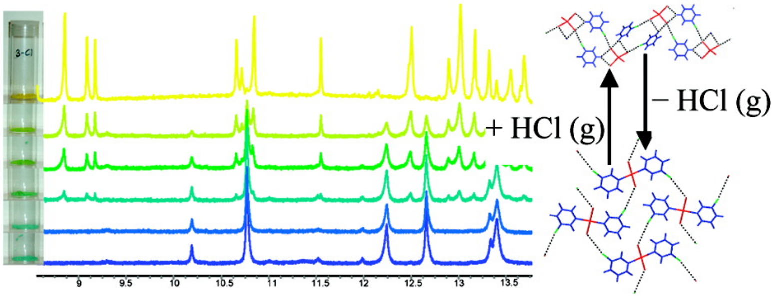
Article

Reversible Gas Uptake by a Nonporous Crystalline Solid Involving Multiple Changes in Covalent Bonding

Guillermo Mnguez Espallargas, Michael Hippler, Alastair J. Florence, Philippe Fernandes, Jacco van de Streek, Michela Brunelli, William I. F. David, Kenneth Shankland, and Lee Brammer

J. Am. Chem. Soc., **2007**, 129 (50), 15606-15614 • DOI: 10.1021/ja075265t



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

Reversible Gas Uptake by a Nonporous Crystalline Solid Involving Multiple Changes in Covalent Bonding

Guillermo Mínguez Espallargas,[†] Michael Hippler,[†] Alastair J. Florence,[‡]
Philippe Fernandes,[‡] Jacco van de Streek,[§] Michela Brunelli,[||] William I. F. David,[⊥]
Kenneth Shankland,[⊥] and Lee Brammer*[,†]

Contribution from the Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom, Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, Institute for Inorganic and Analytical Chemistry, Frankfurt University, 60438 Frankfurt am Main, Germany, European Synchrotron Radiation Facility, 38042 Grenoble, France, and ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom

Received July 14, 2007; E-mail: lee.brammer@sheffield.ac.uk

Abstract: Hydrogen chloride gas (HCl) is absorbed (and reversibly released) by a nonporous crystalline solid, $[CuCl_2(3\text{-Clpy})_2]$ (3-Clpy = 3-chloropyridine), under ambient conditions leading to conversion from the blue coordination compound to the yellow salt $(3\text{-ClpyH})_2[CuCl_4]$. These reactions require substantial motions within the crystalline solid including a change in the copper coordination environment from square planar to tetrahedral. This process also involves cleavage of the covalent bond of the gaseous molecules (H−Cl) and of coordination bonds of the molecular solid compound (Cu−N) and formation of N−H and Cu−Cl bonds. These reactions are not a single-crystal-to-single-crystal transformation; thus, the crystal structure determinations have been performed using X-ray powder diffraction. Importantly, we demonstrate that these reactions proceed in the absence of solvent or water vapor, ruling out the possibility of a water-assisted (microscopic recrystallization) mechanism, which is remarkable given all the structural changes needed for the process to take place. Gas-phase FTIR spectroscopy has permitted us to establish that this process is actually a solid−gas equilibrium, and time-resolved X-ray powder diffraction (both *in situ* and *ex situ*) has been used for the study of possible intermediates as well as the kinetics of the reaction.

Introduction

Although chemical reactions in molecular crystals that proceed without destruction of crystallinity have been known for many years, their study has been largely confined to crystals of organic compounds. Such reactions are typically induced photochemically or thermally[1−3] and require motions on a length scale of a few Ångstroms by neighboring molecules within the crystals either in order that covalent bonds can be formed or subsequent to bond breaking during the reaction. However, many such reactions are irreversible. An illustrative example is carbon−carbon bond formation in cycloaddition reactions between alkenes.[1,2,4,5] Examples of metal−organic compounds that permit irreversible reactions such as polymerizations in the solid state have been known for some time.[6] Reactions of organometallic compounds as solids (surfaces, amorphous, and crystalline) have also been reviewed.[7]

Of particular relevance to the present study are solid−gas reactions involving crystalline metal−organic compounds.[8] Reactions of this type, defined rather broadly, can be divided into three general classes: (i) sorption of gases by crystalline *porous* materials where the gas molecules are incorporated in the interior of the pores; (ii) reactions between *nonporous* crystals and aqueous vapors of volatile acids and bases leading to the incorporation of these molecules into hydrogen-bonded networks; and (iii) absorption of gas molecules by *nonporous* molecular crystals with formation of covalent bonds to the substrate, where retention of crystallinity is unexpected and accordingly extremely rare.

The sorption of gases by crystalline porous materials such as metal−organic frameworks is well established[9,10] and of widespread interest for applications including gas storage,

---

[†] University of Sheffield.

[‡] University of Strathclyde.

[§] Frankfurt University.

[||] European Synchrotron Radiation Facility.

[⊥] ISIS Facility.

(1) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.

(2) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.

(3) MacGillivray, L. R. *CrystEngComm* **2002**, *4*, 37.

(4) Mustafa, A. *Chem. Rev.* **1952**, *51*, 1.

(5) Friscic, T.; MacGillivray, L. R. *Z. Krist.* **2005**, *220*, 351.

(6) Georgiev, I. G.; MacGillivray, L. R. *Chem. Soc. Rev.* **2007**, *36*, 1239.

(7) Coville, N. J.; Cheng, L. *J. Organomet. Chem.* **1998**, *571*, 149.

(8) 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.

(9) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

(10) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (b) Zhao, X.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. *Science* **2004**, *306*, 1012. (c) Forster, P. M.; Eckert, J.; Chang, J.-S.; Park, S.-E.; Férey, G.; Cheetham, A. K. *J. Am. Chem. Soc.* **2003**, *125*, 1309. (d) Lin, X.; Blake, A. J.; Wilson, C.; Sun, X. Z.; Champness, N. R.; George, M. W.; Hubberstey, P.; Mokaya, R.; Schröder, M. *J. Am. Chem. Soc.* **2006**, *128*, 10745.

10.1021/ja075265t CCC: $37.00

chemical separations, and molecular sensing.[9,11−13] Typically physisorption results in gas molecules that are rather weakly bound to the interior surfaces of the pores,[14] but although crystallinity of the solid is retained in some cases after sorption or desorption,[15] often this is not the case.[16] Recent developments have also shown that binding of gas molecules is feasible through specific interactions, for example, hydrogen bonding interactions[17] or coordination bond formation,[18,19] within pores.

Reactions between crystalline powders of the organometallic zwitterion $[Co(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$ and aqueous vapors of volatile acids and bases has been reported by Braga, Grepioni, and co-workers.[20−22] These reactions lead to the formation of salts $[Co(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2H)]X{\cdot}nH_2O$ ($X = Cl^-$, BF_4^-,[21] CF_3COO^-,[21] CHF_2COO^-,[22] CH_2ClCOO^-[22]) if exposed to acids or $[Co(\eta^5\text{-}C_5H_4CO_2)_2](HY){\cdot}nH_2O$ ($Y = NH_3$,[20] NH_2Me,[20] NMe_3[20]) if exposed to bases ($n \geq 0$). Formation and cleavage of hydrogen bonds as well as protonation/deprotonation of the carboxylate/carboxyl groups is required to accommodate the gas molecules in the solid.[23] In some cases, water molecules are also incorporated in the products upon acid or base uptake (i.e., $n > 0$). These reactions are all reversible upon thermal treatment of the resultant salts.

