthesis

### 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 researches have shown that a range of coordination compounds can be prepared without recourse to solution methods (Fernandez-Bertran, 1999; Kaupp *et al.*, 2001; Shan *et al.*, 2002; Braga and Grepioni, 2004; Sheldon, 2005).

On the other hand routes to discrete and network (polymeric) complexes of first row divalent transition metals with pyridine derivatives have been established. These were prepared by thermal or mechanochemical dehydrochlorination of the perchlorometallate salts of the appropriate pyridinium species and the reverse process by solid - vapour reaction. 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 *et al.*, 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).

In recent years solid-state synthesis has gained more attraction, possibly because these reactions are sometimes more convenient than using solvent-based synthesis, are cost effective, and can reduce environmental contamination Garay *et al.*, 2007). 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  $[Pd(NO_3)_2 \cdot en]$  and a tripodal ligand (2,4,6-(tripyridyl)-1,3,5-triazine), was achieved in only ten minutes while a similar reaction

with platinum took more than 4 weeks at 100 °C in  $D_2O$  to be completed (Orita *et al.*, 2002).

This paper is concerned with the design and synthesis of crystalline solids which are planned to offer thermal reactivity towards dehydrochlorination to yield coordination compounds with novel properties. It is aimed at the exploitation of state of the art techniques in crystal engineering to prepare anionic metal complexes which are hydrogen bonded to 2,2'-biimidazolium cation decorated with NH hydrogen bond donor groups. Techniques such as *mechanochemistry* and *solid-gas reactions* were employed in the synthetic parts, whilst *thermal analysis* and *powder X-ray diffraction* methods will be utilised in the characterization of the synthesised materials.

### 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 °C.

#### X-ray Powder Diffraction analysis:

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

#### Thermogravimetric analysis

Thermal analysis of the samples 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, or on a Perkin-Elmer STA 6000 simultaneous thermal analyzer between 50 and 500°C at the heating rate of 5 °C/min. Data was analyzed using Pyris thermal analysis software.

**Synthesis**

Samples were ground by hand using an agate mortar and pestle in air 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<sub>4</sub>biim][CoCl<sub>4</sub>] (1):**

*Mechanochemical synthesis:* 130 mg (1 mmol) of anhydrous CoCl<sub>2</sub> and 207 mg (1 mmol) of 2,2'-biimidazolium chloride were ground in an agate mortar, resulting in the formation of a blue polycrystalline powder. Microanalytical data (%), Calculated for [C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>][CoCl<sub>4</sub>]: C, 21.39; H, 2.39; N, 16.63. Found C, 21.20; H, 2.62; N, 16.30.

*HCl gas absorption:* A vial containing 25 mg of [(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>)CoCl<sub>2</sub>] (2) was placed in a sealed jar, which was flushed with nitrogen gas and then filled with dry HCl gas for 8 hours. Microanalytical data (%), Calculated for [C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>][CoCl<sub>4</sub>]: C, 21.39; H, 2.39; N, 16.63. Found C, 21.74; H, 2.70; N, 16.31.

**[CoCl<sub>2</sub>(H<sub>2</sub>biim)] (2):**

*Mechanochemical synthesis:*

129 mg (1 mmol) of anhydrous CoCl<sub>2</sub> and 134 mg (1 mmol) of 2,2'-biimidazole were forcefully ground in an agate mortar, resulting in the formation of a pink polycrystalline powder. Microanalytical data (%) calculated for [(C<sub>6</sub>H<sub>6</sub>N<sub>4</sub>)CoCl<sub>2</sub>]·2H<sub>2</sub>O: C, 24.02; H, 3.36; N, 18.68. Found C, 24.28; H, 3.39; N, 18.04.

