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Solid-State Structural Transformations of Two Ag^I Supramolecular Polymorphs to Another Polymer upon Absorption of HNO_3 Vapors

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Supporting Information

ABSTRACT: Solid-state structural transformation of two polymorphic forms of $[Ag(8\text{-}HqH)(8\text{-}Hq)]_n$ (**1*α*** and **1*β***, where 8-HqH = 8-hydroxyquinoline and 8-Hq$^-$ = 8-hydroxyquinolate) to $\{[Ag(8\text{-}HqH)_2]NO_3\}_n$ (**2**) has been observed upon solid–gas reaction of compounds **1*α*** and **1*β*** with HNO_3 vapors. Solid–gas reaction of compound **2** with hydrated vapors of NH_3 results in the formation of only the **1*β*** polymorph, while solid–solid reaction of compound **2** with KOH results in the formation of a **1*α*** and **1*β*** mixture with chiral and achiral space groups of $P2_12_12_1$ and *Pbcn*, respectively.

The utilization of intermolecular interactions that generate specific supramolecular motifs has greatly enhanced the systematic approach to both the understanding and design of highly organized molecular arrays in solids.[1] Intermolecular hydrogen bonding and ionic or dipolar interactions have been the most widely employed "directional forces" in this context.[2] In addition to the above-mentioned intermolecular interactions, in silver(I) supramolecular chemistry, similar to thallium(I) supramolecular chemistry,[3] other secondary interactions such as Ag···C, Ag···Ag, and Ag···H also exist that distinguish silver(I) supramolecular polymers from other supramolecular compounds.[4] To develop further our understanding of supramolecular architecture, it is challenging to continue the investigations on the solid-state structural transformations involving coordination polymers and supramolecular networks.[5] In a continuation of studies of supramolecular compounds,[6] in this report we isolated two polymorphs of $[Ag(8\text{-}HqH)(8\text{-}Hq)]_n$ (**1*α*** and **1*β***, where 8-HqH = 8-hydroxyquinoline and 8-Hq$^-$ = 8-hydroxyquinolate) that do novel solid-state structural transformations to $\{[Ag(8\text{-}HqH)_2]NO_3\}_n$ (**2**) by absorption HNO_3 vapors. Because of amphoteric behavior, compounds **1*α*** and **1*β*** are good candidates for studies of the acid/base transformations in the solid state. Similar transformations were observed by Braga et al. in a zwitterionic sandwich complex of $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^1\text{-}C_5H_4COO)]$, which undergoes reversible gas–solid reaction with the hydrated vapors of acids (e.g., HCl, CF_3COOH, CCl_3COOH, CHF_2COOH, $HBrF_4$, and HCOOH) and bases (e.g., NH_3, NMe_3, and NH_2Me) as well as solid–solid reactions with crystalline salts (e.g., KBr, RbBr, CsBr, NaI, and CsI).[7] Compound $[Ag(8\text{-}HqH)(8\text{-}Hq)]_n$ crystallized in at least two different polymorphic forms. These forms have been identified since 1962 by their different powder X-ray diffraction patterns, yet there is no conclusive report on these forms.[8] One form (**1*β***) was crystallographically characterized by Ma et al. in 2006 and refined in space group *Pbcn*.[9] Another form (**1*α***) is reported by us (see the Supporting Information, SI). These polymorphs convert to **2** upon absorption of HNO_3 vapors (Figure 1). Figure S10 in the SI shows the structures of the basic building blocks of compounds **1*α***, **1*β***, and **2**.

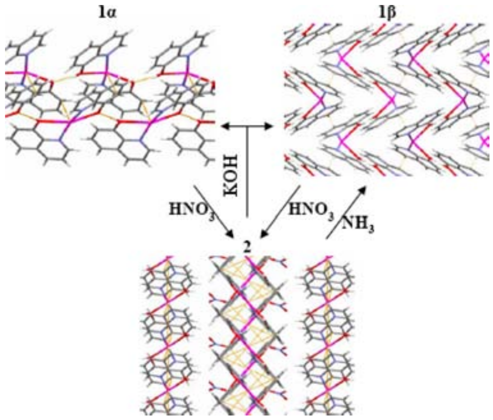

Figure 1. Schematic diagram illustrating the dynamic structural conversions of compounds **1*α*** and **1*β*** to a supramolecular network of **2** by solid–gas and solid–solid reactions. Color code: Ag, violet; O, red; N, blue; C, gray; H, white.