The third class of solid−gas reactions involves not only absorption of gas molecules by *nonporous* molecular crystals but also the resultant formation of metal−ligand covalent bonds. Such reactions converting crystalline reactant into crystalline product are rare. An early example reported by van Koten and co-workers involves the reaction an organoplatinum complex with SO_2 gas.[24] In this reversible reaction, the coordination geometry at the platinum center is converted from square planar to square pyramidal but nevertheless requires the formation of only an axial Pt−S bond enabling SO_2 to be bound upon its uptake by these crystals. In two very recent publications, reactions involving methanol coordination[25] and pyridine coordination[26] have also been identified. In parallel with the present paper, we have also reported reversible ethanol insertion into and elimination from the Ag−O bond of a nonporous crystalline coordination polymer.[27]

Very recent reports by us[28] and by Orpen and co-workers[29] have shown that microcrystalline samples of coordination complexes with pyridine-derived ligands can undergo reaction with hydrated vapors of HCl leading to formation of crystalline hydrogen-bonded salts. These reactions require cleavage of the M−N (M = Cu,[28] Co,[29] Zn,[29]) and H−Cl bonds and formation of N−H and M−Cl bonds, thereby inserting HCl into the M−N coordination bond. However, although water molecules are not included in the crystals of the product salts, given the presence of excess water vapor in the reactions, a highly plausible mechanism for these reactions has been thought to involve a microscopic recrystallization front that migrates across the crystals, analogous to that demonstrated for some anion exchange reactions involving crystalline solids.[30]

In this study, we substantially extend our earlier report and are able to demonstrate that the molecular coordination compound *trans*-$[CuCl_2(3\text{-}Clpy)_2]$ **1** (3-Clpy = 3-chloropyridine) prepared as a microcrystalline powder can react directly with gaseous HCl in the *absence* of water yielding the crystalline salt $(3\text{-}ClpyH)_2[CuCl_4]$ **2**. This definitively rules out the possibility of a water-assisted (microscopic recrystallization) mechanism and requires instead a quite remarkable process that involves transport of HCl through nonporous crystals,[31] coupled with reaction within these crystals that involves multiple changes in covalent bonding and a major change in coordination geometry at the metal center. This reaction has been examined in detail using X-ray powder diffraction and gas-phase IR spectroscopy, including establishing the operation of a solid−gas equilibrium process and investigating the kinetics of the reverse (HCl elimination) reaction.

Experimental Section

General. All reagents were purchased from Aldrich, Lancaster, or Avocado and used as received. HCl gas was purchased from BOC (grade N2.6, 99.6% HCl; H_2O content <10 ppm).

Synthesis of *trans*-$[CuCl_2(3\text{-}Clpy)_2]$ (1). $CuCl_2$ (143.6 mg, 1.068 mmol) was dissolved in MeOH (ca. 5 mL) (solution A), resulting in a green solution. 3-Chloropyridine (222.3 mg, 1.958 mmol) was dissolved separately in MeOH (ca. 5 mL) (solution B) to give a colorless solution. Solution A was added to solution B with the immediate formation of a blue precipitate. The sample was placed in an oven for 5 days at 50 °C for drying.

Synthesis of $(3\text{-}ClpyH)_2[CuCl_4]$ (2). About 200 mg of dry blue crystalline powder **1** was placed in three vials in the presence of vapors of concentrated aqueous HCl (32%) for 2 days.[28] Completion of the reaction was observed after 2 days (complete color change from blue to yellow).

Formation of **1** and **2** and phase purity were confirmed by X-ray powder diffraction.

Preparation of Samples for *ex situ* Powder Diffraction Study of the Release of HCl Gas by 2. About 20 mg of **2** was placed in each of 10 open vials. Under such conditions, conversion to **1** via HCl release is known to occur over a period of 2 days.[28] The vials were sealed

---

[11] Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305.
[12] James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276.
[13] Halder, G. J.; Kepert, C. J.; Moubraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762.
[14] Rowsell, J. L. C.; Spencer, E. C.; Eckert, J.; Howard, J. A. K.; Yaghi, O. M. *Science* **2005**, *309*, 1350.
[15] (a) Serre, C.; Millange, F.; Thouvenot, C.; Nogués, M.; Marsolier, G.; Louer, D. Ferey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519. (b) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428.
[16] (a) Rosi, N.; Eddaoudi, M.; Kim, J.; O'Keefe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 284. (b) Sun, J.; Weng, L.; Zhou, Y.; Chen, J.; Chen, Z.; Liu, Z.; Zhao, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4471.
[17] Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238.
[18] Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763.
[19] Bradshaw, D.; Warren, J. E.; Rosseinsky, M. J. *Science* **2007**, *315*, 977.
[20] Braga, D.; Cojazzi, G.; Emiliani, D.; Maini, L.; Grepioni, F. *Chem. Commun.* **2001**, 2272.
[21] Braga, D.; Cojazzi, G.; Emiliani, D.; Maini, L.; Grepioni, F. *Organometallics* **2002**, *21*, 1315.
[22] Braga, D.; Maini, L.; Mazzotti, M.; Rubini, K.; Grepioni, F. *CrystEngComm* **2003**, *5*, 154.
[23] Related gas-solid acid base reactions are also established for organic compounds, see: Paul, I. C; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217.
[24] Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970.
[25] Supriya, S.; Das, S. K. *J. Am. Chem. Soc.* **2007**, *129*, 3464.
[26] Lennartson, A.; Håkansson, M.; Jagner, S. *New J. Chem.* **2007**, *31*, 344.
[27] Libri, S.; Mahler, M.; Mínguez Espallargas, G.; Singh, D. C. N. G.; Soleimannejad, J.; Adams, H.; Burgard, M. D.; Rath, N. P.; Brunelli, M.; Brammer, L. *Angew. Chem., Int. Ed.* **2007**, *46*, in press.
[28] Mínguez Espallargas, G.; Brammer, L.; van de Streek, J.; Shankland, K.; Florence, A. J.; Adams, H. *J. Am. Chem. Soc.* **2006**, *128*, 9584.
[29] Adams, C. J.; Colquhoun, H. M.; Crawford, P. C.; Lusi, M.; Orpen, A. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 1124.
[30] (a) Khlobystov, A. N.; Champness, N. R.; Roberts, C. J.; Tendler, S. J. B.; Thomson, C.; Schröder. *CrystEngComm* **2002**, *4*, 426. (b) Thompson, C.; Champness, N. R.; Khlobystov, A. N.; Roberts, C. J.; Schröder, M.; Tendler, S. J. B.; Wilkinson, M. J. *J. Microsc. (Oxford)* **2004**, *214*, 261.
[31] (a) Examination by the program *PLATON*[31b] indicates that the crystal structure of the molecular coordination compound $[CuCl_2(3\text{-}Clpy)_2]$ **1** contains no solvent accessible voids and that 76.4% of space is filled (i.e., close packing is achieved). (b) Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7.

sequentially at different stages of this reaction (0, 3, 4, 6, 14, 16, 17, 19, 22, and 49 h), stopping the reaction at these points.

Uptake of Dry HCl by 1 (75% Conversion). Crystalline powder **1** (78.9 mg) (0.22 mmol) was placed in a gas cell of volume ca. 200 cm^3 at room temperature and evacuated using a vacuum line connected to a rotary vacuum pump ($\sim 5 \times 10^{-3}$ Torr) for 30 min prior to the introduction of 0.69 mmol (pressure 65 Torr) of dry gaseous HCl. A change of color of the powder from blue to green occurred within an hour. After 24 h, the powder had become yellow and the sample was removed.

