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Solid–Gas Reactions

Ligand Substitution within Nonporous Crystals of a Coordination Polymer: Elimination from and Insertion into Ag–O Bonds by Alcohol Molecules in a Solid–Vapor Reaction**

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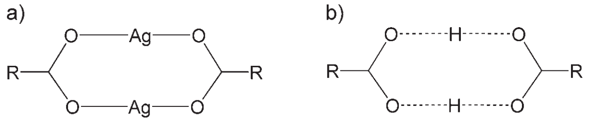
Chemical reactions in the crystalline organic solid state, although uncommon, are well-established and involve covalent bond formation between neighboring molecules as a result of photochemical or thermal activation.[1–4] Carbon–carbon bond forming dimerizations, oligomerizations, and polymerizations involving alkene and alkyne moieties in metal-containing crystals (salts and coordination compounds) have also been studied for many years,[5] though in most cases not in crystal-to-crystal transformations. By comparison, reactions within crystals of organometallic or coordination compounds in which metal–ligand bonds are formed or broken are very limited, not only in number of reports but in variety of reaction observed.[6–8] Most common are reactions that involve loss of coordinated solvent in a porous transition-metal coordination framework compound or solvent-molecule re-coordination upon uptake by the evacuated framework. Typically, a single metal–ligand bond is broken or formed, and transport of the solvent (ligand) molecule in and out of the crystal is relatively facile owing to the available channels.[9] Thermal treatment of the crystal is often needed for solvent removal. A much rarer example of a solid-state metal–ligand bond cleavage reaction is the photolytic cleavage of a Mn–CO bond within a host–guest structure reported by Fujita and co-workers.[10] Three examples of reversible ligand coordination to transition-metal centers involving sorption/desorption in nonporous crystals have been reported. In one case, Pt–S bonds are formed and broken in the reversible absorption of gas-phase SO_2 molecules by a platinum complex;[11] in another, a trinuclear iron complex exchanges coordinated H_2O with MeOH through cleavage and formation of an Fe–O bond;[12] and most recently, reversible loss of a weakly bound pyridine ligand from square-pyramidal copper(II) complexes has been reported.[13] However, all of these examples involve simple cleavage and formation of an individual metal–ligand bond. In recent studies by Rosseinsky and co-workers,[14] from our own work[15,16] and in that of Orpen,[17] the complexity of reactions has been expanded to include the reversible release and uptake of small molecules, involving breaking and formation of more than one covalent bond within crystalline coordination compounds. The present study involves a new class of reactions within nonporous crystals of a coordination polymer in which separate coordination bonds are formed and broken in a ligand-substitution reaction at a silver(I) center.

Previously we have demonstrated the synthesis of coordination network structures based upon silver carboxylate dimer units linked through neutral diimine and diamine ligands. The behavior of Ag^+ ions in these structures has similarities to the behavior of hydrogen ions in structures of carboxylic acids,[18,19] such that the O–Ag–O coordination-bond arrangement in the former mimics the more well-established O–H···O hydrogen-bond arrangement in the latter (Scheme 1). Herein, we extend this analogy a step further, wherein the $\{Ag_2(O_2CR)_2\}$ dimer is expanded by inclusion of an ethanol molecule that is inserted into one of the Ag–O bonds of the dimer, analogous to the well-known expanded carboxylic acid dimer motif in which water or alcohol molecules are incorporated.[20]



Scheme 1. Analogy of a) the silver(I) carboxylate dimer and b) the carboxylic acid dimer.

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More significantly, we have investigated the elimination of ethanol molecules from this expanded dimer and their subsequent extrusion from crystals of the coordination network material $[Ag_4(tmp)_3\{O_2C(CF_2)_3CF_3\}_4(EtOH)_2]_n$ (**1**, tmp = tetramethylpyrazine) to yield the ethanol-free network $[Ag_4(tmp)_3\{O_2C(CF_2)_3CF_3\}_4]_n$ (**2**). This reaction requires a rearrangement of the coordination sphere of the metal center in addition to substantial ligand motions. Surprisingly, the long-range order of the crystal is not lost in the process, which occurs as a single-crystal-to-single-crystal transformation. The reverse process, monitored by X-ray powder diffraction, provides further insight into this unusual solid-state reaction.