*Reaction of 2,2'-biimidazolium chloride with*

- (i) Co(OH)<sub>2</sub>: 207 mg (1 mmol) of 2,2'-biimidazolium chloride was ground with 93 mg (1 mmol) of Co(OH)<sub>2</sub> forming a pink powder, which was dried *in vacuo*. Microanalytical data (%), Calculated for [(C<sub>6</sub>H<sub>6</sub>N<sub>4</sub>)CoCl<sub>2</sub>]·2H<sub>2</sub>O: C, 24.02; H, 3.36; N, 18.68. Found C, 24.42; H, 3.16; N, 18.25.
- (ii) CoCO<sub>3</sub>: 207 mg (1 mmol) of 2,2'-biimidazolium chloride was forcefully ground with 119 mg (1 mmol) of CoCO<sub>3</sub> forming a pink powder, which was dried *in vacuo*. Microanalytical data (%), Calculated for [(C<sub>6</sub>H<sub>6</sub>N<sub>4</sub>)CoCl<sub>2</sub>]·2H<sub>2</sub>O: C, 24.02; H, 3.36; N, 18.68. Found C, 24.68; H, 3.44; N, 18.48.

**[H<sub>4</sub>biim][CuCl<sub>4</sub>] (3):**

*Mechanochemical synthesis:* 170 mg (1 mmol) of CuCl<sub>2</sub>·2H<sub>2</sub>O and 207 mg (1 mmol) of 2,2'-biimidazolium chloride were ground in an agate mortar, resulting in the formation of a yellow polycrystalline powder. Microanalytical data (%), Calculated for [C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>][CuCl<sub>4</sub>]: C, 21.10; H, 2.36; N, 16.41. Found C, 21.14; H, 2.23; N, 16.86.

*HCl gas absorption:* A vial containing 25 mg of [(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)CuCl<sub>2</sub>] (3) was placed in a sealed jar, which was flushed with nitrogen gas and then filled with dry HCl gas for 4 hours. The green colour of the starting compound changed to yellow on completion of the reaction. Microanalytical data (%), Calculated for [C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>][CuCl<sub>4</sub>]: C, 21.10; H, 2.36; N, 16.41. Found C, 21.52; H, 2.63; N, 16.44.

**[CuCl<sub>2</sub>(H<sub>2</sub>biim)] (4):**

170 mg (1 mmol) of CuCl<sub>2</sub>·2H<sub>2</sub>O and 132 mg (1 mmol) of 2,2'-biimidazole were ground in an agate mortar resulting in the formation of a green polycrystalline powder which was dried *in vacuo* to remove excess

water. Microanalytical data (%), Calculated for [(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)CuCl<sub>2</sub>]: C, 26.83; H, 2.25; N, 20.86. Found C, 26.17; H, 2.39; N, 20.93.

*Reaction of 2,2'-biimidazolium chloride with Cu(OH)<sub>2</sub>·CuCO<sub>3</sub>:* 414 mg (2 mmol) of 2,2'-biimidazolium chloride was ground with 221 mg (1 mmol) of Cu(OH)<sub>2</sub>·CuCO<sub>3</sub>, forming a green powder of [CuCl<sub>2</sub>(H<sub>2</sub>biim)<sub>2</sub>]<sub>n</sub>, which was dried *in vacuo*. Microanalytical data (%), Calculated for [(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)CuCl<sub>2</sub>]: C, 26.83; H, 2.25; N, 20.86. Found C, 26.24; H, 2.39; N, 20.74.

**[H<sub>4</sub>biim][ZnCl<sub>4</sub>] (5):**

*Mechanochemical synthesis:* 136 mg (1 mmol) of ZnCl<sub>2</sub> and 207 mg (1 mmol) of 2,2'-biimidazolium chloride were ground in an agate mortar, resulting in the formation of a white polycrystalline powder. Microanalytical data (%), Calculated for [C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>][ZnCl<sub>4</sub>]: C, 20.99; H, 2.35; N, 16.32. Found C, 21.31; H, 2.46; N, 16.15.

*HCl gas absorption:* A vial containing 25 mg of [(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)ZnCl<sub>2</sub>] (5) was placed in a sealed jar, which was flushed with nitrogen gas and then filled with dry HCl gas for 8 hours. Microanalytical data (%), Calculated for [C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>][ZnCl<sub>4</sub>]: C, 20.99; H, 2.35; N, 16.32. Found C, 21.10; H, 2.55; N, 16.42.