Uptake of Dry HCl by 1 (100% Conversion). Crystalline powder **1** (10.0 mg) (0.03 mmol) was placed in a gas cell of volume ca. 625 cm^3 at room temperature (ca. 295 K) and evacuated using a vacuum line connected to a rotary vacuum pump ($\sim 5 \times 10^{-3}$ Torr) for approximately 30 min prior to the introduction of dry gaseous HCl. About 11 mmol of dry HCl gas was introduced into the gas cell (pressure 335 Torr). A change of color of the powder from blue to green occurred within minutes, but the sample was allowed to react for 7 days, during which time it became yellow in color.

X-Ray Powder Diffraction. All of the polycrystalline samples were lightly ground in an agate mortar and pestle and filled into 0.5 mm glass capillaries (dry HCl experiment: 75% conversion), 0.7 mm glass capillaries (dry HCl experiment: 100% conversion), or 0.7 mm borosilicate capillaries (*in situ* and *ex situ* experiments) prior to being mounted and aligned on Station 9.1 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory, UK, using $\lambda = 0.998622$ Å (dry HCl experiment: 75% conversion) or on beam line ID31[32] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France using $\lambda = 0.91912(1)$ Å (dry HCl experiment: 100% conversion) or $\lambda = 0.80103(2)$ Å (*ex situ* and *in situ* experiments). Two-phase Rietveld[33] refinements were undertaken using the program TOPAS[34] using as the starting point the crystal structures determined at room temperature for compounds **1** and **2**[28] or the structure solutions from the simulated annealing (SA) global optimization procedure implemented in the DASH computer program[35,36] (see Supporting Information for details of the structure solution). A small number of minor peaks not attributable to **1** or **2**, nor to ice formation, remain constant throughout the series of patterns measured in both the *in situ* and *ex situ* experiments, as is evident from the residual profile. These peaks are attributed to the presence of a very small amount of an impurity phase. Being constant throughout the reaction, these cannot be taken as an indication of a reaction intermediate.

Product of Reaction of 1 with Dry HCl (75% Conversion). For the yellow product of the exposure of **1** to gaseous dry HCl, X-ray powder diffraction data were collected at SRS station 9.1. Measurements were made at room temperature in the 2θ range 3−40° employing a variable count time (VCT) scheme (3.0−20.0° = 2 s; 20.0−30.0° = 4 s; 30.0−35.0° = 6 s; 35.0−40.0° = 8 s). Indexing of the pattern indicated that two phases were present, namely compounds **1** and **2**, with the latter being the majority phase. Atomic positions and displacement parameters were refined. A spherical harmonic correction of the intensities for preferred orientation was applied for both phases in the final refinement. The ratio of **1**:**2** in the yellow material was determined as 24.1:75.9 from the refinement, and the final value of R_{wp} obtained was 0.0433.

Product of Reaction of 1 with Dry HCl (100% Conversion). For the yellow product of exposure of **1** to gaseous dry HCl, X-ray powder diffraction data were collected at beam line ID31 at ESRF. Measurements were made at room temperature in the 2θ range 3−40° employing a continuous scan mode (20° min^{-1} for 36 min) in which the sample underwent 18 scans. Indexing of the pattern indicated that two phases were present, namely compound **2** and a minor impurity phase, but no traces of compound **1** were observed. Nevertheless, compound **1** was included in the refinement to obtain the composition of the sample more accurately. Atomic positions and displacement parameters were refined for compound **2**. A spherical harmonic correction of the intensities for preferred orientation was also applied for phase **2** in the final refinement. The ratio of **1**:**2** in the yellow material was determined as 0:100 from the refinement, and the final value of R_{wp} obtained was 0.0963.

***Ex situ* Monitoring of HCl Release Reaction.** For each of the 10 samples for which the conversion of **2** to **1** by HCl release was stopped at different stages, X-ray powder diffraction data were collected in the 2θ range 0−40° at 100 K at beam line ID31 at ESRF. The sample temperature was maintained at 100 K by the coaxial nitrogen gas flow of an Oxford Cryosystems Cryostream. A continuous scan mode (20° min^{-1} for 48 min) was employed in which each sample underwent 24 scans. The capillaries were translated after each scan to a sequence of 8 different positions to avoid degradation of the sample in the X-ray beam, resulting in 3 scans being made at each translation position. The data for each sample were rebinned in the range 0−40° to a step size of 0.001°. Inspection of the patterns clearly indicated that complete conversion from **2** to **1** had occurred in the sample for which the vial had been sealed after 49 h. Structure solution and Rietveld refinements were first conducted for the start and end points of the reaction ($t = 0$ h and $t = 49$ h, respectively). Two-phase Rietveld refinements were then performed for each of the 10 samples using the refined structure models obtained for the start and end points.

***In situ* Monitoring of HCl Release Reaction.** The conversion of **2** to **1** through HCl release was also followed *in situ* using the polycrystalline sample of **2** contained in a sealed 0.7 mm borosilicate capillary that was used for the *ex situ* powder pattern for $t = 0$ h. The end of the capillary was removed to permit HCl loss during the subsequent reaction, and the capillary was immediately placed on the diffractometer at beam line ID31, ESRF in the coaxial nitrogen gas flow of an Oxford Cryosystems Cryostream already set at 370 K to accelerate the reaction. A series of powder patterns were then measured over the 2θ range 3−23° in continuous scanning mode at a scan rate of 20° min^{-1}. Successive measurements were made after translation of the capillary to a sequence of 4 positions, a strategy adopted to minimize radiation-induced degradation of the sample in the intense X-ray beam. Each sequence of four measurements and the corresponding translations of the capillary and resetting of the detector angles took 5 min. Eighteen such sequences of measurements were made over a total of 90 min, during which time complete conversion of **2** into **1** could be seen to have taken place due the absence of peaks for **2** and the lack of further growth of the peaks for **1**. The translation position furthest from the base of the capillary was later determined to place a much smaller volume of sample in the beam than other capillary positions and so was excluded from subsequent calculations. The data for each sequence of measurements were summed and rebinned in the range 3−23° to a step size of 0.001°. Two-phase Rietveld refinements were performed for the start and end point of the reaction, using as starting models the crystal structures determined at room temperature.[28] The structures established at 370 K for **1** and **2** from Rietveld refinements of the start and end points of the reaction were then used for two-phase Rietveld refinements from the patterns obtained at the remaining 16 time intervals sampled during the reaction.

Infrared Spectroscopy. Fourier transform infrared (FTIR) spectroscopic experiments were conducted using a double-walled 10 cm glass IR absorption cell fitted with NaCl windows and a suspended sample container. Temperature control was achieved via a flow of silicone oil within the double-wall jacket of the cell. The temperature of the cell was maintained within a range of 0.2 K (1 K at room temperature) using a Haake DC30−K20 circulator bath. To obtain time-dependent concentrations of HCl vapor, gas-phase IR spectra in the region of

---

(32) Fitch, A. N. *Natl. Inst. Stand. Technol.* **2004**, *109*, 133.
(33) Rietveld, H. M. *J. Appl. Cryst.* **1969**, *2*, 65.
(34) Coehlo, A. A. *TOPAS-Academic*; 2004. See http://members.optusnet.com.au/~alancoehlo.
(35) David, W. I. F.; Shankland, K.; Shankland, N. *Chem. Commun.* **1998**, 931.
(36) David, W. I. F.; Shankland, K.; van de Streek, J.; Pidcock, E.; Motherwell, S.; Cole, J. C. *J. Appl. Cryst.* **2006**, *39*, 910.