Compound **1** forms a 1D tape structure in which pairs of tmp ligands link $\{Ag_2(O_2CR)_2(EtOH)\}$ units, which are further connected into zigzag chains through links comprising single tmp molecules (Figure 1).[21] An ethanol molecule is coordinated to one of the two silver atoms of the aforementioned unit and forms an O−H···O hydrogen bond to one of the two carboxylate ligands; it can be regarded as being inserted into one of the Ag−O bonds of the silver(I) carboxylate dimer (Figure 1 c). Heating a single crystal of **1** at 320 K for approximately 48 h resulted in a single-crystal-to-single-crystal transformation yielding compound **2**,[22] in which the overall 1D tape structure is maintained, but extrusion of the EtOH molecules has led to conversion of the $\{Ag_2(O_2CR)_2(EtOH)\}$ unit into the simple silver carboxylate dimer $\{Ag_2(O_2CR)_2\}$. In order for this transformation to take place, cleavage of both covalent (Ag−O(H)Et) and noncovalent ($EtOH\cdots O_{carboxylate}$) bonds as well as formation of new covalent bonds ($Ag{-}O_{carboxylate}$) is required. Thereby an intramolecular ligand substitution has taken place at alternate Ag centers, since ethanol coordination is replaced by bridging carboxylate coordination (Figure 1).

To investigate the reversibility of this process, a freshly prepared sample of **1** was air-dried for 10 min and then gently ground using a pestle and mortar (powder A). One-third of the microcrystalline sample was set aside, and the remainder was heated in the oven at 313 K for 24 h to generate **2** by ethanol loss (powder B). Half of the heated sample was then exposed to vapors of EtOH by placing it in a small vial that was enclosed within a larger sealed vial containing EtOH (powder C). The three resultant powders were examined by synchrotron X-ray powder diffraction (Figure 2).

It is evident from the powder pattern that the starting sample (A) contains both **1** and the ethanol-free analogue **2**, the former as the major phase. This situation may have resulted from both phases being formed in the original synthesis but could also arise from conversion of **1** to **2** during the brief air drying of the sample. Careful inspection revealed

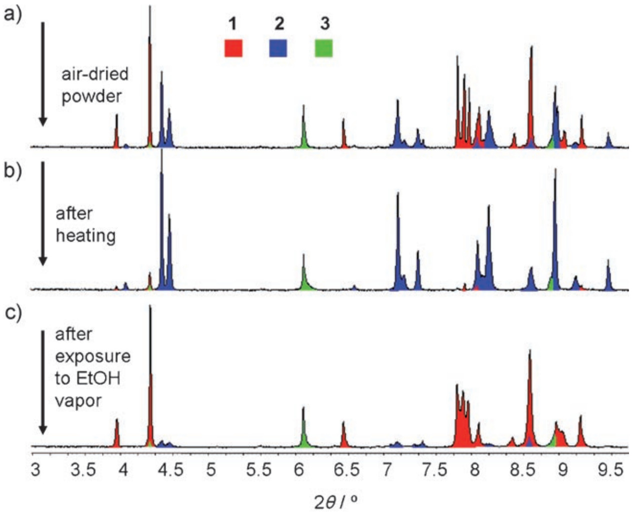
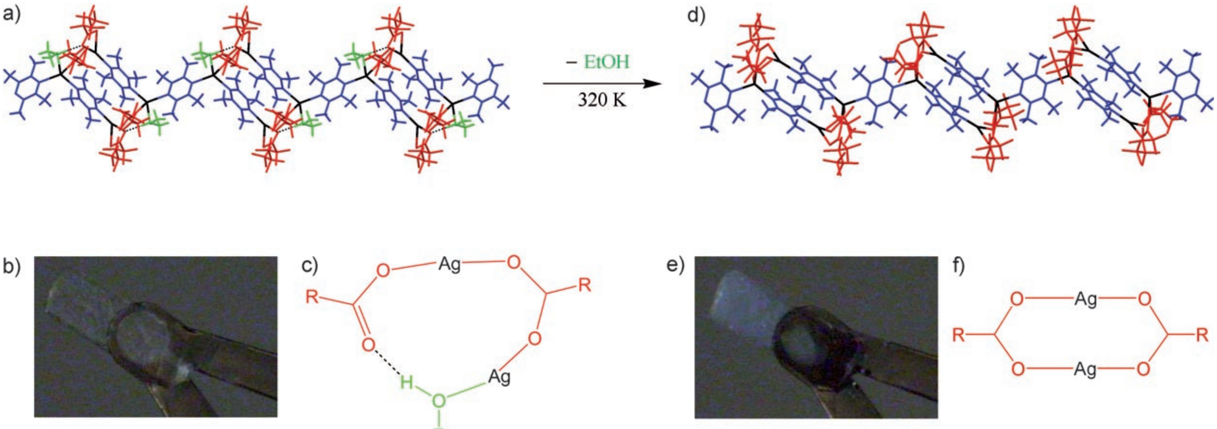


