

## Coordination Chemistry in the Solid State: Reactivity of Manganese and Cadmium Chlorides with Imidazole and Pyrazole and Their Hydrochlorides

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Crystalline coordination compounds  $[\text{MnCl}_2(\text{Hpz})_2]$  **3**,  $[\text{CdCl}_2(\text{Hpz})_2]$  **5**,  $[\text{MnCl}_2(\text{Him})_2]$  **9**, and  $[\text{CdCl}_2(\text{Him})_2]$  **13** (Him = imidazole; Hpz = pyrazole) can be synthesized in solid state reactions by grinding together the appropriate metal chloride and 2 equiv of the neutral ligand. Similarly, grinding together the metal chlorides with the ligand hydrochloride salts produces the halometallate salts  $[\text{H}_2\text{pz}][\text{MnCl}_3(\text{OH}_2)]$  **1**,  $[\text{H}_2\text{pz}][\text{CdCl}_4]$  **4**,  $[\text{H}_2\text{im}]_6[\text{MnCl}_6][\text{MnCl}_4]$  **8**, and  $[\text{H}_2\text{im}]_6[\text{CdCl}_6][\text{CdCl}_4]$  **11**. In contrast, reacting the metal chloride salt with the ligand in concentrated HCl solution yields a second set of salts  $[\text{H}_2\text{pz}][\text{MnCl}_3]$  **2**,  $[\text{H}_2\text{im}][\text{MnCl}_3(\text{OH}_2)_2]$  **7**, and  $[\text{H}_2\text{im}][\text{CdCl}_3(\text{OH}_2)] \cdot \text{H}_2\text{O}$  **12**. Compound **5** can be partly dehydrochlorinated by grinding with KOH to form an impure sample of the pyrazolate compound  $[\text{Cd}(\text{pz})_2]$  **6**, while recrystallizing **9** from ethanol yielded crystals of solvated  $[\text{Mn}_4\text{Cl}_8(\text{Him})_8]$  **10**. The crystal structure determinations of **1**, **2**, **4**, **11**, and **12** are reported.

### Introduction

Although solid-state methods of preparation have been in use in inorganic chemistry for many years, as in the synthesis of mixed-metal oxides and the like, their use in coordination chemistry is much less widespread. Recently, however, there has been growing interest in the formation of metal–ligand bonds by solvent-free methods.<sup>1,2</sup> Not only do such methodologies obviate the need for solvent removal and disposal, they can result in the isolation of species which cannot be obtained in solution, and can also confer other advantages such as control over isomerism or polymorphism.

Within this context, we have recently reported on our studies of the solid-state preparations of imidazolium and pyrazolium salts of tetrachlorometallate anions  $[\text{MCl}_4]^{2-}$  (M = Co, Cu, Zn) and their solid-state conversion into the appropriate coordination compounds  $\text{ML}_2\text{Cl}_2$  (L = Him, imidazole; Hpz, pyrazole) by dehydrochlorination, either thermally (by simply heating the salts) or mechanochemically (by grinding the salts with a base such as KOH).<sup>3,4</sup> These methods have proved remarkably general, and have in certain cases allowed the isolation of compounds that are not accessible by solution-based methods.

We report below on our extension of these studies to salts and coordination compounds of manganese and cadmium.

The similarity of the chemistry of these two metals is well-known, due to neither  $d^{10}$  cadmium(II) nor high-spin  $d^5$  manganese(II) complexes having any crystal-field stabilization effects. This leads to steric factors having an important effect upon the geometries of their complexes, and to them being relatively labile in solution. By utilizing solid-state methods of complex preparation, we hoped to allow the synthesis of phases unavailable by more traditional (solution) methods of preparation.

### Results

**Pyrazole and Pyrazolium Compounds.** Attempts to synthesize the apparently previously unknown salt bis(pyrazolium) tetrachloromanganate(II)  $[\text{H}_2\text{pz}]_2[\text{MnCl}_4]$  by reaction of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with two molar equivalents of pyrazole in 2 M HCl solution afforded instead colorless needle-like crystals of the novel compound  $[\text{H}_2\text{pz}][\text{MnCl}_3(\text{OH}_2)]$  (**1**). Attempts to synthesize the tetrachloromanganate(II) species by grinding  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with two molar equivalents of pyrazolium chloride and by exposing the coordination compound  $[\text{MnCl}_2(\text{Hpz})_2]$  **3** to dry HCl gas resulted in the formation of a (or several) compound(s) of unknown composition, whereas exposure of **3** to vapors from concentrated HCl solution also resulted in the formation of **1** (presumably accompanied by pyrazolium chloride), and a deliberate attempt to synthesize **1** mechanochemically by grinding  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with  $[\text{H}_2\text{pz}]\text{Cl}$  in a 1:1 ratio afforded it in quantitative yield. The compound crystallizes in the *Pbca* space group, and the asymmetric unit contains one pyrazolium cation and a  $[\text{MnCl}_3(\text{H}_2\text{O})]^-$  moiety.

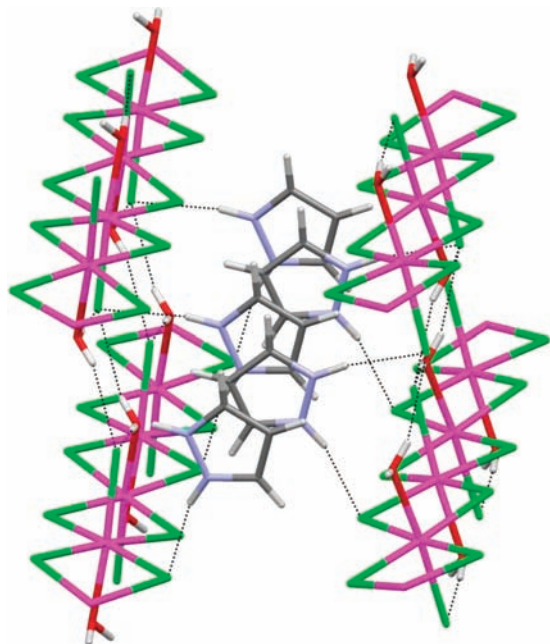
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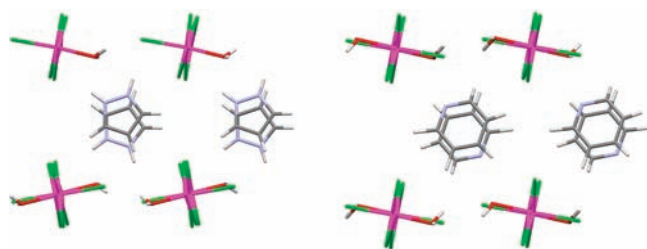
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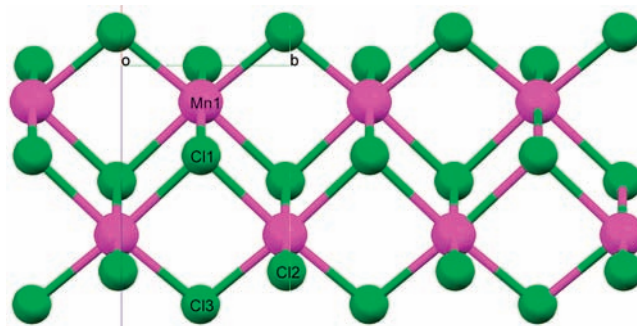
**Figure 1.** Hydrogen bonding between  $[\text{H}_2\text{pz}]^+$  cations and the manganese chloride chains in  $[\text{H}_2\text{pz}][\text{MnCl}_3(\text{OH}_2)]$  **1**.



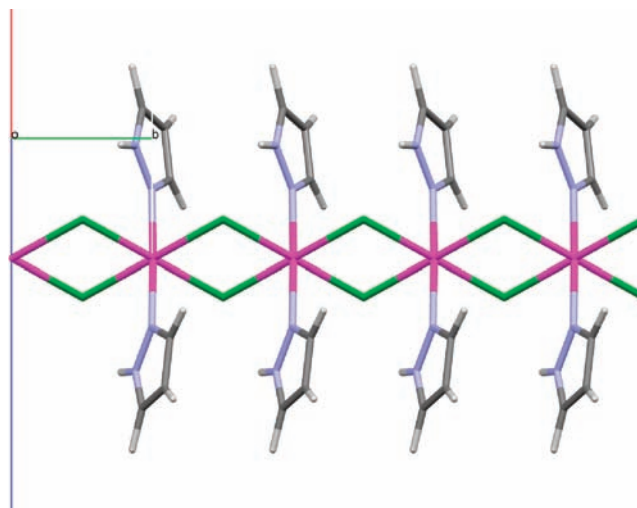
**Figure 2.** Ion packing in  $[\text{H}_2\text{pz}][\text{MnCl}_3(\text{OH}_2)]$  **1** (left) and  $[\text{Hpy}][\text{MnCl}_3(\text{OH}_2)]$  (right).<sup>5</sup>

In the crystal structure the manganese ions are coordinated in a distorted octahedral fashion by five chloride ions and one water molecule. Adjacent octahedra share two  $\mu$ -chlorine ligands, forming an infinite chain of edge-sharing  $\{\text{MnCl}_5(\text{H}_2\text{O})\}$  octahedra along the crystallographic  $a$ -axis, with the water molecules occupying alternate *trans*-axial positions. The water ligands form an in-chain  $\text{O}-\text{H}\cdots\text{Cl}$  hydrogen bond with a chloride ion on the adjacent manganese atom, and another with the axial chloride atom on a neighboring chain (Figure 1). The pyrazolium ions in **1** lie between parallel anionic chains, forming two  $\text{N}-\text{H}\cdots\text{Cl}$  bonds to chloride ions on different chains. Similar polymeric manganese anionic species, which possess magnetic properties of interest and which have the same coordination environment as **1** have been reported with pyridinium (CSD refcode: PYMNCH10) and quinolinium (CSD ecode: QUMNCL) as the counter-cations,<sup>5</sup> and these structures have their protonated nitrogen-donor cations in similar positions to the cations in **1** (Figure 2).