**[ZnCl<sub>2</sub>(H<sub>2</sub>biim)] (6):**

*Mechanochemical synthesis:* 136 mg (1 mmol) of ZnCl<sub>2</sub> and 134 mg (1 mmol) of 2,2'-biimidazole were ground in an agate mortar, resulting in the formation of a white polycrystalline powder. Microanalytical data (%), Calculated for [(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)ZnCl<sub>2</sub>]: C, 26.65; H, 2.24; N, 20.72. Found C, 26.68; H, 2.37; N, 20.87.

*Reaction of 2,2'-biimidazolium chloride with 3Zn(OH)<sub>2</sub>·2ZnCO<sub>3</sub>:*

518 mg (2.5 mmol) of 2,2'-biimidazolium chloride was ground with 275 mg (0.5 mmol) of 3Zn(OH)<sub>2</sub>·2ZnCO<sub>3</sub>. The title compound was formed as a white powder following a mild effervescence. Microanalytical data (%), Calculated for [(C<sub>6</sub>H<sub>6</sub>N<sub>4</sub>)ZnCl<sub>2</sub>]: C, 26.65; H, 2.24; N, 20.72. Found C, 26.04; H, 2.76; N, 20.81.

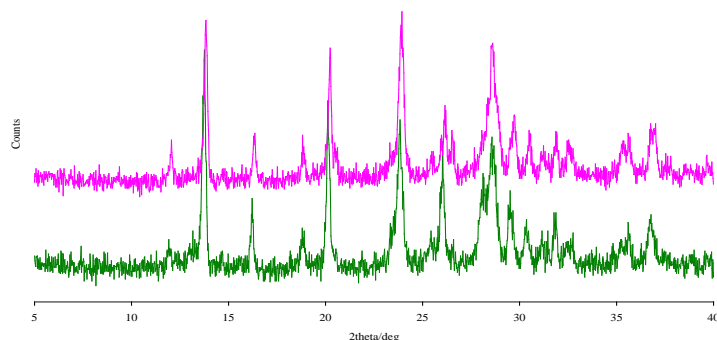
**RESULTS AND DISCUSSION**

The syntheses of complex salts and coordination networks are normally achieved via bulk solution methods (solvothermal methods inclusive) (Zhang *et al.*, 2005; Lundberg, 1966; Lundberg, 1972). The preparation and characterization of [H<sub>4</sub>biim][MCl<sub>4</sub>] complexes (M = Co, 1; Cu, 2; Zn, 3) and [MCl<sub>2</sub>(H<sub>2</sub>biim)] (M = Co, 4; Cu, 5; Zn, 6) by solid state methods are reported herein. The structure of 2,2'-biimidazolium hydrochloride cation has been reported to consist of a planar diprotonated biimidazole moiety and two Cl<sup>-</sup> ions each connected to the dication via a pair of N-H...Cl bonds (Belanger and Beauchamp, 1996).

Mechanochemical grinding of [H<sub>4</sub>biim]Cl<sub>2</sub> and CoCl<sub>2</sub> affords 1 in quantitative yields. Similarly, exposure of the coordination compound [CoCl<sub>2</sub>(H<sub>2</sub>biim)] (2) to vapour from concentrated aqueous HCl solution resulted in the formation of a compound suspected to be [H<sub>4</sub>biim][CoCl<sub>4</sub>] (1) as deduced from the microanalytical data.

Comparison of the X-ray powder diffraction patterns for both synthetic routes (Fig. 1) showed the products to be identical. The crystal structure of **1** is still unknown, but

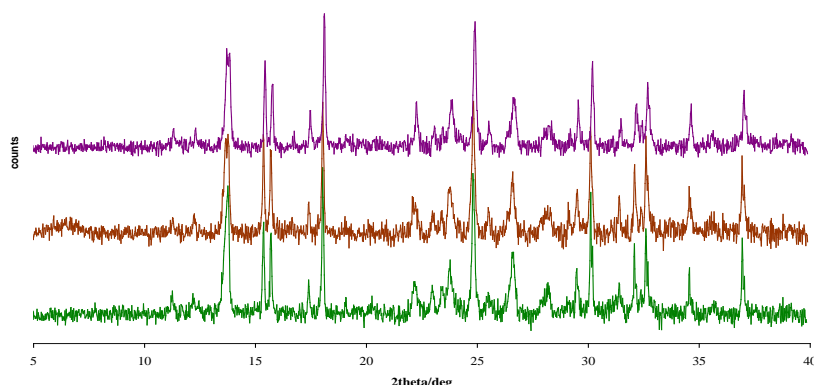
the XRPD patterns for this compound show a close similarity to those of the zinc analogue **3**.