Figure 2. Experimental X-ray powder diffraction pattern a) before heating to remove EtOH (powder A), b) after heating (powder B), and c) after re-exposure to EtOH vapor (powder C). The intensities of the peaks corresponding to **1** (red) and **2** (blue) clearly vary in accord with the loss and uptake of EtOH, while those for compound **3** (green) remain unchanged. The arrows indicate the transition between the powders.



$[Ag_4(tmp)_3\{O_2C(CF_2)_3CF_3\}_4(EtOH)_2]_n$ (**1**)

$[Ag_4(tmp)_3\{O_2C(CF_2)_3CF_3\}_4]_n$ (**2**)

Figure 1. Single-crystal-to-single-crystal reaction involving loss of coordinated ethanol. a) Crystal structure of **1**; b) single crystal of **1** prior to heating; c) $Ag_2(O_2CR)_2(EtOH)$ motif showing how ethanol is inserted into one Ag−O bond of the silver carboxylate dimer; d) crystal structure of **2**; e) single crystal of **2** after heating (same crystal as shown in (b)); f) $Ag_2(O_2CR)_2$ dimer motif after elimination of ethanol. Silver atoms are shown in black, fluorocarboxylate ligands in red, tetramethylpyrazine ligands in blue and ethanol ligands in green. Dashed lines represent O−H···O hydrogen bonds.

a third minor phase, whose pattern matches that for $[Ag_4(tmp)_2\{O_2C(CF_2)_3CF_3\}_4]_n$ (**3**), a 2D network compound that is related to **2** but of different stoichiometry.[23] Clearly compound **3** cannot take up ethanol molecules, as shown by its invariant diffraction intensities during the exposure of the powder to vapors of EtOH.[24] Thus, compound **3** serves as an internal standard during the reaction.