The salt  $[\text{H}_2\text{pz}][\text{MnCl}_3]$  (**2**) was formed when  $\text{MnCl}_2$  and pyrazole were reacted in concentrated aqueous  $\text{HCl}$  in an attempt to synthesize  $[\text{H}_2\text{pz}]_2[\text{MnCl}_4]$ . Upon slow evaporation of the solution at room temperature, colorless



**Figure 3.** Part of the anionic  $\{\text{MnCl}_3^-\}_n$  double chain motif in **2**.



**Figure 4.**  $\{\text{MnCl}_2(\text{Hpz})_2\}_n$  chain in **3**.

needle-like crystals in the  $C2/c$  space group were obtained, containing an asymmetric unit consisting of one  $[\text{H}_2\text{pz}]^+$  cation and an  $[\text{MnCl}_3]^-$  moiety. These  $[\text{MnCl}_3]^-$  units are polymerized to form a chain in which the metal atoms are octahedrally coordinated by chlorine atoms and adjacent octahedra are linked along  $b$  by *trans*-edge sharing. Two such chains run parallel to each other and offset by 1.87 Å (they are symmetry related by the crystallographic  $2_1$  screw axis) and are linked by *cis*-edge sharing (Figure 3) to give a double chain which can be formally derived from the  $\text{MnCl}_2$  structure by dimensional reduction,<sup>6,7</sup> and which is identical to that seen in  $\text{NH}_4\text{CdCl}_3$ .<sup>8</sup> The  $\text{Mn}\cdots\text{Mn}$  distance within the chain is 3.74 Å along the  $b$ -axis, and 3.89 Å between chains. These distances are longer than found in **1** (3.629 Å) but close to the distance in  $\text{MnCl}_2$  (3.71 Å).<sup>9</sup>

Each  $[\text{H}_2\text{pz}]^+$  cation in **2** is associated with  $\{\text{MnCl}_3^-\}_n$  chains through  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds (isomorphous to those shown in Figure 5 for the cadmium analogue). One of the principal features of the crystal structure of **2** is the columnar packing along the  $b$ -axis; these columns are connected by the hydrogen-bond network with the pyrazolium cations.

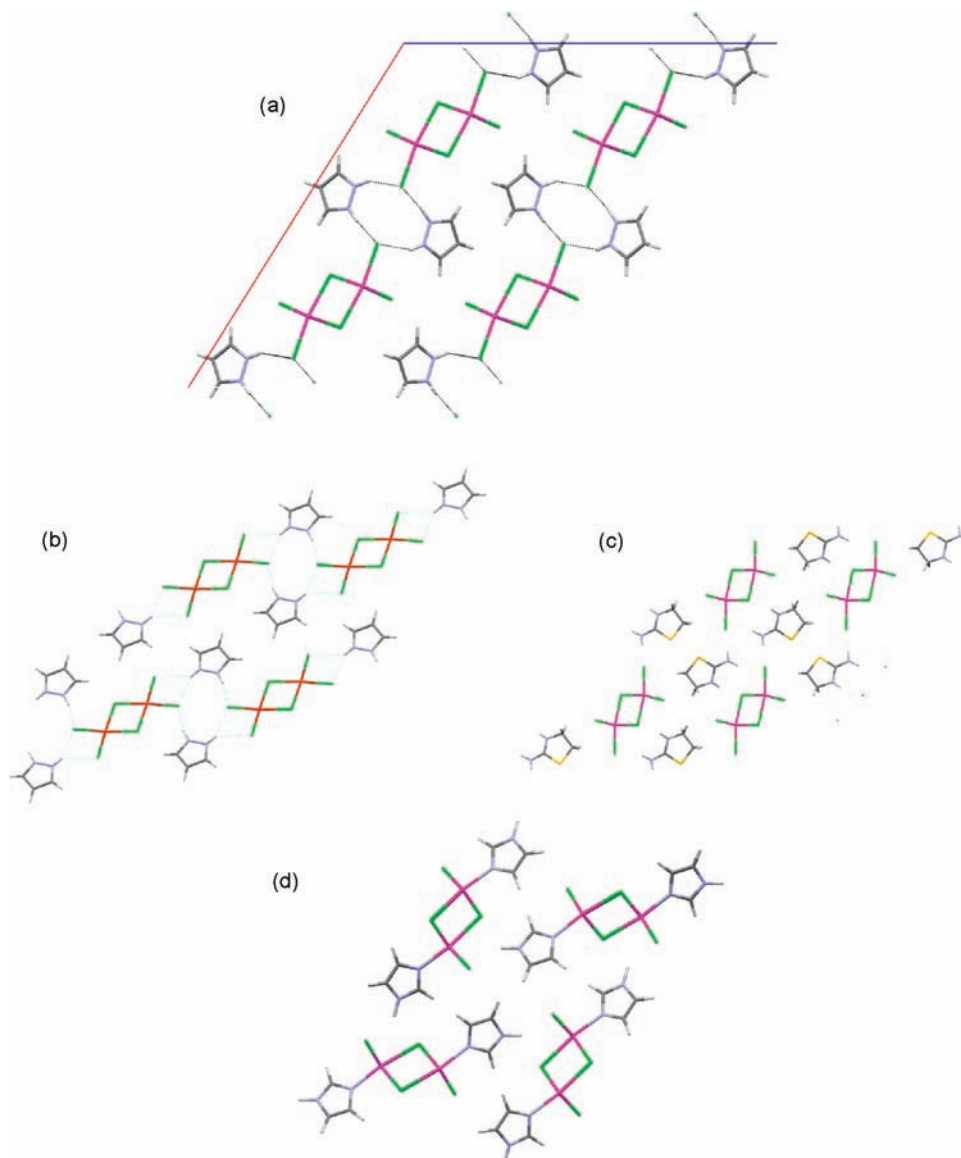
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**Figure 5.** (a) Packing and hydrogen bonding in  $[\text{H}_2\text{pz}][\text{CdCl}_3]$  **4** (which is isostructural with **2**) viewed down the crystallographic  $b$ -axis. The M-Cl chains run directly into the page. The packing motif is very similar to that observed in  $[\text{H}_2\text{pz}]_2[\text{Cu}_2\text{Cl}_6]$  (CSD refcode: GADYUF)<sup>14</sup> (b) and  $[4,5\text{-dihydro-}3\text{H}^+\text{-}1,3\text{-thiazolium}][\text{CdCl}_3]$  (CSD refcode: CAXLES)<sup>11</sup> (c), and is related to that observed in  $[\text{CdCl}_2(\text{Him})]$  (CSD refcode: CLIMZC) (d).

Grinding  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with two molar equivalents of pyrazole gave  $[\text{MnCl}_2(\text{Hpz})_2]$  **3** as an off-white polycrystalline powder, as did grinding  $\text{MnCO}_3$  with two molar equivalents of  $[\text{H}_2\text{pz}]\text{Cl}$  (with concomitant elimination of  $\text{CO}_2$  and water) or grinding **2** with 1 equiv of each of KOH and pyrazole (with concomitant formation of water and KCl). The crystal structure of this compound (CSD refcode: DCPZMN)<sup>10</sup> consists of rows of octahedral manganese(II) units (Figure 4) with *trans* pyrazole ligands, which share equatorial chlorine atoms to form one-dimensional chains. The pyrazole ligands are not coplanar but have an angle of approximately  $47^\circ$  between them, which leads to each being nearly eclipsed with one of the Mn-Cl bonds, and allows formation of an intramolecular NH-Cl hydrogen bond; there are also hydrogen bonds from the NH donors of pyrazole ligands in one chain to Cl acceptors in neighboring chains.

Thermogravimetric analysis was performed on **3** to study its thermal behavior. Mass losses, each of about 26%, were observed at 450 and in the range 527–561 K (the latter apparently being a two-step process). These percentages are in close agreement with that calculated for the removal of one pyrazole ligand from **3** in each step, leading first to formation of a phase of stoichiometry  $\text{MnCl}_2(\text{Hpz})$  and then to  $\text{MnCl}_2$  (the latter step presumably with an intermediate phase).