**Figure 1: XRPD patterns for [H<sub>4</sub>biim][CoCl<sub>4</sub>] **1**. Bottom = mechanochemical; Top = HCl absorption.**

Mechanochemical grinding of neutral 2,2'-biimidazole with anhydrous CoCl<sub>2</sub> in a 1:1 ratio resulted in the formation of a pink polycrystalline powder, which elemental analysis confirmed to have a formula consistent with **2**. Similarly, grinding of [H<sub>4</sub>biim]Cl<sub>2</sub> with equivalent amounts of

Co(OH)<sub>2</sub> or CoCO<sub>3</sub> also affords the title compound in quantitative yield, forming compounds which are identical to each other and the product obtained mentioned earlier as deduced by X-ray powder diffraction (Fig. 2) and elemental analyses.



**Figure 2: XRPD patterns for [CoCl<sub>2</sub>(H<sub>2</sub>biim)]·2H<sub>2</sub>O **2**. Bottom = mechanochemical synthesis; middle = [H<sub>4</sub>biim]Cl<sub>2</sub> + CoCO<sub>3</sub>; top = [H<sub>4</sub>biim]Cl<sub>2</sub> + Co(OH)<sub>2</sub>.**

Mechanochemical grinding of CuCl<sub>2</sub>·2H<sub>2</sub>O with an equivalent amount of [H<sub>4</sub>biim]Cl<sub>2</sub> resulted in [H<sub>4</sub>biim][CuCl<sub>4</sub>] (**3**) as a yellow polycrystalline powder in high yields. Equally, exposure of the coordination compound [(CuCl<sub>2</sub>(H<sub>2</sub>biim))<sub>n</sub>] (**4**) to concentrated aqueous HCl vapour resulted in the formation of **3** in quantitative yield. However, comparison of the XRPD patterns for the two routes (Fig. 3) revealed the presence of some unreacted CuCl<sub>2</sub>·2H<sub>2</sub>O in the sample obtained mechanochemically, despite the reactants being present

in stoichiometric amounts, suggesting that the reaction had not reached completion at the time of the XRPD measurement. An interesting feature displayed by **3** is its ability to extrude two HCl molecules on standing at room temperature to afford the coordination compound. The process is fully reversible, and exposure of the coordination compound **4** to HCl vapours reverts it back to the salt **3**. Similar behaviour by salts containing [CuCl<sub>4</sub>]<sup>2-</sup> anions has been reported by Brammer *et al.*, 2006.

**Figure 1: XRPD patterns for [H<sub>4</sub>biim][CuCl<sub>4</sub>] **55**. Green = mechanochemical; pink = HCl absorption. Key: \* = peaks from CuCl<sub>2</sub>·2H<sub>2</sub>O.**

Mechanochemical treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with unprotonated 2,2'-biimidazole resulted in the formation of the known compound  $[\{\text{CuCl}_2(\text{H}_2\text{biim})\}_n]$  (**4**), whose structure is polymeric, and in which the  $\text{Cu}^{\text{II}}$  ion is coordinated by four basal atoms (two N atoms from a 2,2'-biimidazole molecule and two chloride ions) and one axial chloride ion in a distorted square-pyramidal coordination geometry (Hu *et al.*, 2005). Chloride ions bridge the  $\{\text{Cu}(\text{C}_6\text{H}_6\text{N}_4)\text{Cl}\}$  units into one-dimensional linear chains, which are reinforced by  $\pi$ - $\pi$  interactions. Adjacent linear chains are linked by  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds, resulting in a grid layer (Fig. 4).