Although the detailed mechanism for extrusion and uptake of ethanol is at present unknown, some insight is possible from comparison of the structure of **1** with that of **2**. It is firstly important to note that neither compound **1** nor **2** is porous. Thus, no direct channels for ethanol transport are present. Figure 3 shows pairs of neighboring tapes in the two structures and highlights the resultant movement of the fluorocarboxylate groups upon loss of ethanol. In **1** all $\{Ag_2(O_2CR)_2(EtOH)\}$ units are equivalent, whereas in **2** the repeat unit along the tape involves three consecutive $\{Ag_2(O_2CR)_2\}$ units, leading to a tripling of the unit cell volume.[25] All fluoroalkyl chains adopt an entirely *anti* geometry in **1**, whereas in **2** one carboxylate ligand from each $\{Ag_2(O_2CR)_2\}$ dimer retains the all-*anti* geometry while the other adopts a *gauche* conformation about the C_γ–C_δ bond (i.e. *anti–gauche–anti* overall). Interestingly, the ligands whose carboxylate groups undergo motion to convert from chelating one silver center to bridging a pair of silver centers retain the all-*anti* chain geometry (Figure 3, green circles). It seems probable that ethanol transport in and out of the crystal occurs in a direction orthogonal to the views shown, which corresponds to the *a* axis in the crystal structure of **1**. In **1**, fluorine atoms (shown as spheres in Figure 3) on the C_γ and C_δ carbon atoms of these fluoroalkyl chains provide a barrier to the suggested transport of ethanol molecules along the *a* axis. To permit ethanol transport, these chains would have to move apart before moving closer together to adopt the positions seen in **2** (Figure 3, green circles), in which they reside in the space formerly occupied by the ethanol molecules. The relocation of these chains necessarily leaves space within the fluoroalkyl regions that separate the $\{Ag_4(tmp)_3(O_2C)_4\}_n$ tapes. This space is filled through a change of conformation of all remaining fluoroalkyl chains from all-*anti* conformation to an *anti–gauche–anti* conformation. Three independent (pairs of) chains undergo this conformational change (see yellow, pink, and red ellipses in Figure 3). The reverse of these transformations would then be required to re-admit the ethanol, concluding in insertion of the ethanol molecules into one Ag–O bond in each $\{Ag_2(O_2CR)_2\}$ unit of **2** to permit conversion to **1** and re-formation of the $\{Ag_2(O_2CR)_2(EtOH)\}$ units. The fluoroalkyl chains can be viewed as flexible barriers to ethanol transport within the crystals,[26] perhaps more analogous to a series of curtains rather than doors.

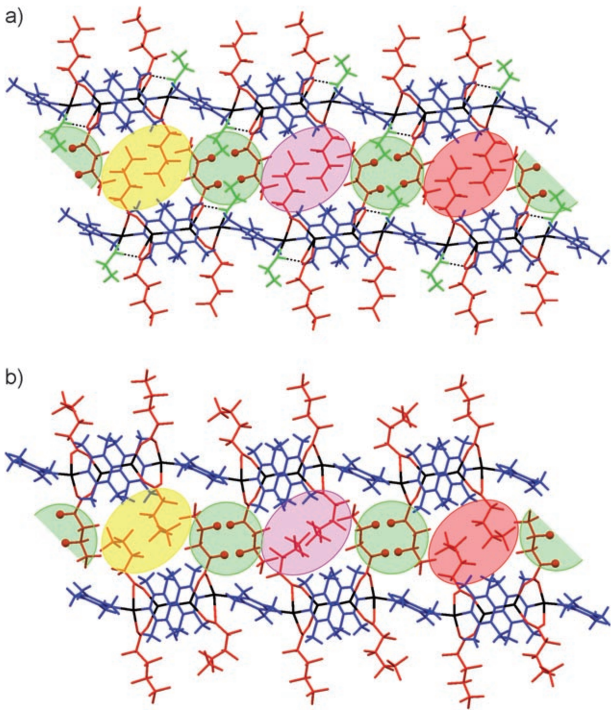


Figure 3. Crystal structures of a) **1** and b) **2** shown in analogous views depicting pairs of neighboring tapes and illustrating the different conformations of the fluoroalkyl chains before and after the loss of ethanol. Atom colors as in Figure 1. Green circles show fluoroalkyl chains close to ethanol molecules in **1** and the same chains after ethanol loss in **2**, all of which retain an all-*anti* conformation. Yellow, pink, and red ellipses show fluoroalkyl chains that adopt an all-*anti* conformation in **1** but which change to an *anti–gauche–anti* conformation in **2**.