Slow evaporation of a concentrated aqueous HCl solution of pyrazole and  $\text{CdCl}_2$  resulted in the formation of colorless needle-like crystals of  $[\text{H}_2\text{pz}][\text{CdCl}_3]$  **4**, whose structure is isomorphous with its manganese analogue **2**. Compound **4** can also be made by grinding  $\text{CdCl}_2$  and  $[\text{H}_2\text{pz}]\text{Cl}$  in a 1:1 ratio. A similar polymeric  $[\text{CdCl}_3]^-$  chain has been reported with 2-amino-4,5-dihydro-3H<sup>+</sup>-1,3-thiazolium cations (CSD refcode: CAXLES),<sup>11</sup> and a

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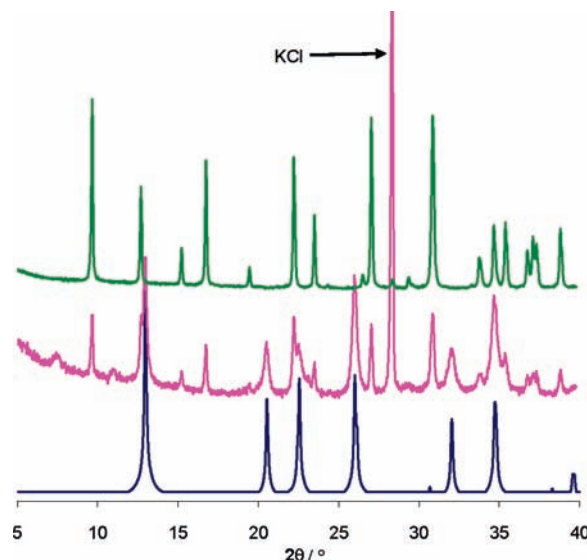
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related one (where the terminal chloride ions are replaced with imidazole) is found in  $[\text{CdCl}_2(\text{Him})]$  (CSD refcode: CLIMZC)<sup>12</sup> (Figure 5). Grinding  $\text{CdCl}_2$  with two equiv of  $[\text{H}_2\text{pz}]\text{Cl}$  produced a material whose powder pattern revealed it to contain **4** and unreacted pyrazolium chloride. A similar mixture is produced by exposure of **5** to HCl gas.

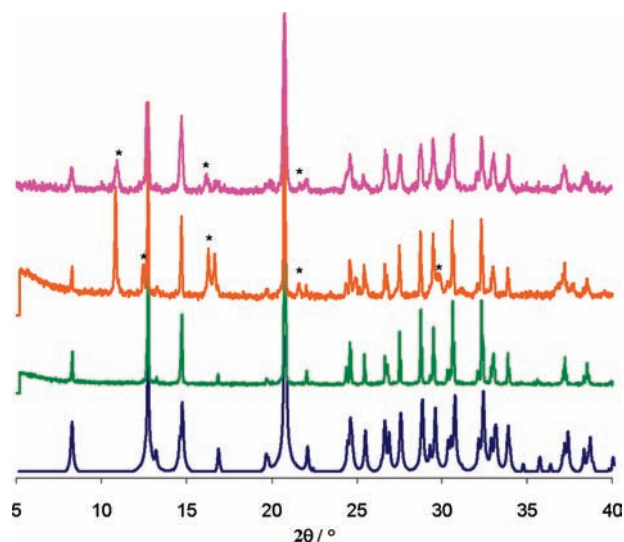
Mechanochemical grinding of  $\text{CdCl}_2$  with two molar equivalents of pyrazole resulted in the formation of  $[\text{CdCl}_2(\text{Hpz})_2]$  (**5**), and the use of an “internal base” to afford coordination compounds from crystalline salts could also be exploited. Thus, mechanochemical reaction of pyrazolium chloride with either  $\text{Cd}(\text{OH})_2$  or  $\text{CdCO}_3$  formed **5** with concomitant elimination of water (and also  $\text{CO}_2$  in the latter case). The crystal structure of **5** determined at room temperature has been reported (CSD refcode: LEDQIV),<sup>13</sup> and it is again isomorphous with its manganese analogue, in this case **3**. In addition, their thermal behaviors are also similar, with thermogravimetric analysis of **5** showing two distinct mass losses of 21.21% and 21.09%, consistent with sequential loss of two pyrazole molecules and intermediate formation of  $\text{CdCl}_2(\text{Hpz})$ .

The cadmium pyrazolate compound  $[\text{Cd}(\text{pz})_2]$  (**6**) has previously been prepared by the addition of aqueous  $\text{NH}_3$  (as the deprotonating agent) to aqueous solutions of  $\text{CdCl}_2$  or  $\text{Cd}(\text{ClO}_4)_2$  and pyrazole. Compound **6** was structurally characterized by ab initio XRPD analysis,<sup>15</sup> and was found to contain tetrahedral metal centers coordinated to four pyrazolate ions through the nitrogen atoms. Attempted mechanochemical elimination of two molecules of HCl from  $[\text{CdCl}_2(\text{Hpz})_2]$  (**5**) by grinding with two molar equivalents of KOH resulted in the formation of a mixture of  $[\text{Cd}(\text{pz})_2]$  (**6**), KCl, and some unreacted starting material **5** (Figure 6). Attempts to obtain **6** in a phase-pure form invariably yielded mixtures of product and starting material.

**Imidazole and Imidazolium Compounds.** An attempt to afford a single crystal sample of  $[\text{H}_2\text{im}]_2[\text{MnCl}_4]$  by slow evaporation of a solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and two molar equivalents of imidazolium chloride in concentrated hydrochloric acid resulted in the formation of  $[\text{H}_2\text{im}][\text{MnCl}_3(\text{H}_2\text{O})_2]$  (**7**), whose structure has been previously reported to consist of discrete imidazolium cations and a polymeric  $\{[\text{MnCl}_3(\text{H}_2\text{O})_2]_n\}^{n-}$  anionic chain (CSD refcode: ADEPOP).<sup>16</sup> Recrystallization of a sample of **7** by diffusion of diethyl ether into an ethanol solution yielded the perchloromanganate species  $[\text{H}_2\text{im}]_6[\text{MnCl}_4][\text{MnCl}_6]$  (**8**) whose structure is also known (CSD recode: DEF-WOB),<sup>17</sup> and which could more simply be prepared by mechanochemical grinding of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with 3 equiv of imidazolium chloride. Exposure of the coordination compound  $[\text{MnCl}_2(\text{Him})_2]$  (**9**) (vide infra) to vapors from concentrated aqueous HCl in a sealed vial and analysis of the product by PXRD (Figure 8) revealed the presence of both **8** and **9**; this mixture was also observed on grinding  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with two equiv of imidazolium chloride,



**Figure 6.** XRPD patterns for  $[\text{Cd}(\text{pz})_2]_n$  **6**. Blue = calculated from the crystal structure;<sup>15</sup> pink = mixture of **5**, **6** and KCl from grinding **5** with KOH; green =  $[\text{CdCl}_2(\text{Hpz})_2]$  **5**.



**Figure 7.** XRPD patterns of  $[\text{H}_2\text{im}]_6[\text{MnCl}_4][\text{MnCl}_6]$  **8**. Blue = calculated from the crystal structure;<sup>17</sup> green = mechanochemical ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} + 3[\text{H}_2\text{im}]\text{Cl}$ ); orange =  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} + 2[\text{H}_2\text{im}]\text{Cl}$ ; pink = HCl absorption by **9**. Key: \* = peaks from **9**.

indicating that a phase of composition  $[\text{H}_2\text{im}]_2[\text{MnCl}_4]$  is not formed (Figure 7).

Grinding  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with 2 equiv of imidazole gave  $[\text{MnCl}_2(\text{Him})_2]$  (**9**) as a white polycrystalline powder. Similarly, grinding  $\text{MnCO}_3$  with two molar equivalents of  $[\text{H}_2\text{im}]\text{Cl}$  afforded **9** in quantitative yield, with concomitant elimination of  $\text{CO}_2$  and water (removed in vacuo). Figure 8 compares the X-ray diffraction powder patterns of **9** formed by these synthetic routes. Comparison of these patterns with that of  $[\text{CdCl}_2(\text{Him})_2]$  (**13**) does not show any similarity, an indication that **9** and **13** are not isostructural. Other manganese chloride–imidazole phases are known, including  $[\text{MnCl}_2(\text{Him})_2(\text{H}_2\text{O})_2]$  (CSD refcode: POVXAA),<sup>18</sup>  $[\text{Mn}(\text{Him})_4(\text{H}_2\text{O})_2]\text{Cl}_2$  (CSD

