

## Reversible Extrusion and Uptake of HCl Molecules by Crystalline Solids Involving Coordination Bond Cleavage and Formation

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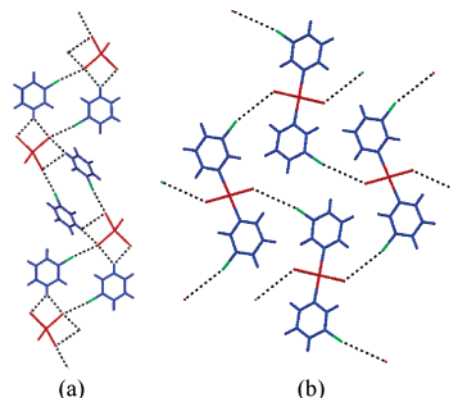
Solid-state reactions have long been studied in organic compounds,<sup>1</sup> especially photochemical reactions<sup>2</sup> and thermally induced rearrangements,<sup>3</sup> and have also been investigated in metal–organic systems.<sup>4</sup> Representative examples of the latter are provided by Real, who has studied the topochemical ligand substitution in [Fe(pyrimidine)(OH)<sub>2</sub>{M(CN)<sub>2</sub>}<sub>2</sub>]·H<sub>2</sub>O (M = Ag, Au), where loss of H<sub>2</sub>O takes place with the subsequent coordination of the uncoordinated pyrimidine nitrogen atom,<sup>5</sup> while Orpen has reported the thermal dehydrochlorination of 4-picolinium salts of [MCl<sub>4</sub>]<sup>2-</sup> (M = Pd, Pt) with the formation of coordination complexes.<sup>6</sup>

Solid–gas reactions, a different type of solvent-free reaction, are uncommon in the field of organometallic chemistry,<sup>4,7</sup> where there has been much effort toward the design of materials capable of interacting with a range of gases, including O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, NO, and CO.<sup>8</sup> A beautiful example was reported in this area by van Koten for the uptake and release of SO<sub>2</sub> by an organoplatinum complex involving the corresponding formation and breaking of a covalent bond (Pt–S).<sup>9</sup> Also, Braga has reported the absorption of volatile acids and bases by crystals of [Co(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>H)(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>)] leading to the formation of the corresponding salts.<sup>10</sup>

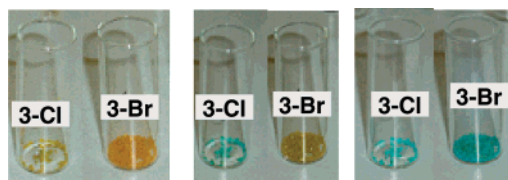
Here we present the direct elimination of HCl from crystalline materials and the subsequent reversible uptake via a gas–solid reaction. The ionic networks in crystalline (3-halopyridinium)<sub>2</sub>[CuCl<sub>4</sub>] (**1a**, X = Cl; **2a**, X = Br<sup>11</sup>) were found to extrude HCl through cleavage of N–H and Cu–Cl bonds and formation of Cu–N bonds, yielding molecular crystals of formula [CuCl<sub>2</sub>(3-halopyridine)<sub>2</sub>] (**1b**, X = Cl; **2b**, X = Br). In this reaction, the copper(II) centers change their coordination geometry from distorted tetrahedral to square planar (Figure 1), with a corresponding color change from yellow (ionic material) to blue (molecular material) (Figure 2). Remarkably, this process is fully reversible upon exposure of crystals of the coordination compound to vapors of concentrated aqueous HCl, leading to re-formation of the yellow crystalline tetrachlorocuprate(II) salts.

Compounds **1a** and **2a** are isostructural and form networks propagated by bifurcated asymmetric N–H···Cl<sub>2</sub>Cu hydrogen bonds and Cu–Cl···X–C halogen bonds<sup>12</sup> (Figure 1a). The interaction geometries are presented in Table 1. It is worth noting that one of the chloride ligands is not involved in a significant noncovalent interaction, unlike the related cobalt compounds recently described by our group in which all the halides are involved in either halogen bonds or bifurcated hydrogen bonds.<sup>13</sup>

After manual grinding of crystals of **1a** or **2a** for ca. 60 s, the homogeneous yellow powders were left in open sample vials and



**Figure 1.** (a) One-dimensional networks formed in crystals **1a** and **2a**, propagated via bifurcated N–H···Cl<sub>2</sub>Cu hydrogen bonds and Cu–Cl···X–C halogen bonds, and (b) two-dimensional networks formed in crystals **1b** and **2b**, propagated via Cu–Cl···X–C halogen bonds. Copper atoms and halide ligands are shown in red, organic halogen atoms in green, and all other atoms in blue.