Reversible reactions in molecular crystals in which metal–ligand coordination bonds are formed or broken are rare, particularly for cases in which crystallinity is retained. Sorption of guest molecules from the vapor phase by nonporous crystals is also rare. The present study describes a coordination polymer that remarkably exhibits both of these unusual traits. The key to its behavior is flexibility. Flexibility in the Ag coordination sphere[27] and relatively weak Ag–O bonds allow facile insertion and elimination of ethanol. Flexibility in the fluoroalkyl chain conformation allows transport of ethanol molecules in and out of these nonporous crystals. These behaviors and the extension of such mechanisms for sorption and desorption in a wider range of crystalline materials are currently under investigation. Improving our understanding of, at present, unusual processes such as these has the potential to provide new opportunities in the development of functional crystalline materials for sorption, sensing, and solid-state reactions.

Experimental Section

Crystal syntheses: All starting materials were purchased from Aldrich, Lancaster, Avocado, or Fluorochem and used as received. Light was excluded from all reactions as a precaution to minimize decomposition to form silver metal. Compound **1** was prepared in 38% yield by layering an ethanol solution of Ag_2CO_3 and nonafluoropentanoic acid onto a dichloromethane solution of tetramethylpyrazine at a temperature of approximately 5 °C. Colorless crystals suitable for single crystal diffraction were formed after one day. Compound **2** was prepared in a single-crystal-to-single-crystal transformation upon heating **1** at 320 K for 48 h. Single crystals of compound **3** were formed as a minor product in the synthesis of **1**.

X-ray crystallography: Single crystal X-ray data were collected at 250 K for compound **1**, 120 K for compound **2**, and 100 K for **3** on Bruker CCD diffractometers using $Mo_{K\alpha}$ radiation. In each case data were corrected for absorption using empirical methods (SADABS) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.[28] Crystal structures were solved and refined against all F^2 values using the SHELXTL suite of programs.[29] Non-hydrogen atoms were refined anisotropically (except as noted), and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Disorder in some fluoroalkyl chains was modeled for the structures of **1** and **2**. In **1**, one fluoroalkyl chain was modeled in two orientations in a 60.1(11):39.9(11) ratio for both the β- and γ-CF_2 groups. In **2**, one fluoroalkyl chain was modeled in two orientations in a 60.5(17):39.5(17) ratio for both the β- and γ-CF_2 groups. Carbon and fluorine atoms in some chains could only be modeled isotropically for **2**. For the single-crystal-to-single-crystal reaction, X-ray data were first collected on a crystal of **1** (250 K). The crystal was then heated to 320 K for 48 h, enabling conversion to **2**, and finally cooled to 120 K prior to collection of a new data set on the same crystal (now compound **2**). Crystallographic data are summarized in tabulated form in the Supporting Information. CCDC 654182 (**1**), 654183 (**2**), and 654184 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

X-ray powder diffraction: The polycrystalline samples A, B, and C, prepared as described in the main text, were loaded into 1.0-mm glass capillaries. X-ray powder diffraction data were collected at 100 K on beam line ID31[30] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France using wavelength $\lambda = 0.93369(3)$ Å. Full details are provided in the Supporting Information.