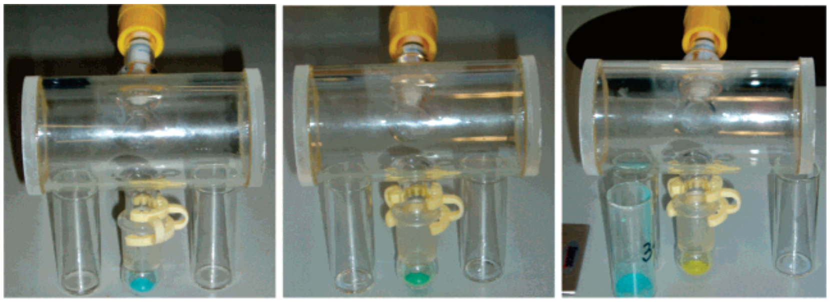

(a) (b) (c)

Figure 1. Reaction of crystalline **1** (blue) with *dry* gaseous HCl yields crystalline **2** (yellow). Shown after (a) 0 h, (b) 1 h, and (c) 24 h (alongside original vial of unreacted **1**).

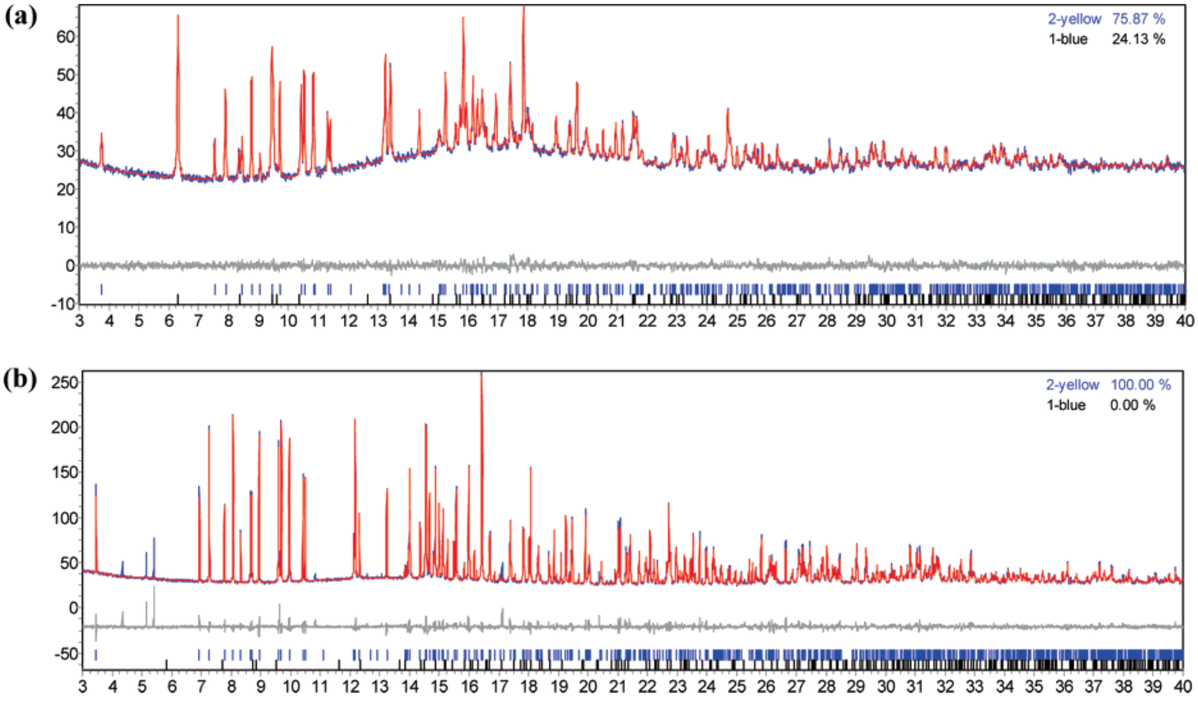


Figure 2. Observed (blue) profile, profile calculated from two-phase fit (red) and difference plot [($I_{obs} - I_{calcd}$)] (gray) for the two-phase Rietveld refinement of the product of exposure for (a) 24 h and (b) 7 days of **1** to dry HCl gas (2θ range 3.0−40.0°; maximum resolution (a) 1.46 Å and (b) 1.34 Å).

2500−6500 cm^{-1} were acquired using a FTIR spectrometer (Perkin-Elmer Paragon 1000, resolution 1 cm^{-1}, no apodization). The spectrometer was operated in the single-beam mode, that is, sample and background (empty cell) spectra were recorded separately. The area under the HCl absorption spectrum was integrated from 2600 to 3100 cm^{-1} after background subtraction and baseline correction to obtain a measure for the HCl concentration (which was previously calibrated, see Supporting Information). The absorption cell was loaded with ca. 50 mg of polycrystalline compound **2** and then connected to a vacuum line to remove all the H_2O and other gases present. Sixteen scans were accumulated over a period of 2 min for each IR spectrum to provide a satisfactory signal-to-noise ratio. Additional scans to improve accuracy further were not made since continuous extrusion of HCl was expected. Scans were continued until no increase in the HCl signal was observed.

Having established that the reaction is a gas−solid equilibrium (*vide infra*), the equilibrium position was further studied as a function of temperature. The study was performed using a cylindrical glass IR absorption cell of length 10 cm fitted with NaCl windows and a suspended sample container, but without a double-walled jacket, as seen in Figure 4a (*vide infra*). The cell was loaded with ca. 50 mg of a fresh sample of polycrystalline compound **2** and the reaction was allowed to reach equilibrium at room temperature over a period of 2 months (although only hours are needed). After this time, IR spectra were acquired by accumulating 64 scans (total 10 min). The cell was then placed in an oven at 40 °C for 24 h to permit equilibrium to be reached at the elevated temperature, after which another spectrum was acquired (accumulating only 16 scans to avoid significant cooling of the unjacketed cell). The cell was raised to 50 °C for a period of 72 h and subsequently to 60 °C for a period of 24 h. After each temperature rise, a spectrum was obtained (again accumulating 16 scans). Finally, the cell was then left at room temperature for 120 h to permit re-establishment of equilibrium at the reduced temperature, and another spectrum was collected.

Results and Discussion

HCl Gas Uptake by 1 in the Absence of Water. Blue coordination compound **1** was placed in the sample holder of a gas cell equipped with NaCl windows and a valve suitable for introduction and removal of gases, as shown in Figure 1a. To eliminate the presence of water, the cell was evacuated using a vacuum line (ca. 5×10^{-3} Torr) for ca. 30 min. Upon introduction of dry gaseous HCl, a color change was visible within minutes, and over a 24-hour period, the crystalline solid changed color from blue to yellow (Figure 1), indicating the formation of tetrahedral $[CuCl_4]^{2-}$ anions.

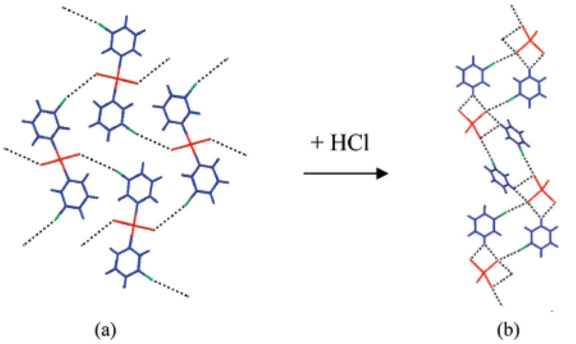


Figure 3. Crystal structures showing (a) 2D network formed in **1**, propagated via Cu−Cl···Cl−C halogen bonds represented as dotted lines and (b) 1D network formed by **2**, propagated via N−H···Cl_2Cu hydrogen bonds and Cu−Cl···Cl−C halogen bonds, indicated as dotted lines. Copper atoms and chloride ligands shown in red, carbon-bound chlorine atoms in green, and all other atoms in blue.