The concept of accessing coordination compounds by reacting the protonated ligand with a basic metal salt as the source of the metal could also be exploited here, and grinding  $[\text{H}_4\text{biim}]\text{Cl}_2$  with basic copper carbonate ( $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ ) also affords **4** in quantitative yields, with concomitant elimination of  $\text{CO}_2$  and water. Elemental and X-ray powder diffraction analyses confirmed the products to be **4**. Figure 5 compares the calculated and the observed powder patterns.

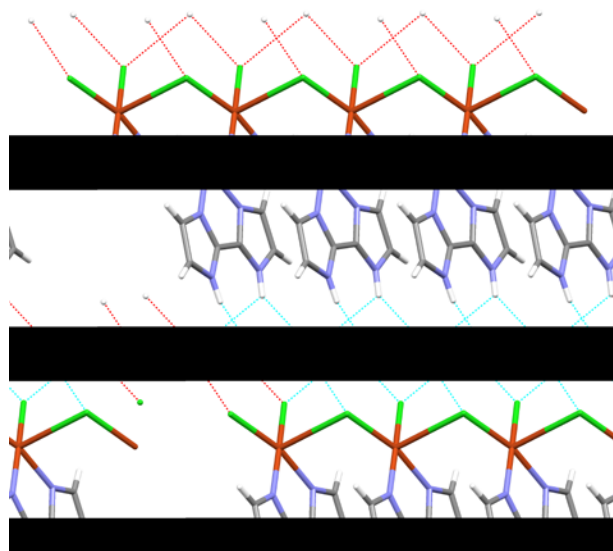


Figure 4:  $\{\text{CuCl}_2(\text{H}_2\text{biim})\}_n$  chain in **4**.

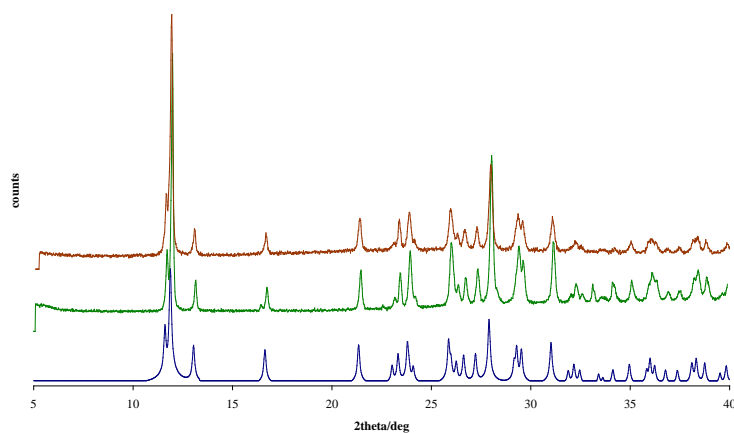


Figure 5: XRPD patterns for  $[\text{CuCl}_2(\text{C}_6\text{H}_6\text{N}_4)]_n$  **4**. Bottom = calculated from the crystal structure; green mechanochemical synthesis; brown =  $2[\text{H}_4\text{biim}]\text{Cl}_2 + \text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ .

Mechanochemical treatment of  $\text{ZnCl}_2$  with an equivalent amount of  $[\text{H}_4\text{biim}]\text{Cl}_2$  led to the formation of  $[\text{H}_4\text{biim}][\text{ZnCl}_4]$  (**5**) as a white polycrystalline powder in quantitative yield. Exposure of the coordination compound **6** to vapour from concentrated aqueous  $\text{HCl}$  also affords the title compound **5**. Figure 6 compares the observed XRPD patterns for these products. The crystal structure of the complex is still

unknown but elemental analyses of the products suggest a formula consistent with that of **5**; in addition, the X-ray diffraction powder pattern shows a close resemblance to that of its cobalt analogue **1**. Thermogravimetric analysis (see Fig. 7) on a sample of **5** showed a first mass loss of 21.75% which is equivalent to the loss of 2 molecules of  $\text{HCl}$  at 506 K.