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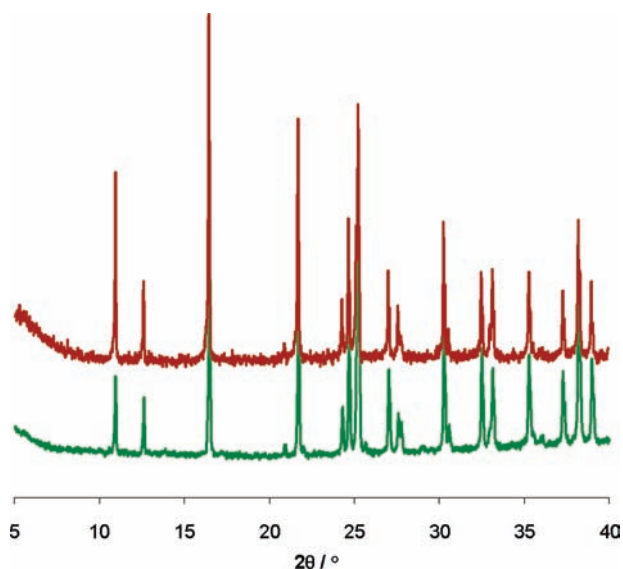
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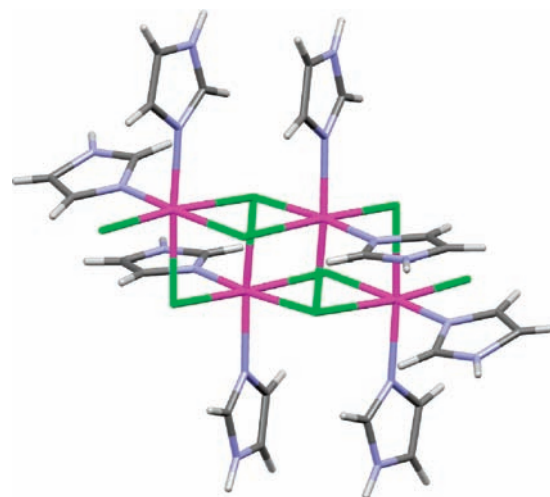
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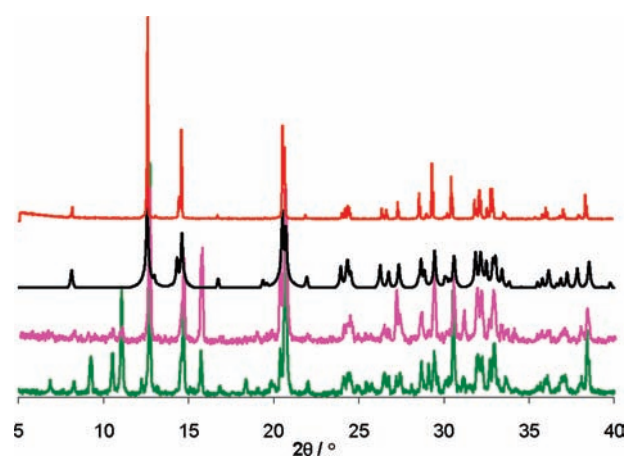
**Figure 8.** XRPD patterns for  $[\text{MnCl}_2(\text{Him})_2]$  **9**. Green = mechanochemical; brown =  $\text{MnCO}_3 + 2[\text{H}_2\text{im}]\text{Cl}$ .

refcode: CAFXEM),<sup>19</sup> and  $[\text{Mn}(\text{Him})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  (CSD refcode: CABPEA),<sup>20</sup> but none of these generate a powder pattern that matches that of **9** (or **13**). Thermogravimetric analysis of **9** revealed processes at 455 K, with a mass loss corresponding to one imidazole ligand, and at 592 and 658 K. The combined mass loss of the two latter processes is again close to that expected for loss of an imidazole ligand, implying formation of  $\text{MnCl}_2$  above 658 K.

The crystal structure of **9** is still unknown. Attempts to grow single crystals by dissolving  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and imidazole in absolute ethanol gave colorless crystals whose structure contains the tetranuclear manganese(II) cluster  $[\text{Mn}_4\text{Cl}_8(\text{Him})_8]$  (**10**) (Figure 9) with ethanol in the lattice (CSD refcode: NOJCIZ).<sup>21</sup> The cluster is based upon two  $\text{Mn}_4\text{Cl}_4$  cubes which share one face, and which each lack one manganese vertex, giving a  $\text{Mn}_4\text{Cl}_6$  unit. This contains two different octahedral coordination environments for the manganese atoms, one of which is coordinated by four bridging chloride ligands and two imidazole nitrogen atoms, while the other is coordinated by three bridging and one terminal chloride atoms and two imidazole nitrogen atoms. The remaining two metal centers are generated by inversion symmetry. A partial occupancy ethanol solvent molecule is present, and the crystal structure displays several  $\text{N}-\text{H} \cdots \text{Cl}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds. The structure and magnetic properties of a similar chlorido-bridged tetranuclear cluster of cadmium(II) with 2(2-pyridyl)-4,4',5,5'-tetramethyl-4,5-dihydro-1*H*-imidazol-1-*oxy*-3-*N*-oxide (NIToPY) have been reported,<sup>22</sup> and the  $\text{M}_4\text{Cl}_8$  core is similar to that



**Figure 9.** Structure of the  $[\text{Mn}_4\text{Cl}_8(\text{Him})_8]$  molecule in **10**.



**Figure 10.** XRPD patterns for  $[\text{H}_2\text{im}]_6[\text{CdCl}_4][\text{CdCl}_6]$  **11**. Green = 2:1 mechanochemical synthesis; pink = HCl absorption by **13**; black = calculated from the crystal structure; red = 3:1 mechanochemical synthesis.

observed in  $\text{M}_4\text{Cl}_8(\text{thf})_6$  ( $\text{M} = \text{Co}, \text{Fe}$ ) and  $\text{Mn}_5\text{Cl}_{10}(\text{thf})_8$ .<sup>23</sup>

Grinding imidazolium chloride and  $\text{CdCl}_2$  led to the formation of a white crystalline powder, which was recrystallized from acetonitrile solution to give colorless crystals of  $[\text{H}_2\text{im}]_6[\text{CdCl}_6][\text{CdCl}_4]$  (**11**); this could be deliberately synthesized in the solid state by grinding  $\text{CdCl}_2$  and  $[\text{H}_2\text{im}]\text{Cl}$  in a 1:3 ratio, whereas use of a 1:2 ratio resulted in the formation of a mixture of **11** and an unidentified second product. The same mixture of known and unknown products was also observed on exposing the coordination compound **13** to vapors from concentrated HCl solution or to dry HCl gas. Figure 10 compares the calculated and the observed X-ray powder diffraction patterns for this compound.

The crystal structure of **11** is isomorphous with that of **8**, containing imidazolium cations and discrete  $[\text{CdCl}_4]^{2-}$  and  $[\text{CdCl}_6]^{4-}$  anions. In the structure,  $\text{N}-\text{H} \cdots \text{Cl}$  hydrogen bonds link (rotationally disordered) imidazolium cations and both kinds of anion, forming hydrogen bonded chains along the *c*-axis (Figure 11). Two such chains are connected to each other via another  $\text{N}-\text{H} \cdots \text{Cl}$  hydrogen bond, involving (ordered) cations

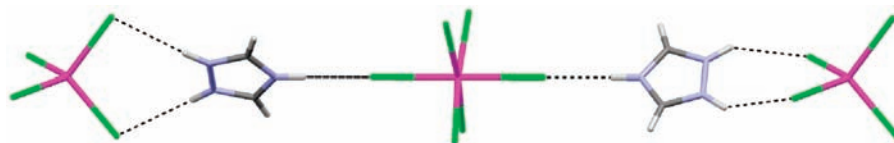
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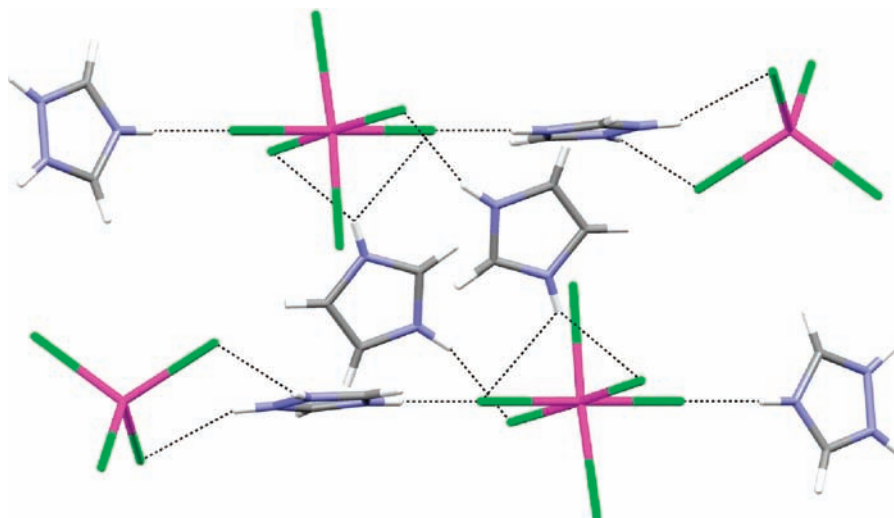
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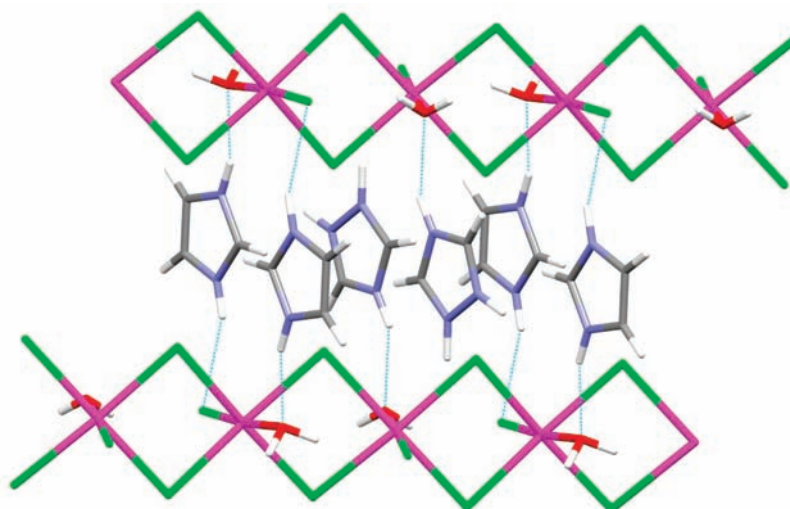
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**Figure 11.** N–H····Cl bridges between  $[\text{CdCl}_4]^{2-}$  and  $[\text{CdCl}_6]^{4-}$  along the crystallographic  $c$ -axis in **11**.