**Figure 2.** Solid-state reactions **1a** → **1b** (3-Cl) and **2a** → **2b** (3-Br) lead to a change in color from yellow (ionic compound) to blue (molecular compound). After 0 h (left); 4 h (middle); and 7 days (right).

a color change from yellow to blue occurred over a period of a few hours for **1a** and over a few days for **2a** (Figure 2). Importantly, in sealed vials, no change in color is observed over periods of many months. The crystalline materials **1a** and **2a** eliminate two molecules of HCl per formula unit to produce the coordination compounds **1b** and **2b**, respectively. Structure determination from X-ray powder diffraction and subsequent Rietveld refinement (Figure 3) show that **1b** and **2b** are isostructural. The structures consist of 2D layers propagated solely by Cu–Cl···X–C halogen bonds (see Figure 1b).<sup>14</sup> The homogeneous composition of **1b** and **2b** was also confirmed by elemental analysis.

To examine the elimination of HCl more closely, a vial containing crystalline material **2a** was enclosed within a larger vial together with a separate vial containing an aqueous solution of AgNO<sub>3</sub>. HCl was eliminated from **2a**, resulting in precipitation of AgCl and acidification of the AgNO<sub>3</sub> solution, while the yellow powder (**2a**) changed color to blue (**2b**), as seen in Figure 4. Thus, absorption of HCl (as protons and Cl<sup>-</sup> ions) by the AgNO<sub>3</sub> solution has promoted the extrusion of HCl from **2a**. In the absence of a

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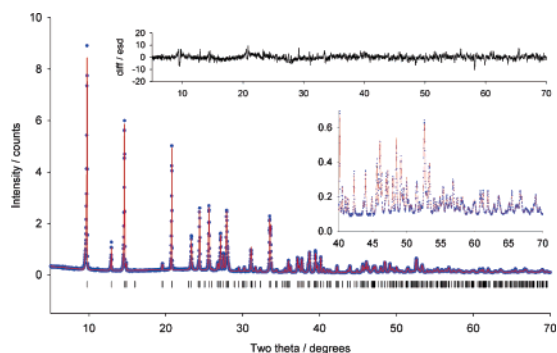
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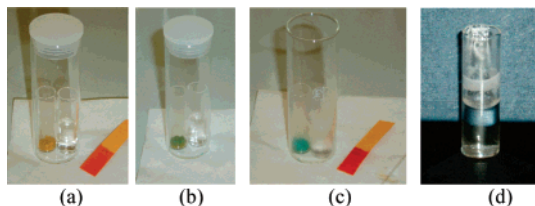
**Table 1.** Selected Bond Lengths, Hydrogen Bonds, and Halogen Bonds for Compounds **1a**, **2a**, **1b**, and **2b**

	Cu–Cl (Å)	Cu–N (Å)	C–X (Å)	Cl⋯X (Å) [R <sub>CIX</sub> ] <sup>a</sup>	Cu–Cl⋯X (°)	Cl⋯X–C (°)	H⋯Cl <sup>b</sup> (Å) [R <sub>HCl</sub> ] <sup>a</sup>	N–H⋯Cl (°)
(3-ClpyH) <sub>2</sub> [CuCl <sub>4</sub> ] <b>1a</b>	2.2323(7)		1.722(3)	3.2369(9) [0.925]	158.18(3)	165.79(9)	2.425 [0.82]	138.93
	2.2398(7)						2.426 [0.82]	135.29
	2.2427(7)		1.730(2)	3.3044(9) [0.944]	172.72(3)	175.53(9)	2.179 [0.74]	154.72
	2.2965(7)						2.855 [0.97]	106.94
(3-BrpyH) <sub>2</sub> [CuCl <sub>4</sub> ] <b>2a</b>	2.234(2)		1.882(6)	3.225(2) [0.896]	158.74(7)	167.6(2)	2.377 [0.81]	136.32
	2.242(2)						2.456 [0.83]	137.84
	2.247(2)		1.885(6)	3.241(2) [0.900]	170.71(7)	176.06(19)	2.195 [0.74]	154.31
	2.300(2)						2.795 [0.95]	110.92
[CuCl <sub>2</sub> (3-Clpy) <sub>2</sub> ] <b>1b</b>	2.294(2)	1.989(4)	1.731(5)	3.734 [1.067]	120.89	158.52	n/a	n/a
[CuCl <sub>2</sub> (3-Brpy) <sub>2</sub> ] <b>2b</b>	2.304(5)	2.025(9)	1.929(10)	3.675 [1.021]	120.53	157.73	n/a	n/a

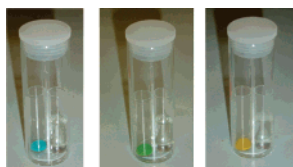
<sup>a</sup>  $R_{XX'} = d(X\cdots X')/(r_X + r_{X'})$ , where  $r_X$  and  $r_{X'}$  are the van der Waals radii<sup>15</sup> of the halogen atoms X and X', respectively (following the definition of Lommerse et al.<sup>16</sup>);  $R_{HX}$  is defined analogously for the H⋯X separation. <sup>b</sup> Geometries calculated using hydrogen atom positions normalized to standard nuclear positions, as established by neutron diffraction (N–H = 1.01 Å).