The crystallinity and identity of the yellow product as the ionic material **2** was confirmed by X-ray powder diffraction. Rietveld refinement of the final product shows that the reaction had not reached completion in 24 h (75% conversion; see Figure 2a), although 100% conversion can be obtained by extending the period of reaction with the HCl gas (Figure 2b). The same polymorph of **2** is formed as when **1** reacts with *aqueous* HCl vapor.[28] This process involves multiple changes in covalent bonding. Specifically, HCl molecules are inserted into all Cu−N bonds requiring rupture of the covalent bond of the gaseous molecules (H−Cl) and of coordination bonds of molecular solid compound (Cu−N) in order that N−H and Cu−Cl bonds can be formed. The crystalline product, the salt $(3\text{-ClpyH})_2[CuCl_4]$ **2** (3-ClpyH = 3-chloropyridinium), now contains four Cu−Cl bonds in a distorted tetrahedral arrangement rather than two Cu−Cl and two Cu−N bonds in the square planar geometry of **1**, consistent with the change in color. The resultant ionic compound forms 1D chains where the 3-chloropyridinium cations and $[CuCl_4]^{2-}$ anions are linked via bifurcated N−H···Cl_2Cu hydrogen bonds[37] and intermolecular Cu−Cl···Cl−C halogen bonds,[38] the latter being also present in the crystal structure of **1**, which forms 2D layers (Figure 3).

Establishment of a Solid−Gas Equilibrium. The reverse of the HCl uptake process, that is, the extrusion of HCl in the absence of water to convert salt **2** into neutral coordination compound **1**, was monitored by time-resolved Fourier transform infrared (FTIR) spectroscopy to establish the variation in concentration of HCl gas with time. The possible formation of a solid−gas equilibrium in this reaction had been previously

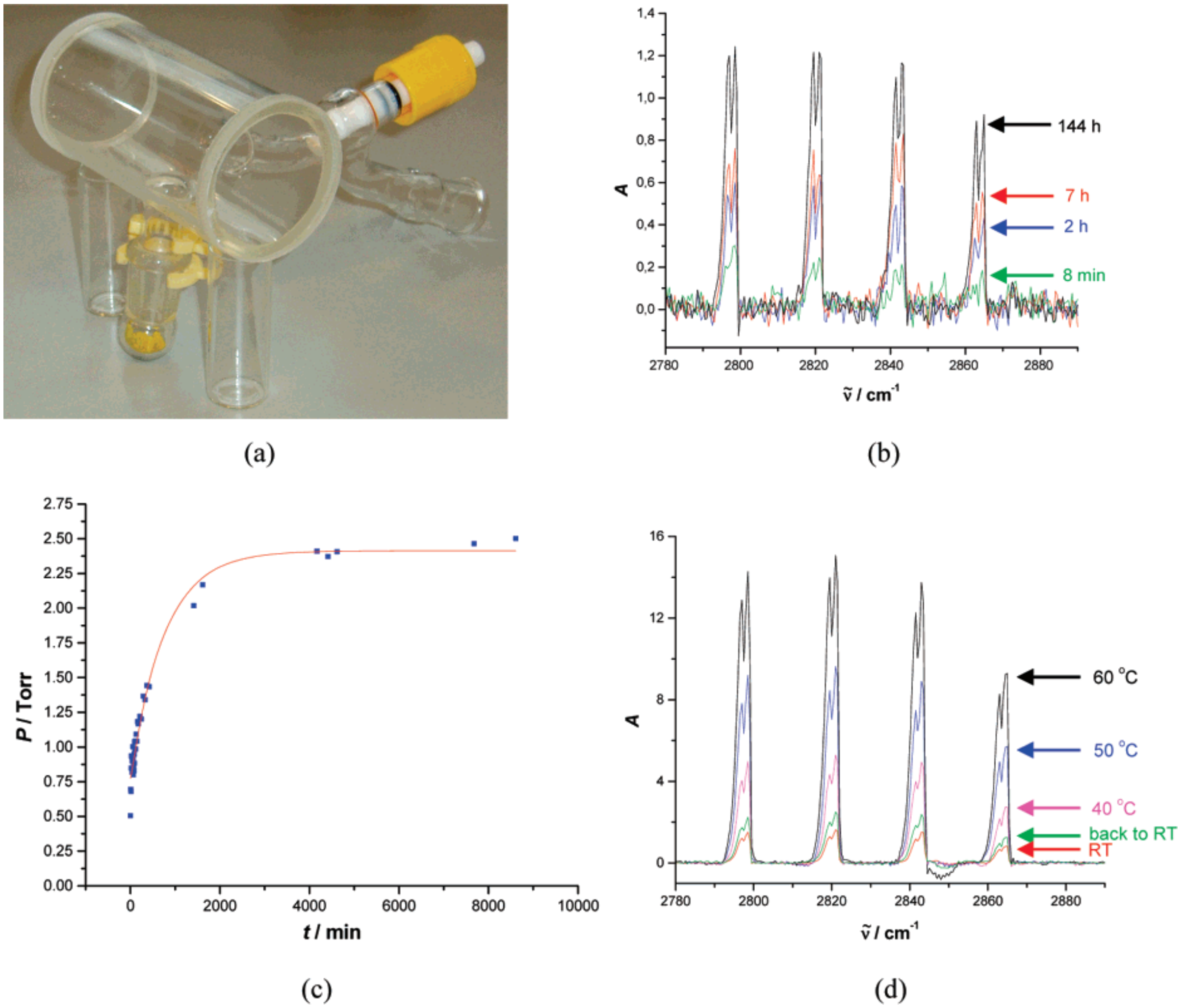


Figure 4. (a) Gas cell used for the IR spectroscopy measurements containing a sample of **2**; (b) variation with time of the IR absorbance for HCl, after 8 min (green), 2 h (blue), 7 h (red), and 144 h (black); (c) variation of HCl pressure with time at 35 °C (exponential fit); (d) variation with temperature of the IR absorbance for HCl at equilibrium.

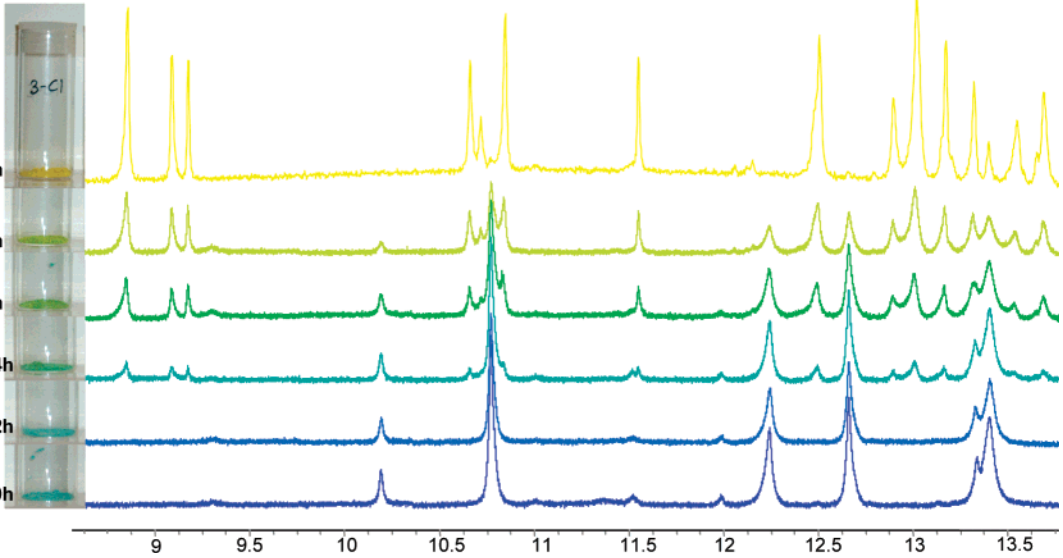


Figure 5. Samples from the *ex situ* reaction study showing the change in color over time as **1** (yellow) is converted to **2** (blue) through extrusion of gaseous HCl (left) together with the corresponding synchrotron X-ray powder patterns ($T = 100$ K).