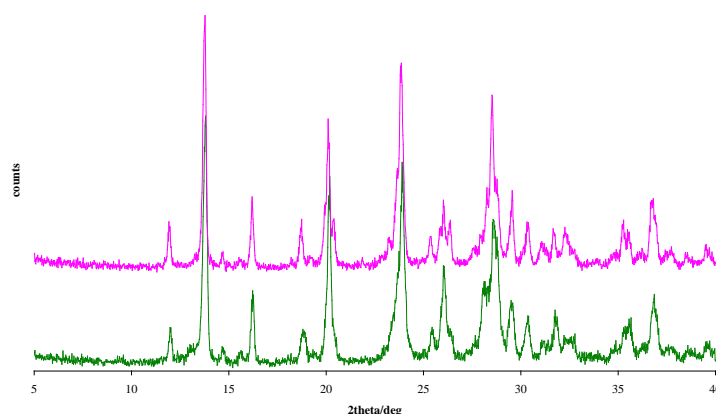


Figure 6: XRPD patterns for  $[H_4biim][ZnCl_4]$  5. Bottom = mechanochemical synthesis; top = HCl absorption.

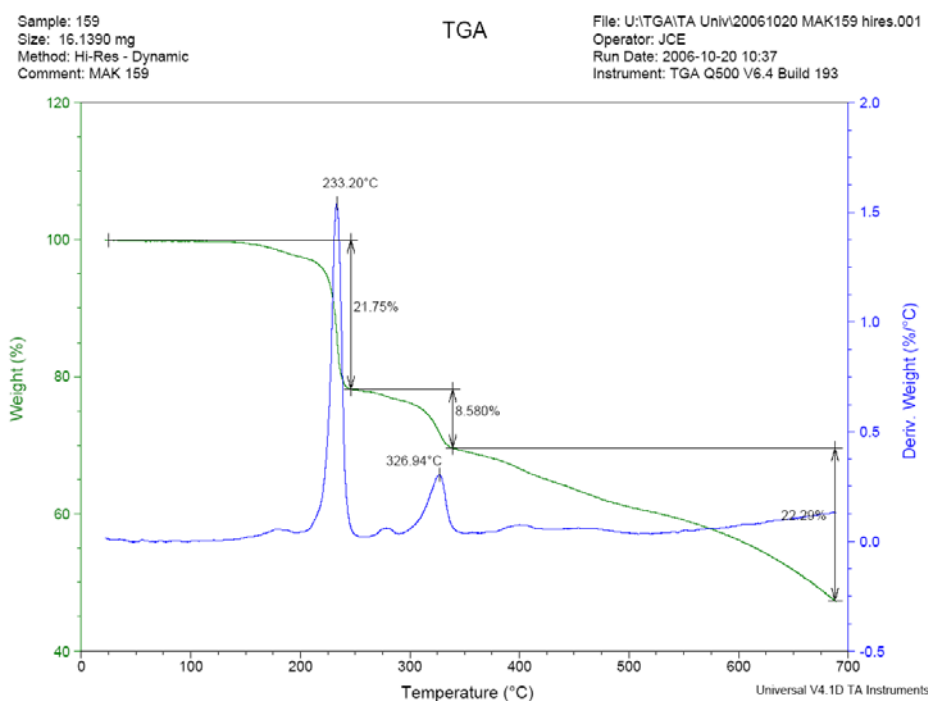


Figure 7: TGA diagram for  $[H_4biim][ZnCl_4]$  5.

Grinding equivalent amounts of  $ZnCl_2$  and  $H_2biim$  led to the formation of the title compound  $[ZnCl_2(H_2biim)]$  (**6**) in quantitative yield. Similarly, treatment of basic zinc carbonate ( $3Zn(OH)_2 \cdot 2ZnCO_3$ ) with five molar equivalents of  $[H_4biim]Cl_2$  afforded **6** after the elimination of  $CO_2$  and water (removed *in vacuo*). The crystal structure of **6** is reported to consist of discrete

$Zn(H_2biim)Cl_2$  molecules. The metal has a distorted tetrahedral  $N_2Cl_2$  coordination sphere, consisting of two chloro ligands and a neutral bidentate  $H_2biim$  ligand (Gruia *et al.*, 2007). N-H $\cdots$ Cl interactions between  $Zn(H_2biim)Cl_2$  molecules form infinite chains along the *b*-axis (Fig. 8). Figure 9 compares the calculated and the experimental powder patterns.