Single-crystal X-ray diffraction analysis (Tables S2 and S3 in the SI) of compound **1*α*** shows that the complex is a chiral one-dimensional supramolecular network, as illustrated in Figure 1. 8-Hydroxyquinoline acts as a bidentate chelating ligand with two forms of protonated (8-HqH) and deprotonated (8-Hq$^-$) ligands. The Ag^I ions in **1*α*** are coordinated by two N and two O atoms of 8-HqH and 8-Hq$^-$ ligands (Figure S10a in the SI). Our search shows that the Ag^I ions in compound **1*α*** may also be involved in an η^1 interaction with the phenyl group of neighboring [Ag(8-HqH)(8-Hq)] units (Figure S11a in the SI). Thus, the Ag^I coordination sphere is completed, and rather than a AgN_2O_2 coordination sphere, the complex could be considered to contain an $O_2N_2Ag\cdots C$ coordination sphere with a Ag···C distance of 3.199 Å. A π–π stacking[10] interaction between the parallel aromatic rings of adjacent units is also observed in **1*α*** (Figure S12a in the SI). The mean molecular planes are close to parallel and are separated by a distance of ~3.7 Å, close to that of the planes in graphite.[10,11] The existence of a moderate electrostatic hydrogen-bonding network between O3(8-Hq$^-$)

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and H2W(8-HqH) with bond distances of 1.681 Å (Figures 1 and S12a in the SI), η^1-Ag···C interactions (Figures 1 and S11a in the SI), and π–π stacking (Figure S12a in the SI) in **1*α*** results in the formation of a one-dimensional supramolecular network. In the other polymorphic form (**1*β***), the Ag^I ion is located on a 2-fold axis and chelated by two 8-HqH and 8-Hq^- molecules with distorted tetrahedral geometry.[9] This achiral polymorph (**1*β***) forms a three-dimensional supramolecular network, which could be observed along the *b* axis in Figure 1. The Ag^I ions in **1*α*** are coordinated by two N and two O atoms of 8-HqH and 8-Hq^- ligands (Figure S10b in the SI). The Ag^I complexes in **1*β*** were linked to each other via hydrogen bonding to form a supramolecular chain structure (Figure S12b in the SI).[9] Our search shows that the Ag^I ions in compound **1*β*** may also be involved in two η^1 interactions with the phenyl group of neighboring [Ag(8-HqH)(8-Hq)] units (Figure S11b in the SI). Thus, the complex could be considered to contain an $O_2N_2Ag{\cdots}C_2$ coordination sphere with a Ag···C distance of 3.358 Å. No π–π stacking interaction exists in **1*β***. The crystals of **1*α*** and **1*β*** turned black (probably because of the surface corrosive nature of HNO_3 after conversion of both polymorphs to compound **2** in the presence of extra HNO_3 vapors) upon exposure to diluted HNO_3 fumes for 5 h and were not suitable for single-crystal X-ray crystallography. Both of them have similar PXRD patterns, with some differences in peak intensities, which differed from those of **1*α*** and **1*β*** (Figure S3 in the SI). In this solid–gas reaction, in addition to HNO_3 vapors, various forms of nitric oxides including NO_2 formed from decomposition of HNO_3. Thus, in addition to the reaction of HNO_3 vapors with **1*α*** and **1*β*** polymorphs, the reaction between water droplets that formed on the surface of compounds **1*α*** and **1*β*** with NO_2 gas, which exists in the enclosed vessel of the reaction, results in the formation of compound **2**. It should be mentioned that similar reactions of both polymorphs with HCl vapors result in the formation of AgCl, which is due to the strong affinity of the Ag^I ion toward chloride ions in the presence of the 8-HqH coordinating ligand (Figures S4 and S5 in the SI).