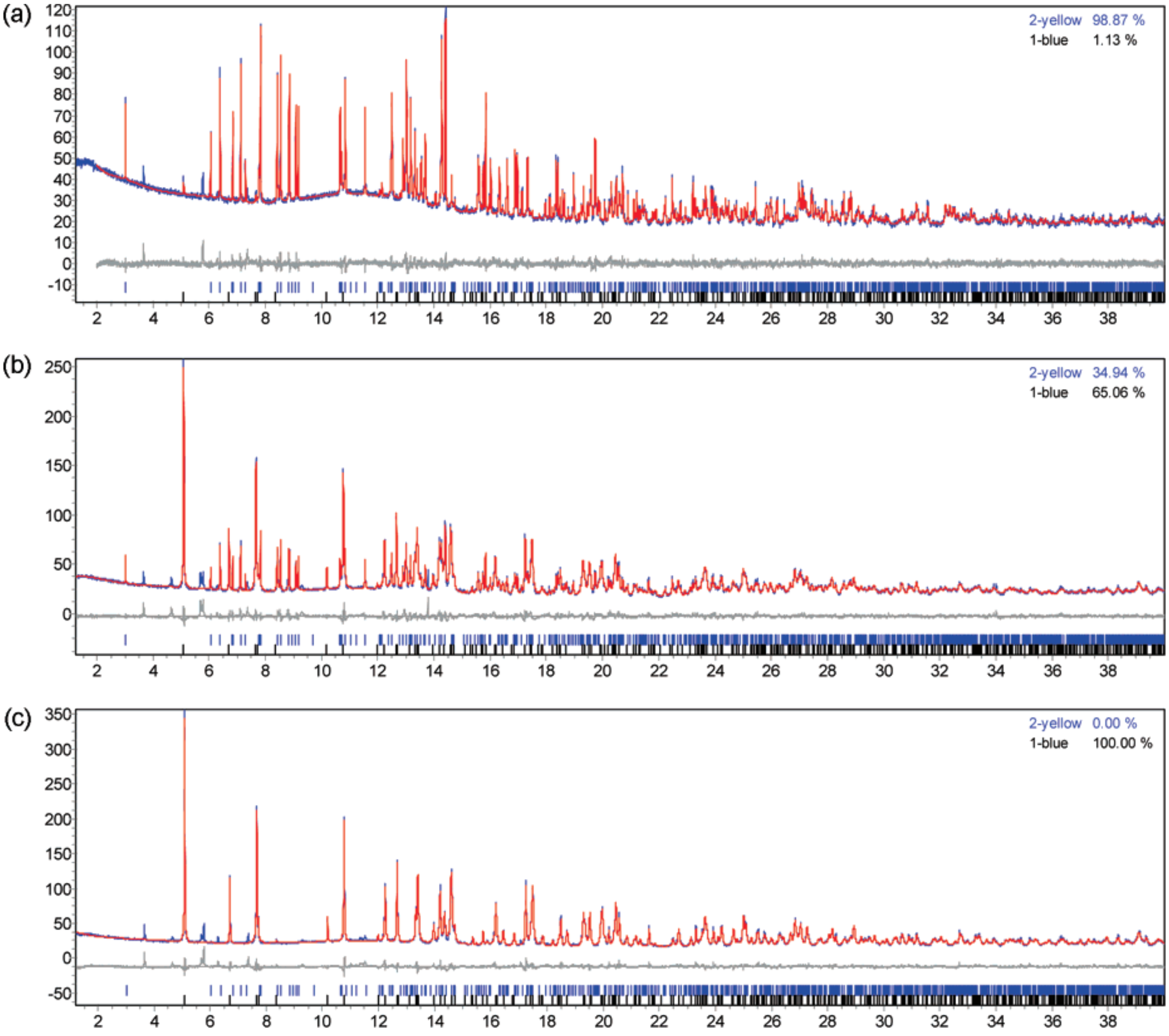


Figure 6. Observed (blue) and calculated (red) profiles and difference plot [($I_{obs} - I_{calcd}$)] (gray) of the two-phase Rietveld refinement after having stopped the reaction of **2** → **1** after (a) 0 h; (b) 6 h; and (c) 49 h (2θ range 2.0−40.0°, maximum resolution of 1.17 Å). A full set of patterns is provided in Supporting Information.

anticipated but not confirmed. Specifically, no change of color is observed over many months if crystalline **2** is placed inside a sealed vessel. However, release of HCl by **2** can be promoted within a closed system by trapping the eliminated HCl gas with

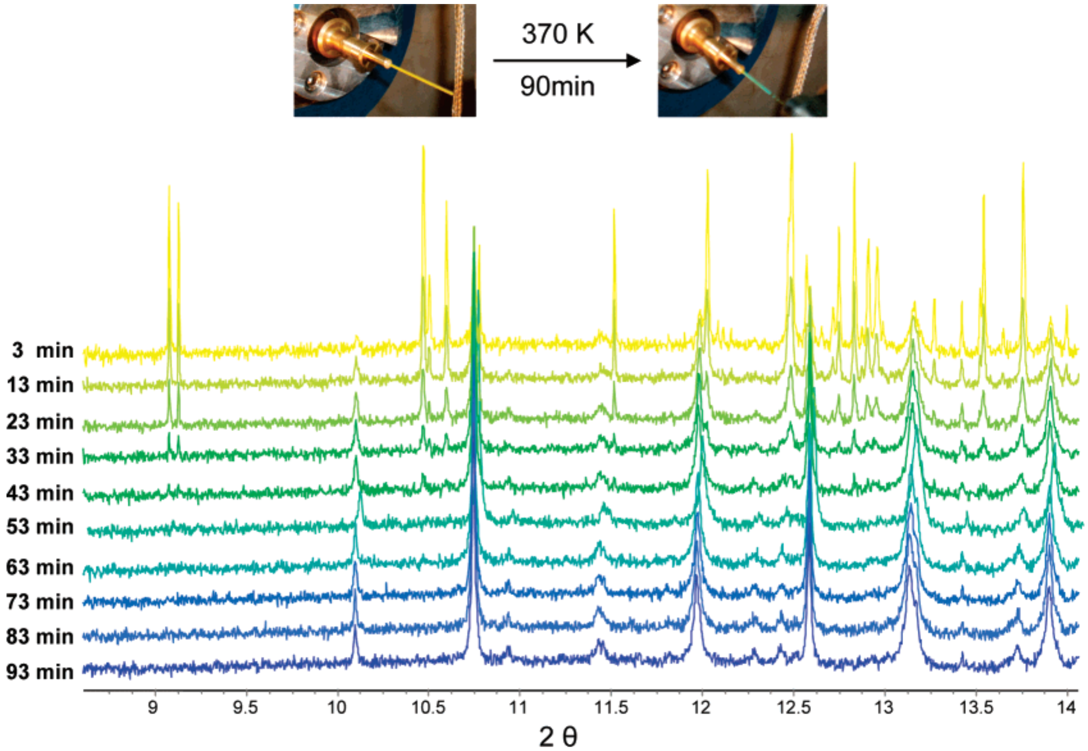


Figure 7. (Top:) Powder sample of **2** (yellow) prior to reaction and as **1** (blue) after reaction. (Bottom) Powder patterns ($T = 370$ K) of samples from *in situ* study depicting the transformation of crystalline **2** (yellow pattern) to **1** (blue pattern).