**Figure 12.** Linked chains in **11**.



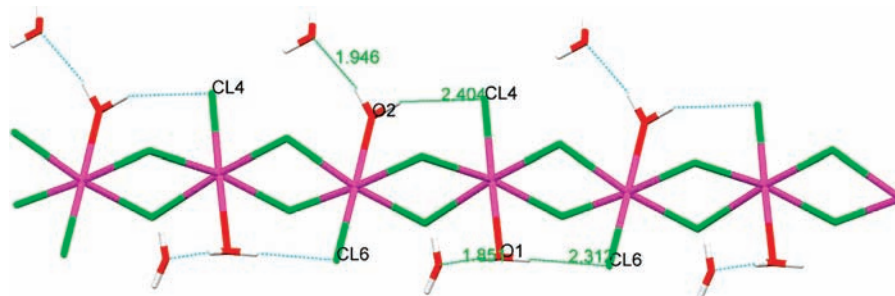
**Figure 13.** Packing of  $[\text{H}_2\text{im}]^+$  cations between Cd–Cl chains in **12**.

and equatorial chlorine atoms on the  $[\text{CdCl}_6]^{4-}$  anions, effectively forming a 2-dimensional network (Figure 12).

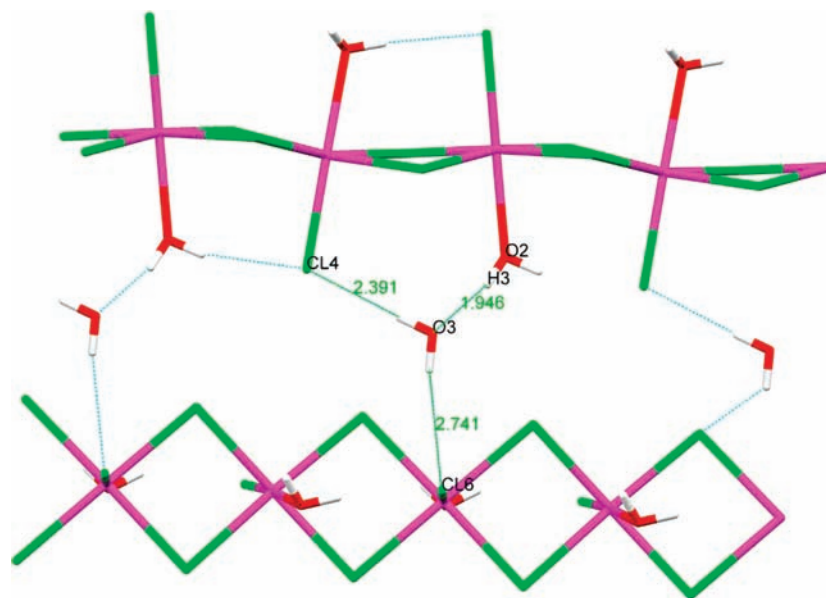
An attempt to synthesize  $[\text{H}_2\text{im}]_2[\text{CdCl}_4]$  from solution by reacting  $\text{CdCl}_2$  with 2 equiv of imidazole in concentrated  $\text{HCl}$  acid gave colorless crystals of  $[\text{H}_2\text{im}][\text{CdCl}_3(\text{OH}_2)] \cdot \text{H}_2\text{O}$  (**12**), containing discrete imidazolium cations and a polymeric chain of stoichiometry  $[\text{CdCl}_3(\text{H}_2\text{O})]^-$ . The cadmium centers are coordinated by one water and five chloride ligands, leading to a distorted octahedral coordination sphere. Adjacent octahedra are bridged by two  $\mu$ -chloride ligands, forming an infinite  $-\text{Cd}-\text{Cl}_2-\text{Cd}-\text{Cl}_2-$  chain along the  $a$ -axis with water ligands occupying alternate *trans*-axial positions

(Figure 13). Two different lattice water environments are present in the asymmetric unit and contribute to the various N–H····Cl, N–H····O and O–H····Cl interactions which form a three-dimensional hydrogen bond network (see below). Similar anionic cadmium-containing chains have been reported with ephedrinium cations.<sup>24</sup> The imidazolium cations lie between parallel  $\{\text{CdCl}_3(\text{H}_2\text{O})\}_n$  chains, forming N–H····Cl bonds with the axial chloride ligands of one chain and N–H····O bonds with water ligands on the other chain, effectively forming

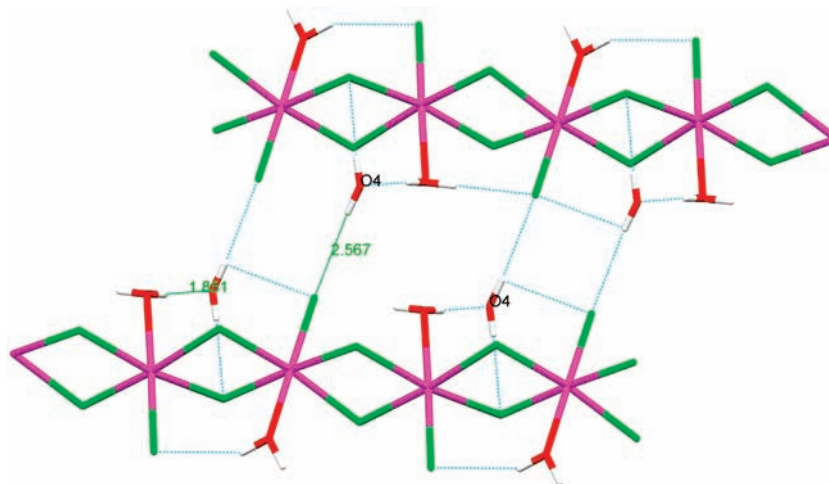
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**Figure 14.** O–H·····Cl and O–H·····O hydrogen bonds in **12**.



**Figure 15.** O3–H·····Cl and O3–H·····O hydrogen bonds in **12**.



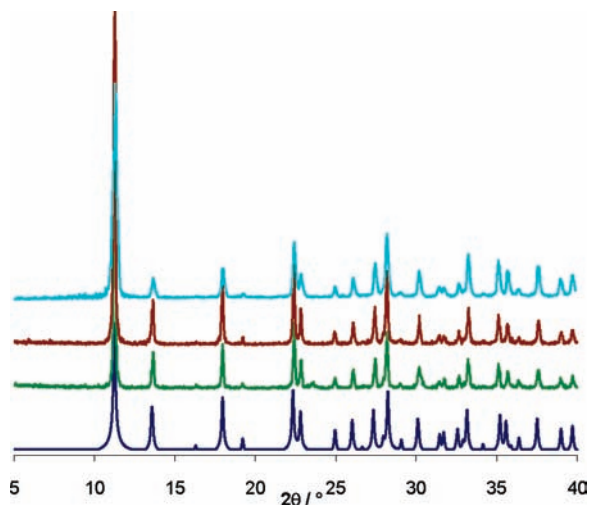
**Figure 16.** O4–H·····Cl and O4–H·····O hydrogen bonds in **12**.

the chains into a two-dimensional network through hydrogen bonding (Figure 13).

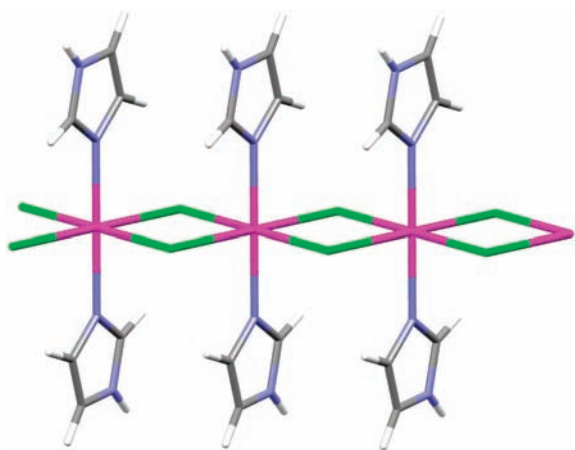
The water ligands form intramolecular O–H·····Cl hydrogen bonds with the chloride ions on the adjacent cadmium atom and O–H·····O bonds with the lattice water molecules (Figure 14). The lattice water molecules form further hydrogen bonds; O3 bridges between two chains via O–H·····Cl and O–H·····O to connect the

$\{\text{CdCl}_3(\text{H}_2\text{O})\}^-_n$  chains oriented perpendicular to each other (Figure 15), and O4 connects parallel  $\{\text{CdCl}_3(\text{H}_2\text{O})\}^-_n$  chains in a similar fashion to the imidazolium cations (Figure 16).