Single crystals of compound **2** were obtained from another reaction (Figure S3 in the SI). The structure determination of **2** by X-ray crystallography (Tables S2 and S4 in the SI) showed that one HNO_3 molecule was added to each [Ag(8-HqH)(8-Hq)] unit. Two types of Ag^I ions exist in **2**, Ag1 and Ag2. The coordination number in **2** is 4, and each Ag^I ion is coordinated by two N and two O atoms of two 8-HqH ligands (Figure S10c in the SI). The bond angles of **2** are different from the bond angles of **1*α*** and **1*β***. Compound **2** has O–Ag–O and N–Ag–N bond angles of 180°, and the Ag^I ions have square-planar coordination geometry, but these bond angles are 158.18 and 162.48° in compound **1*α*** and 93.6 and 157.2° in compound **1*β***. Thus, HNO_3 absorption of **1*α*** and **1*β*** results in the formation of **2** with regular square-planner geometry around Ag^I ions. Again a search for Ag···C approaches indicates that Ag atoms in compound **2** may also be involved in $2\eta^2$ interactions with the two phenyl groups of neighboring $[Ag(8\text{-HqH})_2]^+$ units (Table S5 in the SI). Thus, each Ag^I ion has short interactions with four C atoms of two neighboring phenyl groups (Figure S13 in the SI), and rather than an AgN_2O_2 coordination sphere, the Ag^I ions could be considered to contain a tetrahapto center with an $O_2N_2Ag{\cdots}C_4$ coordination sphere. These $2\eta^2$-Ag···C interactions result in the formation of parallel chains in **2** (Figure 1). The distance of Ag···C interactions observed in these three compounds (Table S5 in the SI) is less than the sum of the van der Waals radii for Ag and C atoms (3.42 Å).[12] Some other silver(I) polycyclic aromatic polymeric complexes containing weak Ag–C(sp^2) bonds with a mean Ag–arene distance of 2.82–3.37 Å have been reported.[13] With this level of data (Table S2 in the SI), it really is not possible to conclude anything about the protonation state of the ligand (i.e., to locate H atoms), but the charge balance of compound **2**, after entrance of a NO_3^- anion to the structures of **1*α*** and **1*β***, needs protonation of the 8-Hq^- ligand in $[Ag(8\text{-HqH})(8\text{-Hq})]_n$. On the other hand, the appearance of a very broad band at the frequency range of 2200–3500 cm^{-1} in the IR spectrum (Figure S9 in the SI) indicates that protonation of the 8-Hq^- ligand in **2** has occurred and probably the hydrogen-bonding network exists in **2**. In this solid-state structural transformation, the coordination bond rearrangement for the Ag–N and Ag–O bonds occurs and any new bond is not formed (Tables S3 and S4 in the SI). Indeed a monohapto interaction in **1*α*** and two monohapto interactions in **1*β*** were substituted with two weaker dihapto interactions in compound **2** (Figure 2 and Table S5 in the SI). As could be observed from PXRD patterns (Figure S14 in the SI), when we did the solid–gas reaction of compound **2** with hydrated vapors of NH_3, only the **1*β*** polymorph was obtained, while by solid–solid reaction of compound **2** crystals with KOH, a mixture of **1*α*** and **1*β*** was formed (Figures 1 and 2).

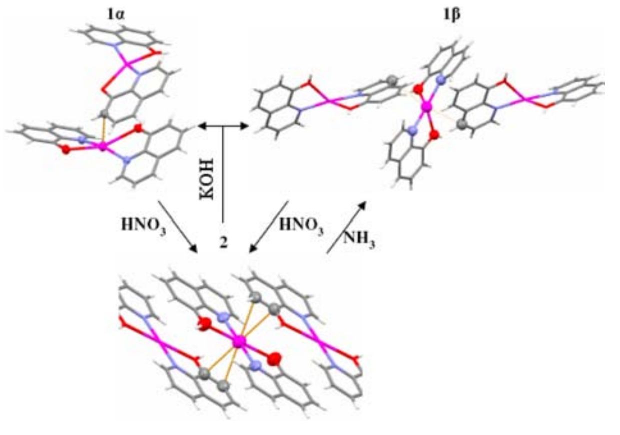

Figure 2. Schematic representation of the solid-state structural transformations of compounds **1*α*** and **1*β*** to compound **2** by solid–gas and solid–solid reactions, showing a coordination bond rearrangement around Ag^I ions. Color code: Ag, violet; O, red; N, blue; C, gray; H, white.