an aqueous solution containing Ag^+ ions (through formation of insoluble AgCl).[28]

Compound **2** (yellow salt) was placed in a gas cell under vacuum (ca. 5×10^{-3} Torr), and the gas-phase IR spectrum was measured at intervals over a period of 1 week (Figure 4). The pressure of HCl increased rapidly with time at the outset but reached a maximum pressure, indicating the establishment of a gas−solid equilibrium (Figure 4c). At 35 °C, the pressure reached ca. 2.5 Torr after 2 days[39] and resulted in no perceptible change in color of the solid; this corresponds to a 10.9(2)% conversion of **2** to **1** at equilibrium for 50 mg of **2** used in a cell of volume ca. 200 cm^3. The equilibrium constant ($K = P_{HCl}{}^2$) is calculated at $1.03(5) \times 10^{-5}$ [$\Delta G^{\ominus}_{m} = 29.5(1)$ kJ.mol^{-1}] and indicates good sensitivity of **1** to HCl gas in the range 200−20 000 ppm. Futhermore, we have also shown that the position of the equilibrium can be displaced by changing the temperature (Figure 4d). Specifically, the equilibrium pressure of HCl increases with increase in temperature, indicating that HCl extrusion is endothermic. Importantly, a reduction in temperature returns the equilibrium pressure to its original lower value, further confirming the ability of the blue coordination compound (**1**) to react directly with gaseous HCl in the absence of water.

Study of the Reaction Path and Reaction Kinetics. To understand better the path of the reaction, we have followed the extrusion of HCl from **2** by time-resolved synchrotron X-ray powder diffraction on beam line ID31[32] at the European Synchrotron Radiation Facility in Grenoble, France. We reasoned that a plausible mechanism could involve stepwise loss of the two equivalents of HCl, requiring the formation of a transient intermediate phase resulting from the loss of one molecule of HCl per formula unit of the ionic compound, as has been suggested in studies of thermal treatment of a related platinum system.[40] The high intensity and narrow line width of a third generation synchrotron source provides the optimum chance of detecting such a phase even if present in very low relative abundance. Both *ex situ* and *in situ* approaches to monitoring the reaction have been undertaken.

(a) *Ex situ* Monitoring of the HCl Release. A large sample of **2** was prepared and divided into 9 vials. One was sealed immediately to prevent conversion to **1** beyond the equilibrium established at room temperature. Each of the others was sealed in sequence at intervals of a few hours over a total period of 2 days during which full conversion to **1** occurs.[28] Given that equilibrium should be established upon sealing the vials following irreversible loss of some HCl to the atmosphere, the samples should represent a sequence of snapshots of the reaction during its progress (Figure 5). In this way, the procedure is analogous to the well-established protocol of sampling aliquots of a solution-phase reaction and quenching the reaction prior to (spectroscopic) analysis. X-ray powder patterns were measured at 100 K to a resolution of 1.17 Å for each sample in a flame-sealed capillary (Figure 5). It can be observed that the peaks corresponding to **2** diminish in intensity with time whereas those corresponding to **1** increase. Rietveld analysis revealed an excellent fit to a two-phase model for each pattern, indicating the absence of a detectable intermediate crystalline phase in the reaction (Figure 6). Furthermore, there is no evidence for formation of an amorphous phase during the reaction. A small

---

[37] Brammer, L.; Swearingen, J. K.; Bruton, E. A.; Sherwood, P. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4956.

[38] Zordan, F.; Brammer, L.; Sherwood, P. *J. Am. Chem. Soc.* **2005**, *127*, 5979.

[39] From the exponential curve fit to the data in Figure 4c, the pressure at equilibrium is 2.41(4) Torr [321(5) Pa]. This compares with a corresponding pressure of 1.37(4) Torr [183(5) Pa] for the measurements made at 25 °C. (Full details in Supporting Information.)