Grinding of  $\text{CdCl}_2$  with two molar equivalents of imidazole affords  $[\text{CdCl}_2(\text{Him})_2]$  (**13**), as does treatment of either of the internal bases  $\text{Cd}(\text{OH})_2$  or  $\text{CdCO}_3$  with 2 equiv of  $[\text{H}_2\text{im}]\text{Cl}$  with the elimination of water



**Figure 17.** XRPD patterns for  $[\{\text{CdCl}_2(\text{Him})_2\}_n]$  **13**. Blue = Calculated from the crystal structure; green =  $\text{CdCl}_2 + 2 \text{Him}$ ; brown =  $2 \text{H}_2\text{imCl} + \text{CdCO}_3$ ; turquoise =  $2 \text{H}_2\text{imCl} + \text{Cd}(\text{OH})_2$ .



**Figure 18.**  $\{\text{CdCl}_2(\text{Him})_2\}_n$  chain in **13**.<sup>25</sup>

(removed in vacuo) and carbon dioxide (in the latter). XRPD patterns (Figure 17) and elemental analyses confirmed the products from these synthetic routes to be identical to the known structure of **13** (CSD refcode: CLIMCD), which consists of cadmium atoms which are linked to their neighbors in the *a* direction by double chloride bridges in infinite  $-\text{Cd}-\text{Cl}_2-\text{Cd}-\text{Cl}_2-$  ribbons.<sup>25</sup> Octahedral coordination at cadmium is completed by two  $\text{Cd}-\text{N}$  (imidazole) bonds which are perpendicular to the plane of the Cd and Cl atoms (Figure 18). As for other the other  $\text{MCl}_2\text{L}_2$  compounds herein, **13** showed successive mass losses corresponding to loss of the organic ligands upon heating and eventual formation of the metal dichloride.

### Discussion and Conclusions

The work presented herein extends our recent investigations into the solid-state preparation of perchlorometallate salts of protonated nitrogen bases and of metal-halide coordination

compounds.<sup>3,4,26,27</sup> Thus, we were able to synthesize all four of the coordination compounds  $\text{MCl}_2\text{L}_2$  ( $\text{L} = \text{Hpz}$  or  $\text{Him}$ ) by simply grinding together in a mortar and pestle 2 equiv of the ligand *L* with one of the metal precursor  $\text{MCl}_2$ , and it was also possible to form the salts  $[\text{H}_2\text{pz}][\text{MnCl}_3(\text{OH}_2)]$  **1**,  $[\text{H}_2\text{pz}][\text{CdCl}_3]$  **4**,  $[\text{H}_2\text{im}]_6[\text{MnCl}_4][\text{MnCl}_6]$  **8**, and  $[\text{H}_2\text{im}]_6[\text{CdCl}_4][\text{CdCl}_6]$  **11** by reaction of the protonated ligand  $\text{H}_2\text{L}$  with the metal chlorides under the same conditions. Schemes 1–4 summarize the outcomes of our solid-state and solid–gas reactions. We note that some of the reactions presented herein do form pastes upon grinding, which then require further drying to yield analytically pure products. As no attempts were made to try and control the environment experienced by the reactions it is possible that moisture may be playing a part in them, either adventitiously during the grinding process, by having previously been absorbed by hygroscopic reagents, or even by being present in hydrated metals salts (such as  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) used as starting materials. This is most obviously the case for formation of the aquated compound **1**.

Our previous work has dealt with metals such as platinum and palladium<sup>26</sup> and cobalt<sup>4</sup> which generally (for reasons of crystal-field stability) have more predictable coordination geometries and environments than the cadmium and manganese compounds presented herein. All of the halide-bridged polymeric structures encountered herein belong to common general structure types,<sup>28</sup> but we would not have been able to predict in advance which one would be found. When performing solid-state synthesis, if the product formed is not that anticipated, then characterization of the phase(s) produced is challenging. Thus, although it is possible to cleanly generate **1**, **4**, **8**, and **11** in the solid-state, it would not be straightforward to confirm their structure without the a priori knowledge of their stoichiometry from single-crystal studies since none of them have the anticipated  $[\text{H}_2\text{L}]_2[\text{MCl}_4]$  formulation. The matter is complicated further when it is realized that a second series of salts  $[\text{H}_2\text{pz}][\text{MnCl}_3]$  **2**,  $[\text{H}_2\text{im}][\text{MnCl}_3(\text{OH}_2)_2]$  **7**, and  $[\text{H}_2\text{im}][\text{CdCl}_3(\text{OH}_2)] \cdot \text{H}_2\text{O}$  **12** also exists; these were all crystallized from concentrated HCl solutions, and none of them have been formed by grinding, implying that they are probably the results of a series of complex equilibria in the chloride rich solutions.

In the cases of the  $\text{ML}_2\text{Cl}_2$  coordination compounds **3**, **5**, **9**, and **13**, thermogravimetric analysis suggests loss of organic ligands upon heating. They all first lose the appropriate mass for one heterocyclic ligand, leading to phases of composition  $\text{MLCl}_2$ . Both manganese<sup>29</sup> and cadmium<sup>12,30</sup> are known to form phases of this stoichiometry upon heating  $\text{ML}_2\text{Cl}_2$  (e.g., for *L* = pyridine), and it seems likely that similar compounds are being formed in the current systems. The loss of the second organic ligand apparently occurs in two steps for **3**, **9**, and **13**, with 60% of the mass being lost first and the remaining 40% following between 30 and 60 degrees higher, implying intermediate formation of compounds of stoichiometry  $\text{ML}_{0.4}\text{Cl}_2$ . Again, ligand-poor phases (for example of stoichiometry  $\text{ML}_{0.66}\text{Cl}_2$ ) have been observed in the thermal decomposition of related pyridine compounds.<sup>29–31</sup> It has been postulated that phases with stoichiometries between

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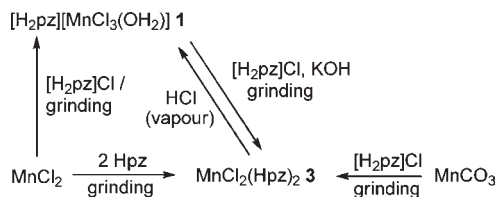
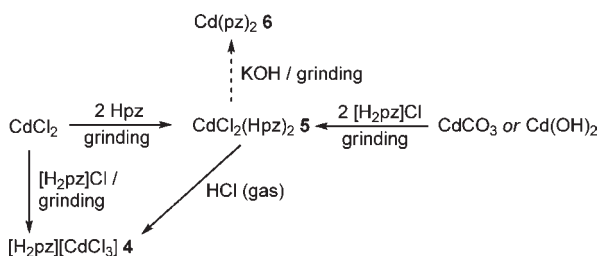
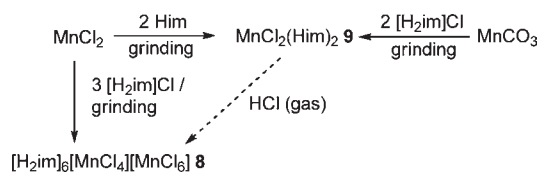
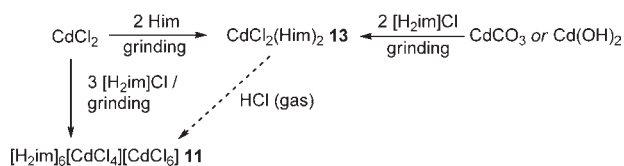
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**Scheme 1.** Outcomes of the Solid-State Manganese–Pyrazole Reactions**Scheme 2.** Outcomes of the Solid-State Cadmium–Pyrazole Reactions<sup>a</sup><sup>a</sup> A dotted line indicates a partial reaction.**Scheme 3.** Outcomes of the Solid-State Manganese–Imidazole Reactions<sup>a</sup><sup>a</sup> The dotted line indicates a partial reaction.**Scheme 4.** Outcomes of the Solid-State Cadmium–Imidazole Reactions<sup>a</sup><sup>a</sup> The dotted line indicates a partial reaction.

$\text{ML}_2\text{Cl}_2$  and  $\text{MCl}_2$  result from the elimination of the ligands L from neighboring polymeric chloride-bridged chains and subsequent chain linkage by chloro-bridging,<sup>31,32</sup> so that (for example) the  $\text{MLCl}_2$  phase corresponds to a double stranded chain, as observed in the crystal structure of  $\text{Cd}(\text{Him})\text{Cl}_2$ .<sup>12</sup> These transformations are all apparently aided by the fact that the compounds involved have parallel M–Cl chains running throughout their structures, allowing condensation to occur without major structural rearrangements. It has been shown that such an arrangement is very common

for  $\text{CdCl}_2\text{L}_2$  compounds (L = a pyridine or substituted pyridine),<sup>33</sup> and indeed all three  $\text{MCl}_2\text{L}_2$  species of known structure herein adopt it (the structure of **9** is not known).