Compound **1*α*** was only observed in a mixture when refluxed filtrate was evaporated (see the SI), and we could not obtain a purified precipitate of the **1*α*** polymorph in order to study of nanostructural morphology during the mentioned transformations. The large amount of precipitate obtained during reflux reaction was characterized to be the *β* form by matching PXRD patterns (Figure S1 in the SI). In order to study the morphology and size of compound **1*β*** nanostructures during transformation to compound **2**, four samples were prepared by microwave-assisted syntheses[14] (see the SI). Figure 3a shows a SEM image of **1*β***, which indicates the formation of a mixture from microrods and nanoparticles. When sample **1*β*b** undergoes a solid–gas reaction with HNO_3 vapors, compound **2** nanostructures (sample **2**b) were formed. Figure S6b in the SI shows the IR spectrum of sample **2**b, which is different from sample **1*β*b** (Figure S6a in the SI) and approved the formation of **2** nanostructures. This solid–gas reaction of compound **1*β*** powder was tested by three other samples with different morphologies (Figures S16–S18a,b in the SI). In each case, different

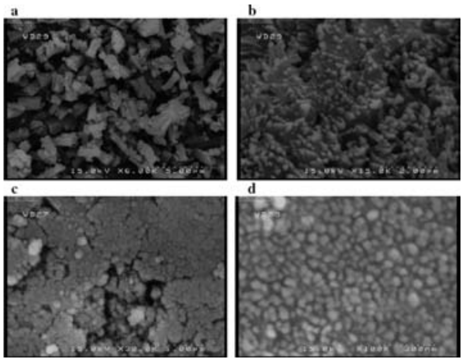

Figure 3. SEM images of (a) compound **1***β* (sample **1***β*b) prepared by a microwave-assisted process, (b) compound **2** (sample **2**b) prepared from gas–solid reaction of HNO_3 vapors with sample **1***β*b, (c) a mixture of compound **1***α* and **1***β* nanoparticles prepared from solid–solid reaction of sample **2**b with KOH, and (d) compound **1***β* nanoparticles prepared from gas–solid reaction of NH_3 hydrated vapors with sample **2**b.

morphologies of compound **2** with comparison to samples **1***β*a, **1***β*c, and **1***β*d were formed. Similar results were observed in our recent work.[6,15] As we mentioned, this transformation was not reversible by HNO_3 desorption, but we could obtain compound **1***β* nanostructures from sample **2**b, **2**c, and **2**d by solid–gas reaction of these samples with hydrated vapors of NH_3. Solid–solid reaction of compound **2** nanostructures with KOH was also performed. Parts c and d of Figure S6 in the SI show the IR spectra of the resulting samples from solid–solid and gas–solid reactions of sample **2**b, which are similar to the IR spectrum of sample **1***β*b (Figure S6a in the SI). Parts c and d of Figure 3 show the SEM images of a mixture of compound **1***α* and **1***β* nanoparticles and compound **1***β* nanoparticles, obtained from the reaction of sample **2**b with KOH and NH_3, respectively. Similar results observed from these solid–solid and solid–gas reactions of other **2**a, **2**c, and **2**d samples (Figures S16–S18c,d in the SI).

In summary, solid-state structural transformation of two polymorphs, **1***α* and **1***β*, has been observed to **2**, upon solid–gas reaction of compounds **1** with HNO_3 vapors. Solid–gas reaction of compound **2** with hydrated vapors of NH_3 forms only the **1***β* polymorph, while solid–solid reaction of compound **2** with KOH forms a mixture of **1***α* and **1***β* with chiral and achiral space groups $P2_12_12_1$ and *Pbcn*, respectively. Probably in the presence of KOH, because of its higher base strength in comparison with hydrated vapors of NH_3, a mixture of two thermodynamically stable (**1***β*) and unstable (**1***α*) products were formed. The morphology and size of compound **2** nanostructures are different from those of compound **1***β*. This phenomenon could possibly be related to a change in color, crystal system, and space group of compound **1***β* during the solid-state structural transformation to compound **2**.[16]

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format and full synthetic and analytical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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