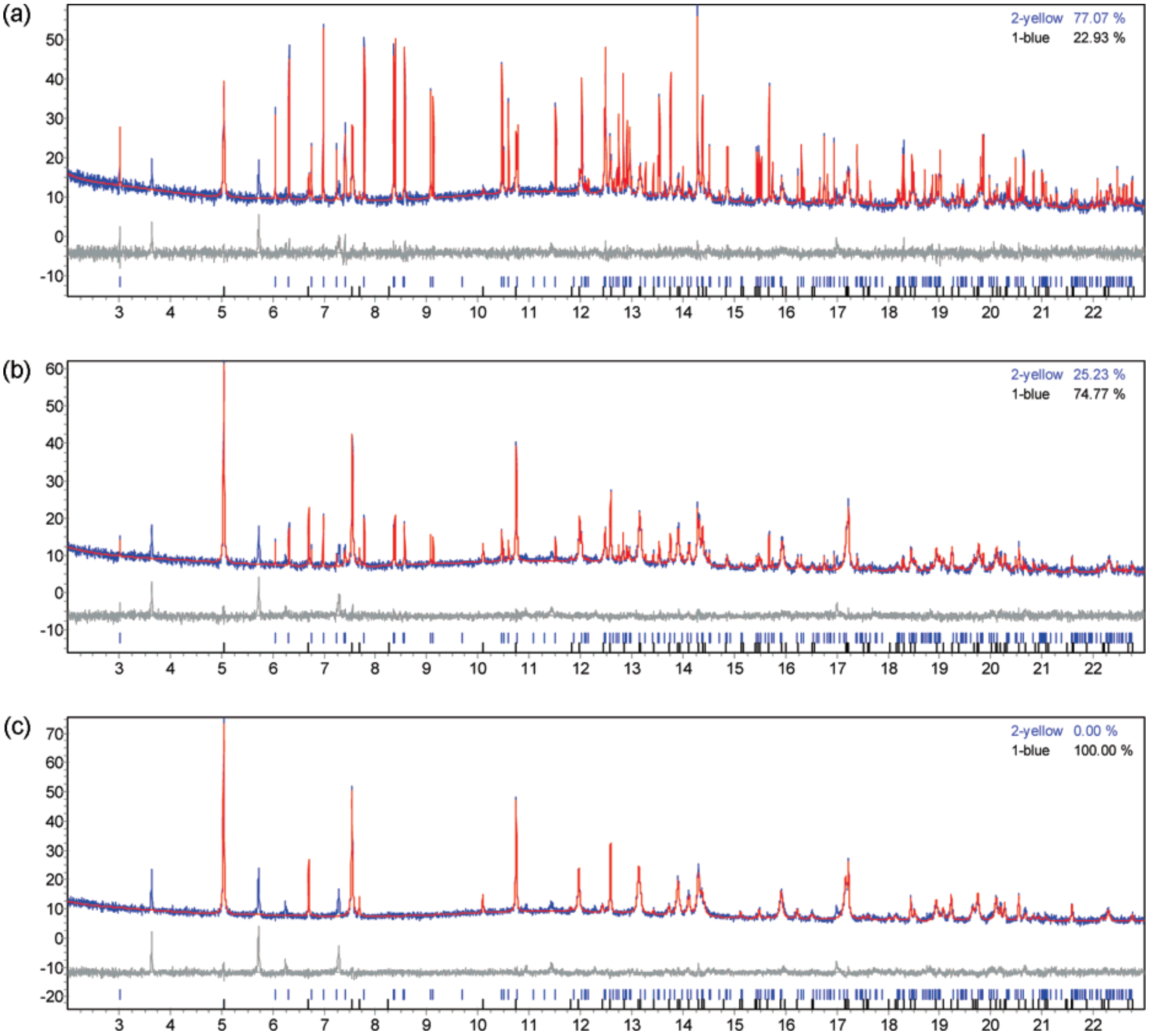


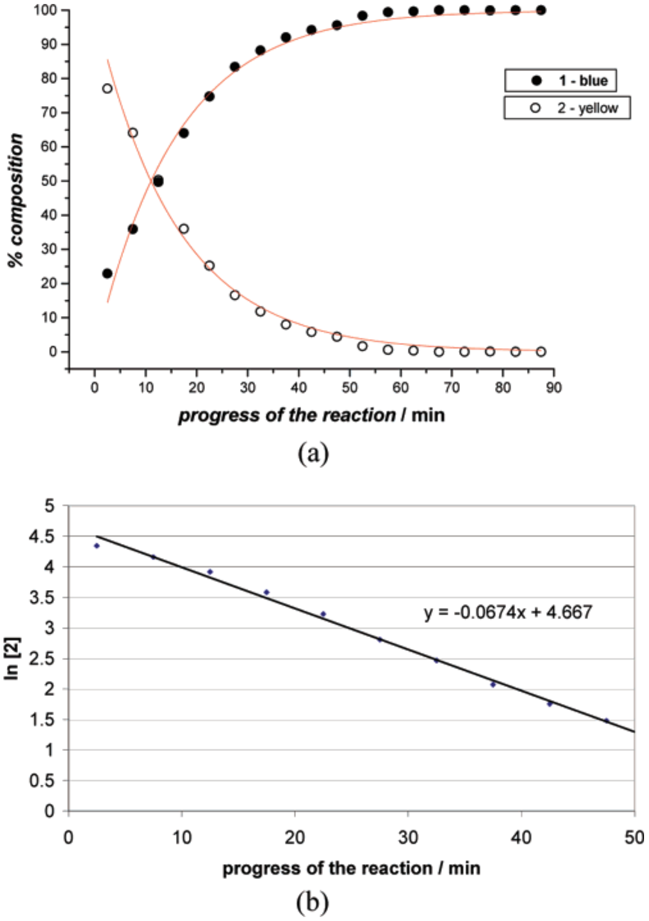
Figure 8. Observed (blue) and calculated (red) profiles and difference plot [$(I_{\mathrm{obs}} - I_{\mathrm{calcd}})$] (gray) of the two-phase Rietveld refinement after (a) 2.5 min; (b) 22.5 min; and (c) 87.5 min of the reaction of **2** → **1** at 370 K (2θ range 2.0−23.0°, maximum resolution 2.01 Å). A full set of patterns is provided in Supporting Information.

number of minor peaks not attributable to **1** or **2**, nor to ice formation, remain constant throughout the series of patterns measured, as is evident from the residual profile. These peaks are attributed to the presence of a very small amount of an impurity phase. Being constant throughout the reaction, these cannot be taken as an indication of a reaction intermediate. It is plausible that this impurity phase corresponds to a solvate of the coordination compound, **1·MeOH**, since a similar compound has been previously reported for the Pt analogous compound.[38] However, it has not been possible to confirm this due to the small number and low intensity of the peaks.

The decreasing fractional composition of **2** and increasing composition of **1** follow an exponential (and inverse exponential) progression analogous to that observed by IR spectroscopy for the evolution of HCl gas (Figure 4c), consistent with a first-order reaction and indicating complete conversion in a period of ca. 17 h (see Supporting Information).

(b) *In situ* Monitoring of the HCl Release. Although compelling, one might argue that establishment of equilibrium upon sealing each sample vial in the *ex situ* study could in principle lead to removal of an intermediate crystalline or amorphous phase and thereby prevent its observation in the aforementioned diffraction studies. Thus, we undertook an *in situ* X-ray powder diffraction study of the conversion of **2** to **1**, again employing synchrotron radiation. An open capillary containing a microcrystalline sample of **2** was placed on the diffractometer under a flow of N_2 gas at an elevated temperature (370 K) to accelerate the reaction.

Powder patterns were measured continuously within 5 min intervals to a resolution of 2.01 Å over a period of 90 min (Figure 7 shows the powder patterns measured every 10 min). Again, Rietveld analysis provided a very good two-phase fit for each pattern, and the same impurity peaks as those found in the *ex situ* experiments were present, remaining constant during the reaction (Figure 8). The changes in fractional composition of **1** and **2** obtained from the Rietveld fit follow a very similar (but smoother) trajectory to those obtained from the *ex situ* studies and indicate complete conversion of **2** to **1** after ca. 70 min at 370 K for the sample used (Figure 9). Again, no evidence for an intermediate phase is found. A logarithmic plot of the change in composition versus time shows a linear relationship (Figure 9b) permitting the first-order rate constant to be determined as 1.1×10^{-3} s^{-1} for the sample studied.



(a)

(b)

Figure 9. (a) Exponential variation with time of the percentage composition of **1** and **2** in the reaction products obtained during the *in situ* monitoring of HCl release. (b) Logarithmic plot to determine the first-order rate constant for conversion of **2** to **1** ([**2**] = mole fraction of **2**).

Conclusions

The reversible uptake of HCl molecules from the gas phase by a nonporous crystalline solid has been established to proceed in the absence of any solvent and with retention of crystallinity, despite the many chemical and geometrical changes needed for this process to take place. Specifically, cleavage and formation of coordination bonds (cleavage of H−Cl and Cu−N and formation of Cu−Cl and N−H bonds) and hydrogen bonds (N−H···Cl_2Cu), as well as a change in the geometry of the metal center from square planar to distorted tetrahedral, are required. The results provide clear evidence that this process in which HCl molecules are trapped by insertion into metal−ligand coordination bonds is not a microscopic recrystallization process but a true gas−solid reaction. IR spectroscopic studies of the reverse reaction, the release of HCl gas, have established that this reversible process is actually an equilibrium process, whose equilibrium position varies with temperature. *In situ* and *ex situ* powder diffraction studies of the transformation resulting from release of HCl gas do not indicate the presence of an intermediate of the reaction. It has also been established that the release of HCl follows first-order reaction kinetics. The change in color between blue (no HCl) and yellow (HCl included) suggests potential exploitation in sensing of HCl, and it has been established that the sensitivity of coordination compound **1** to HCl gas is good in the range 200−20 000 ppm. This is currently being explored alongside studies that establish the generality of the reaction to other metal coordination compounds and other hydrogen halides. In this regard, preliminary diffraction results for reactions involving HBr suggest similar behavior to that found for HCl.

More generally, these results describe unprecedented flexibility within molecular crystals and indicate that the molecular solid state can be far more dynamic than it is generally perceived to be. The observations are pertinent to the development of responsive molecular crystalline materials for sensing, gas sorption, and catalysis and to efforts to develop solvent-free or solvent-minimized reactions for green chemistry.[41,42]

Acknowledgment. Support from the Cambridge Crystallographic Data Centre and the Centre for Molecular Structure and Dynamics of the Science and Technology Funding Council, UK is gratefully acknowledged. We thank the Synchrotron Radiation Source, Daresbury, UK and the European Synchrotron Radiation Facility, Grenoble, France for access to experimental facilities. We are grateful to Dr. Sam Hawxwell (New York University) for assistance with some of the studies conducted at ESRF.

Supporting Information Available: Full details of experimental work including additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA075265T

---

(40) Adams, C. J.; Crawford, P. C.; Orpen, A. G.; Podesta, T. J.; Salt, B. *Chem. Commun.* **2005**, 2457.
(41) Braga, D.; Grepioni, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4002.
(42) Lazuen Garay, A.; Pichon, A.; James, S. L. *Chem. Soc. Rev.* **2007**, *36*, 846.