A similar principle seems to be at work in the polymeric salts. We have previously shown how the close proximity of H and Cl atoms within the crystal structures of hydrogen-bonded salts can be exploited in the elimination of HCl with associated formation of coordination complexes, especially in cases where the salt and coordination complex have similar packing motifs.<sup>27,34</sup> Thus, although the structure of  $\text{CdCl}_2(\text{Hpz})$  is not known, the similarities (shown in Figure 5) between the packing motifs observed for the salt  $[\text{H}_2\text{pz}][\text{CdCl}_3]$  **4** and  $\text{CdCl}_2(\text{Him})$  imply that the thermal decomposition of the former may well lead to a phase  $\text{CdCl}_2(\text{Hpz})$  with a structure similar to the latter. However, as the coordination compounds **3**, **5**, **9**, and **13** are all of stoichiometry  $\text{MCl}_2\text{L}_2$  (i.e., a M:L ratio of 1:2) but none of the salts have that ratio (M:L ratios of 1:1 for **1**, **2**, **4**, **7**, and **12**, and 2:3 for **8** and **11**) the interconversion of these salts and the coordination compounds by (de)hydrochlorination cannot proceed cleanly. Although exposing **3**, **5**, **9**, and **13** to concentrated hydrochloric acid vapor or HCl gas produced materials that contained (by inspection of their XRPD patterns) **1**, **4**, **8**, and **11** respectively, they were not and could not have been pure phases because of the stoichiometry of the reactions. Equally, converting the salts into the coordination compounds would require reaction with both an external base and some additional ligand.

Overall, we conclude that although the synthesis of known coordination compounds or salts of cadmium and manganese by solid-state routes is perfectly feasible, the controlled synthesis of new phases is not reliable given that phases of unexpected stoichiometry are formed in a number of cases (although this is of course also a problem in solution chemistry). Of the compounds herein only **9** has not been made in solution, and attempts to make unknown species such as  $[\text{H}_2\text{pz}]_2[\text{MnCl}_4]$  by solid-state reaction of appropriate precursors in the correct stoichiometry were unsuccessful. Similarly, while solid-state interconversion of salts and coordination compounds can be achieved, it may be non-quantitative because of differences in the stoichiometry of the stable phases in the two series.

The isostructural nature of the cadmium and manganese structures observed in the pairs **2** and **4**, **3** and **5**, and **8** and **11** implies that it should be possible to prepare solid solutions of these compounds. We have recently shown how solid-state methods such as those presented herein allow this to be achieved with precise control over stoichiometry, in contrast to the approximate stoichiometry afforded in samples prepared from solution.<sup>35</sup>

## Experimental Section

**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 20–30 s) is only that necessary to be sure that all the reagents have been thoroughly mixed. All other reagents were purchased from Aldrich, Strem,

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or Lancaster and used without further purification. Product samples were dried in vacuo or in the oven at 50 °C. No attempts were made to control the atmosphere surrounding the reaction.

**[H<sub>2</sub>pz][MnCl<sub>3</sub>(H<sub>2</sub>O)] (1).** *Mechanochemical synthesis:* 198 mg (1 mmol) of MnCl<sub>2</sub>·4H<sub>2</sub>O was forcefully ground with 105 mg (1 mmol) of pyrazolium chloride to form a pinkish paste, which dries into a pink powder which was further dried in vacuo. Microanalytical data (%) for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>][MnCl<sub>3</sub>(H<sub>2</sub>O)], Calculated: C, 14.51; H, 2.84; N, 11.28. Found C, 14.92; H, 3.01; N, 11.62. *Vapor Absorption:* A vial containing 63 mg of an off-white powder of **3** was placed in a jar containing concentrated HCl. The powder changes to a pinkish color after 8 h. Microanalytical data (%) for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>][MnCl<sub>3</sub>(H<sub>2</sub>O)], Calculated: C, 14.51; H, 2.84; N, 11.28. Found C, 14.85; H, 3.26; N, 11.63.

**[H<sub>2</sub>pz][MnCl<sub>3</sub>] (2).** *Solution synthesis:* 198 mg (1 mmol) of MnCl<sub>2</sub>·4H<sub>2</sub>O and 136 mg (2 mmol) of pyrazole were dissolved in concentrated HCl solution, which was then allowed to evaporate slowly at room temperature. After a few days colorless needle-like crystals were obtained.

**[MnCl<sub>2</sub>(Hpz)<sub>2</sub>] (3).** *Mechanochemical synthesis:* 198 mg (1 mmol) of MnCl<sub>2</sub>·4H<sub>2</sub>O and 136 mg (2 mmol) of pyrazole were forcefully ground in an agate mortar, resulting in the formation of an off-white polycrystalline powder. This was dried in vacuo to remove excess water. Microanalytical data (%) for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>MnCl<sub>2</sub>], Calculated: C, 13.51; H, 3.08; N, 21.38. Found C, 13.46; H, 3.12; N, 21.47. *Reaction of pyrazolium chloride with MnCO<sub>3</sub>:* 115 mg (1 mmol) of MnCO<sub>3</sub> and 209 mg (2 mmol) of pyrazolium chloride were forcefully ground in an agate mortar, resulting in the formation of a light-brown polycrystalline powder. This was dried in vacuo to remove excess water. Microanalytical data (%) for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>MnCl<sub>2</sub>], Calculated: C, 13.51; H, 3.08; N, 21.38. Found C, 13.13; H, 3.46; N, 21.19. *Mechanochemical elimination:* 248 mg (1 mmol) of **1**, 68 mg (1 mmol) of pyrazole and 56 mg (1 mmol) of KOH were forcefully ground in an agate mortar, resulting in the formation of an off-white polycrystalline powder, which was dried in vacuo. Microanalytical data (%) for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>MnCl<sub>2</sub>] + KCl, Calculated: C, 21.41; H, 2.40; N, 16.65. Found C, 21.01; H, 2.85; N, 16.28.

**[H<sub>2</sub>pz][CdCl<sub>3</sub>] (4).** *Solution synthesis:* To a solution of 136 mg (2 mmol) of pyrazole in conc. HCl (5 mL) was added 183 mg (1 mmol) of CdCl<sub>2</sub>. On slow evaporation at room temperature, white crystals were obtained after a few weeks. Microanalytical data (%) for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>][CdCl<sub>3</sub>], Calculated: C, 18.37; H, 2.57; N, 14.28. Found C, 18.13; H, 2.55; N, 14.48.

**[CdCl<sub>2</sub>(Hpz)<sub>2</sub>] (5).** *Mechanochemical synthesis:* 183 mg (1 mmol) of CdCl<sub>2</sub> and 136 mg (2 mmol) of pyrazole were forcefully ground in an agate mortar, resulting in the formation of a white polycrystalline powder of [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>]. Microanalytical data (%) for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>], Calculated: C, 22.56; H, 2.52; N, 17.54. Found C, 22.58; H, 2.58; N, 17.74. *Reaction of pyrazolium chloride with (i) Cd(OH)<sub>2</sub>:* 209 mg (2 mmol) of pyrazolium chloride was ground with 146 mg (1 mmol) of Cd(OH)<sub>2</sub>, forming a white polycrystalline powder of [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>], which was dried in vacuo. Microanalytical data (%), Calculated for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>]: C, 22.56; H, 2.52; N, 17.54. Found C, 22.83; H, 2.60; N, 17.99. *(ii) CdCO<sub>3</sub>:* 209 mg (2 mmol) of pyrazolium chloride was ground with 172 mg (1 mmol) of CdCO<sub>3</sub>, forming a white polycrystalline powder of [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>], which was dried in vacuo. Microanalytical data (%), Calculated for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>]: C, 22.56; H, 2.52; N, 17.54. Found C, 22.99; H, 2.58; N, 17.83.

**[Cd(pz)<sub>2</sub>]<sub>n</sub> (6).** *Mechanochemical elimination:* 320 mg (1 mmol) of [CdCl<sub>2</sub>(Hpz)<sub>2</sub>] **5** was forcefully ground with 112 mg (2 mmol) of KOH. The reaction proceeded with no significant color change, forming a white polycrystalline powder which was dried in vacuo. XRPD pattern reveals the presence

of three compounds - [Cd(pz)<sub>2</sub>]<sub>n</sub>, KCl, and another which resembles [CdCl<sub>2</sub>(Hpz)<sub>2</sub>] **5**. Several attempts to synthesize the title compound by this route always ended up with starting material. Microanalytical data (%), Calculated for [(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>Cd] + 2KCl: C, 18.21; H, 1.53; N, 14.16. Found C, 18.69; H, 1.77; N, 14.18.