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[20] The CSD (version 5.28, April 2007) contains 13 crystal structures in which one, two, or four methanol molecules are inserted into the cyclic hydrogen-bonding pattern of the carboxylic acid dimer to give a $R_3^3(10)$, $R_4^4(12)$ or $R_6^6(16)$ motif. (CSD refcodes: AHIFAY, AQUMUU, CILLUE, DIVWEK, IYUQIC, IYUQOI, MIGBAF, MITCOH, TATREL, TPTPCM, UCUKUY, WERCOL, XUNJIZ). There are eight examples involving insertion of either one or two ethanol molecules leading to $R_3^3(10)$ or $R_4^4(12)$ motifs, respectively (CSD refcodes: FIDNEM, JIDCEE, MAPNIB, OLOCEX, POFPIJ, SURYUZ, VURBAL, ZIVDUD). However, we are not aware of any examples of alcohol insertion into carboxylic acid dimers occurring in solid-state reactions.
[21] Crystal data for **1**: $C_{48}H_{48}Ag_4F_{36}N_6O_{10}$, $M_r = 992.20\ \mathrm{g\,mol^{-1}}$, triclinic, space group $P\bar{1}$, $a = 8.957(4)$, $b = 13.838(6)$, $c = 15.726(7)$ Å, $\alpha = 108.113(7)$, $\beta = 104.157(7)$, $\gamma = 102.380(8)°$, $V = 1704.7(14)$ Å^3, $Z = 1$, $\rho_{\mathrm{calcd}} = 1.933\ \mathrm{Mg\,m^{-3}}$, $\mu = 1.286\ \mathrm{mm^{-1}}$, 10258 ($R$(int) = 0.030) reflections used in refinement. Final $R1 = 0.0751$ ($F^2 > 4\sigma(F^2)$), $wR2 = 0.2568$ (all data).
[22] Crystal data for **2**: $C_{44}H_{36}Ag_4F_{36}N_6O_8$, $M_r = 946.14\ \mathrm{g\,mol^{-1}}$, triclinic, space group $P\bar{1}$, $a = 15.4430(8)$, $b = 17.2340(7)$, $c = 18.3084(8)$ Å, $\alpha = 84.548(3)$, $\beta = 81.374(3)$, $\gamma = 69.370(3)°$, $V = 4504.0(4)$ Å^3, $Z = 3$, $\rho_{\mathrm{calcd}} = 2.093\ \mathrm{Mg\,m^{-3}}$, $\mu = 1.452\ \mathrm{mm^{-1}}$, 26585 ($R$(int) = 0.151) reflections used in refinement. Final $R1 = 0.0961$ ($F^2 > 4\sigma(F^2)$), $wR2 = 0.3506$ (all data).
[23] The Ag/tmp ratio in **3** is 2:1 rather than 4:3 as found in **2**. Compound **3** has been prepared and structurally characterized by single crystal X-ray diffraction. The structure of **3** can be envisioned as related to **2** through removal of the singly bridging tmp ligands and connection of neighboring $\{Ag_4(tmp)_2\{O_2C(CF_2)_3CF_3\}_4\}$ units through additional bridging Ag–O bonds (see Figure S1 in the Supporting Information).
[24] The lack of ethanol uptake by crystals of **3** may in part be related to the fact that the fluoroalkyl chains are more closely packed than in **2**.
[25] The relationship between the unit cells of **1** and **2** does not involve a simply tripling of one unit cell axis. Owing to the change in translational symmetry along the coordination tapes resulting from ethanol loss, use of the unit cell vectors from **1** to describe a unit cell in **2** would require tripling of all three unit cell axes and result in a nonprimitive triclinic cell of 27 times the volume of that in **1**. The primitive cell of **2** is, however, only approximately 3 times the volume of that in **1** but requires a different choice of unit cell vectors such that the tapes lie along the ⟨001⟩ vector in **1**, whereas they lie along the ⟨12−1⟩ vector in **2**. The relationship between the two unit cells is explored in greater detail in the Supporting Information.
[26] a) A related mechanism involving alkyl-group motions has been proposed for the uptake of gas molecules by crystalline *p*-*t*Bu-calix[4]arene in one of its polymorphs, which although contain-

ing void spaces is nonporous. Guest molecules in these crystals remain confined by dispersion forces and no subsequent covalent bond breaking or formation is involved; b) see J. L. Atwood, L. J. Barbour, A. Jerga, B. L. Schottel, *Science* **2002**, *298*, 1000; c) S. J. Delgarno, P. V. Thallapally, L. J. Barbour, J. L. Atwood, *Chem. Soc. Rev.* **2007**, *36*, 236.

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