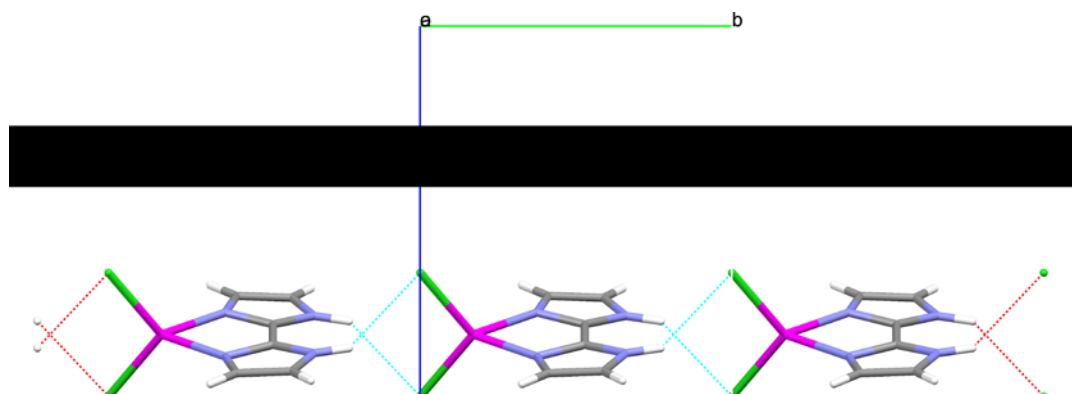


Figure 8: N-H...Cl interactions between [Zn(H<sub>2</sub>biim)Cl<sub>2</sub>] 6 molecules along the *b*-axis.

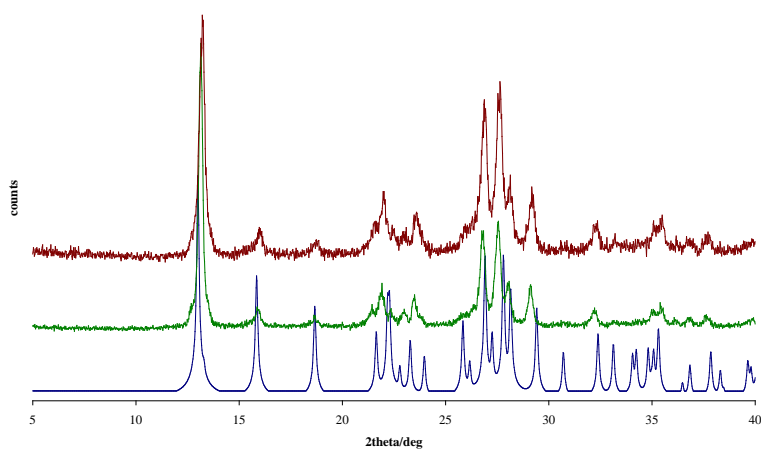


Figure 9: XRPD patterns for [Zn(H<sub>2</sub>biim)Cl<sub>2</sub>] 6. Bottom = calculated from the crystal structure; centre = mechanochemical synthesis; top = 5[H<sub>4</sub>biim]Cl<sub>2</sub> + 3Zn(OH)<sub>2</sub>·2ZnCO<sub>3</sub>.

Scheme 1 summarizes the reactions studied in this Section highlighting those that proceeded according to plan and those that formed unexpected products or are not attempted at all.

M	i	ii	iii	iv	v	vi	vii
Co	√	X	√	X	?	√	√
Zn	√	X	√	X	?	√	√
Cu	√	X	√	X	?	√	√

**Scheme 1:** Syntheses and inter-conversion of  $[H_4biim][MCl_4]$  and  $[MCl_2(H_2biim)]$  crystalline phases (M = Co, Cu or Zn). Key: √ = OK; X = did not proceed as unexpected; ? = not attempted.

Abbreviations

$H_2biim$  = Neutral 2,2'-biimidazole molecule.

$H_4biim$  ( $[C_6H_8N_4]^{2+}$ ) = 2,2'-biimidazolium dication.

$H_4biimCl_2$  = 2,2'-Biimidazolium chloride.

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