**[H<sub>2</sub>im][MnCl<sub>3</sub>(H<sub>2</sub>O)] (7).** Single crystals of **7** were obtained as previously reported.<sup>16</sup>

**[H<sub>2</sub>im]<sub>6</sub>[MnCl<sub>6</sub>][MnCl<sub>4</sub>] (8).** *Mechanochemical synthesis:* 198 mg (1 mmol) of MnCl<sub>2</sub>·4H<sub>2</sub>O and 209 mg (2 mmol) of imidazolium chloride were ground in an agate mortar, forming **8** as a white paste which dries into a white crystalline powder, which was dried in vacuo. Microanalytical data (%), Calculated for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]<sub>6</sub>[MnCl<sub>6</sub>][MnCl<sub>4</sub>] + 2[(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>MnCl<sub>2</sub>] + 2[C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]Cl: C, 21.52; H, 3.01; N, 16.73. Found C, 21.64; H, 3.53; N, 16.94. *Vapor Absorption:* A vial containing 20 mg of solid **9** was placed in a jar containing concentrated HCl. In about 2 h the white powder became pinkish as **8** was formed. Microanalytical data (%) Calculated for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]<sub>6</sub>[MnCl<sub>6</sub>][MnCl<sub>4</sub>] + 2[(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>MnCl<sub>2</sub>] + 2[C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]Cl: C, 21.52; H, 3.01; N, 16.73. Found C, 21.28; H, 3.20; N, 16.66.

**[MnCl<sub>2</sub>(Him)<sub>2</sub>] (9).** *Mechanochemical synthesis:* 198 mg (1 mmol) of MnCl<sub>2</sub>·4H<sub>2</sub>O and 136 mg (2 mmol) of imidazole were forcefully ground in an agate mortar, resulting in the formation of a white polycrystalline powder of **9**. This was dried in vacuo to remove excess water. Microanalytical data (%) for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>MnCl<sub>2</sub>], Calculated: C, 27.51; H, 3.08; N, 21.38. Found C, 27.40; H, 3.76; N, 21.35. *Reaction of imidazolium chloride with MnCO<sub>3</sub>:* 115 mg (1 mmol) of MnCO<sub>3</sub> and 209 mg (2 mmol) of imidazolium chloride were forcefully ground in an agate mortar, resulting in the formation of light-brown polycrystalline powder of **9**. This was dried in vacuo to remove excess water. Microanalytical data (%) for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>MnCl<sub>2</sub>], Calculated: C, 27.51; H, 3.08; N, 21.38. Found C, 27.51; H, 3.77; N, 21.19.

**[Mn<sub>4</sub>Cl<sub>8</sub>(Him)<sub>8</sub>]·1.234EtOH (10).** *Solution synthesis:* To a solution of imidazole 136 mg (2 mmol) in absolute alcohol (5 mL) was added 198 mg (1 mmol) of MnCl<sub>2</sub>·4H<sub>2</sub>O. On evaporation at room temperature, white crystals were obtained after a few weeks.

**[H<sub>2</sub>im]<sub>6</sub>[CdCl<sub>6</sub>][CdCl<sub>4</sub>] (11).** *Mechanochemical synthesis:* 183 mg (1 mmol) of CdCl<sub>2</sub> and 314 mg (3 mmol) of imidazolium chloride were ground in an agate mortar, forming **11** as a white crystalline powder. Microanalytical data (%), Calculated for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]<sub>6</sub>[CdCl<sub>4</sub>][CdCl<sub>6</sub>]: C, 21.75; H, 3.04; N, 16.91. Found C, 21.79; H, 3.25; N, 16.82. *Solution synthesis:* A small amount of **11** was dissolved in acetonitrile. The solution was allowed to evaporate slowly at room temperature and colorless needle-like crystals were obtained after a few weeks.

**[H<sub>2</sub>im]<sub>2</sub>[Cd<sub>2</sub>Cl<sub>6</sub>(OH)<sub>2</sub>]·2H<sub>2</sub>O (12).** *Solution synthesis:* To a solution of imidazole 136 mg (2 mmol) in concentrated HCl (5 mL) was added 183 mg (1 mmol) of CdCl<sub>2</sub>. On evaporation at room temperature, colorless needle-like crystals were obtained after a few days.

**[CdCl<sub>2</sub>(Him)<sub>2</sub>] (13).** *Mechanochemical synthesis:* 183 mg (1 mmol) of CdCl<sub>2</sub> and 136 mg (2 mmol) of imidazole were forcefully ground in an agate mortar, resulting in the formation of a white polycrystalline powder of **13** which was dried in vacuo. Microanalytical data (%), Calculated for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>]: C, 22.56; H, 2.52; N, 17.54. Found C, 22.42; H, 2.58; N, 17.63. *Reaction of imidazolium chloride with (i) CdCO<sub>3</sub>:* 209 mg (2 mmol) of imidazolium chloride was ground with 172 mg (1 mmol) of CdCO<sub>3</sub> forming a white polycrystalline powder, which was dried in vacuo. Microanalytical data (%), Calculated for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>]: C, 22.56; H, 2.52; N, 17.54. Found C, 22.54; H, 2.50; N, 17.51. *(ii) Cd(OH)<sub>2</sub>:* 209 mg (2 mmol) of imidazolium chloride was ground with 146 mg (1 mmol) of Cd(OH)<sub>2</sub> forming a white polycrystalline powder, which was dried in vacuo. Microanalytical data (%), Calculated for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>]: C, 22.56; H, 2.52; N, 17.54. Found C, 22.63; H, 2.59; N, 17.48.

Table 1. Summary Crystallographic Data

crystal data	1	2	4	11	12
<i>T</i> /K	100(2)	100(2)	100(2)	173(2)	173(2)
formula	[C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> ][MnCl <sub>3</sub> (H <sub>2</sub> O)]	[C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> ][MnCl <sub>3</sub> ]	[C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> ][CdCl <sub>3</sub> ]	[C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> ] <sub>6</sub> [CdCl <sub>4</sub> ][CdCl <sub>6</sub> ]	[C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> ] <sub>2</sub> [Cd <sub>2</sub> Cl <sub>6</sub> (H <sub>2</sub> O) <sub>2</sub> ]·2H <sub>2</sub> O
formula weight	248.41	230.38	287.86	993.86	647.74
color	colorless	colorless	colorless	colorless	colorless
morphology	needle	needle	needle	needle	needle
<i>D</i> <sub>calc</sub> /Mg m <sup>-3</sup>	1.891	2.036	2.436	1.867	2.124
crystal system	orthorhombic	monoclinic	monoclinic	tetragonal	monoclinic
space group	<i>Pbca</i>	<i>C2/c</i>	<i>C2/c</i>	<i>I4<sub>1</sub>/a</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	7.2477(14)	22.561(5)	22.886(6)	12.1221(12)	7.5463(17)
<i>b</i> /Å	14.614(3)	3.7413(7)	3.8529(10)	12.1221(12)	21.385(5)
<i>c</i> /Å	16.473(3)	20.895(4)	20.990(6)	24.730(24)	12.531(3)
β/deg	90	121.54(3)	121.99(4)	90	95.505(7)
<i>V</i> /Å <sup>3</sup>	1744.7(6)	1503.2(7)	1569.7(7)	3633.9(7)	2012(8)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
<i>Z</i>	8	8	8	4	4
data collected	18480	7613	7374	19245	6014
unique data	2006	1721	1778	2091	4125
<i>R</i> (int)	0.0375	0.0324	0.0283	0.0346	0.0188
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (%)	1.89, 4.58	3.00, 7.81	1.82, 5.01	2.03, 4.37	2.53, 6.46

**X-ray Single Crystal Analysis.** Single crystal X-ray data (see Table 1) were collected at 100 K on a Bruker APEX diffractometer using Mo-K<sub>α</sub> X-radiation. Data were corrected for absorption using empirical methods (SADABS)<sup>36</sup> based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. Crystal structures were solved and refined against all *F*<sup>2</sup> values using the SHELXTL suite of programs.<sup>37</sup> Non-hydrogen atoms were refined anisotropically and hydrogen atoms were generally placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters, except for the hydrogen atoms of the water molecules in **1** and **12**, which were located in the difference map and refined freely (though with the O–H distance restrained to 0.84 Å in **12**). In the structure of **11**, one of the imidazolium cations is disordered about a crystallographic 2-fold rotational axis. In the structure of **12** one of the imidazolium cations also shows some disorder, which was modeled by refining two alternative orientations with the sum of their occupancies constrained to 1, with the disordered carbon and nitrogen atoms sharing the same position and the same anisotropic displacement parameters.

**X-ray Powder Diffraction Analysis.** All crystalline phases were analyzed at room temperature by powder X-ray diffraction

on a Bruker D8 diffractometer using Cu–K<sub>α</sub> X-radiation. In all the cases the experimental pattern matched that calculated on the basis of the single crystal structure determination at room temperature, indicating phase purity *except* when the powder patterns of the products of mechanochemical eliminations (reactions with KOH or K<sub>2</sub>CO<sub>3</sub>) show an extra peak at 2θ = 28° due to the presence of KCl.

**Thermogravimetric Analysis.** Thermal analysis of the samples was carried out on a TA Q500 V6.4 build 193 instrument under N<sub>2</sub> flow over the temperature range 20–700 °C at variable (high resolution mode) heating rate and analyzed by TA Universal analysis 2000 software.

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**Supporting Information Available:** Details of the crystal structures of **1**, **2**, **4**, **11**, and **12** as cif files, thermal ellipsoid plots, tables of hydrogen bond lengths and angles, complete powder patterns for all syntheses, and TGA traces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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