**Figure 3.** Observed (blue) and calculated (red) profiles and difference plot  $[(I_{\text{obs}} - I_{\text{calc}})/\sigma(I_{\text{obs}})]$  of the Rietveld refinement for **1b** ( $2\theta$  range 5.0–70.0°).



**Figure 4.** Solid-state reaction of **2a** → **2b** in closed vial in the presence of AgNO<sub>3</sub> solution after: (a) 0 h; (b) 2 h; (c) 24 h (solution is more acidic). (d) Detail of AgCl formed in vial containing AgNO<sub>3</sub> solution.



**Figure 5.** Reversibility of the reaction: uptake of HCl by compound **1b** after: 0 h (left); 2 h (middle); 2 days (right). Note that intermediate color green is a mixture of **1b** (blue) and **1a** (yellow).

HCl capture agent, no apparent reaction occurs in a sealed vessel. These observations led us to investigate the reversibility of the reactions by studying the conversion of the molecular crystalline compounds **1b** and **2b** into **1a** and **2a** through a gas–solid reaction. Exposure of the blue powders of the molecular compounds to 32% aqueous HCl vapors led to conversion back to the yellow ionic compounds **1a** and **2a** over a period of 2 days (Figure 5). The structures of the yellow crystalline products were determined by X-ray powder diffraction and confirmed to match **1a** and **2a** (see Supporting Information, compounds **1c** and **2c**).

The reversible crystalline solid-state interconversion between ionic (3-halopyridinium)<sub>2</sub>[CuCl<sub>4</sub>] chains and 2D molecular networks

of [CuCl<sub>2</sub>(3-halopyridine)<sub>2</sub>] via release and uptake of HCl has been established under ambient conditions. Crystal structures have been determined by powder XRD. The transformations require cleavage and formation of *covalent* bonds as well as noncovalent interactions and involve a change in the coordination geometry at the metal center.

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**Supporting Information Available:** Synthetic procedures, X-ray structural data (for both single crystal and powder experiments), and additional pictures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.
- (2) (a) Stoermer, R.; Laage, E. *Ber.* **1921**, *54*, 77. (b) Schmidt, G. M. *Pure Appl. Chem.* **1971**, *27*, 647. (c) MacGillivray, L. R. *CrystEngComm* **2004**, *6*, 77.
- (3) (a) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217. (b) Ouyang, X.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 12400. (c) Sureshan, K. M.; Murakami, T.; Miyasou, T.; Watanabe, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9174.
- (4) Coville, N. J.; Cheng, L. *J. Organomet. Chem.* **1998**, *571*, 149.
- (5) Niel, V.; Thompson, A. L.; Muñoz, M. C.; Galet, A.; Goeta, A. E.; Real, J. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3760.
- (6) Adams, C. J.; Crawford, P. C.; Orpen, A. G.; Podesta, T. J.; Salt, B. *Chem. Commun.* **2005**, 2457.
- (7) Meijer, M. D.; Klein Gebbink, R. J. M.; van Koten, G. In *Perspectives in Supramolecular Chemistry—Crystal Design: Structure and Function*; Desiraju, G., Ed.; Wiley: Chichester, U.K., 2003; Vol. 7, Chapter 9.
- (8) (a) Taylor, R. J.; Drago, R. S.; George, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 6610. (b) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1992**, *114*, 5905. (c) Padden, K. M.; Krebs, J. F.; MacBeth, C. E.; Scarrow, R. C.; Borovik, A. S. *J. Am. Chem. Soc.* **2001**, *123*, 1072. (d) Bianchini, C.; Zanobini, F.; Aime, S.; Gobetto, R.; Psaro, R.; Sordelli, L. *Organometallics* **1993**, *12*, 4757.
- (9) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970.
- (10) Braga, D.; Grepioni, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4002.
- (11) Crystal structure of **2a** previously reported: Willett, R. D.; Awwadi, F.; Butcher, R.; Haddad, S.; Twamley, B. *Cryst. Growth Des.* **2003**, *3*, 301.
- (12) The term halogen bond refers to the interaction between a halogen and an electron-rich atom. See: (a) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *Acc. Chem. Res.* **2005**, *38*, 386. (b) Zordan, F.; Brammer, L.; Sherwood, P. *J. Am. Chem. Soc.* **2005**, *127*, 5979.
- (13) Mínguez Espallargas, G.; Brammer, L.; Sherwood, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 435.
- (14) These compounds are isostructural to the Pd analogues reported in ref 12b.
- (15) Bondi, A. J. *J. Chem. Phys.* **1964**, *68*, 441.
- (16) Lommerse, J. P. M.; Stone, A. J.; Taylor, R.; Allen, F. H. *J. Am. Chem. Soc.* **1996**, *118*, 3108.

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