View Article Online / Journal Homepage / Table of Contents for this issue

Published on 30 January 2007. Downloaded by University of Chicago on 25/10/2014 05:22:17.

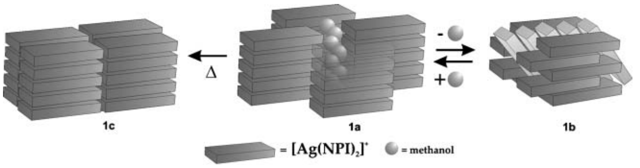
Single-crystal to single-crystal phase transitions of bis(*N*-phenylisonicotinamide)silver(I) nitrate reveal cooperativity properties in porous molecular materials†

Partha S. Mukherjee,[a] Nazario Lopez,[b] Atta M. Arif,[c] Francisco Cervantes-Lee[b] and Juan C. Noveron*[b]

Received (in Austin, TX, USA) 13th November 2006, Accepted 9th January 2007
First published as an Advance Article on the web 30th January 2007
DOI: 10.1039/b616502h

Two single-crystal to single-crystal phase transitions in *trans*-[Ag(NPI)$_2$](NO$_3$)·2CH$_3$OH (1a), (NPI = *N*-phenylisonicotinamide) were characterized with X-ray crystallography; the first transition is reversible and arises from a desolvation transition induced by vacuum and generated 1b; the second transition was induced by heat at 140 °C and generated 1c.

Recent progress in crystal engineering has expanded into understanding the relationship between single-crystal structure and structural dynamism with respect to non-covalent interactions.[1–12] Of particular interest are phase transitions of porous materials because of their implications to numerous applications such as separation science, catalysis, sensing, and gas storage.[6–12] Recently, it was demonstrated that open channels in solids are not necessarily a requirement for the solid to behave as a porous material. Dynamic cooperativity in the ensemble may transport guest molecules into the crystal matrix, even in the absence of traditional open channels.[13–15] This new paradigm for what is a porous material is intriguing and represents a new facet in crystal engineering that could play a role in functional materials design. Here we report two single-crystal to single-crystal phase transformations of a porous crystalline material derived from [AgL$_2$]NO$_3$, where L = *N*-phenylisonicotinamide (NPI), studied with single-crystal X-ray crystallography and differential scanning calorimetry (DSC). The first transition was induced by vacuum and involves a desolvation/solvation process in which the pores of the crystalline framework close and open reversibly, and the second transition was induced by heat and generated an irreversible thermodynamically stable crystal phase, Scheme 1.



Scheme 1

The NPI ligand was made by the stoichiometric reaction of isonicotinic acid chloride, aniline and triethylamine in chloroform. The Ag-complex was prepared by slow evaporation of a mixture of the nitrate salt of Ag(I) and NPI in methanol over two days to yield a crystalline batch (93%) of product. Single-crystal X-ray crystallographic studies and elemental analysis revealed structure **1a**, Scheme 1, with the molecular formulation of *trans*-[Ag(NPI)$_2$](NO$_3$)·2CH$_3$OH.[17a]

The supramolecular structure of **1a** exhibits channels (8 Å in diameter) filled with methanol molecules along the *a*-axis, Fig. 1. There are four types of hydrogen bonds in the unit cell of which two are between the ligand and solvent in the form of N–H(amide)···O(methanol) and O=C(amide)···HO(methanol) with average distances of 2.88 and 2.86 Å, respectively, and between adjacent methanol molecules (2.73 Å), and NPI with nitrate ions *via* N–H(amide)···O(nitrate), 2.99 Å. The average distance between the nearest Ag centers is 3.31 Å, which is significantly longer than other crystals with suspected Ag–Ag interactions such as silver acetate (2.79 Å).[18] The average distance between Ag(I) and the nearest nitrate ion is 2.64 Å. The bond angle of N(1)–Ag–N(3) is 158°, which is smaller than those present in analogous Ag-complexes (169°).[19] Despite the expected planar structure of NPI, **1a** reveals that the ligand twist half way forming a torsion angle at C(2)–C(3)–C(6)–N(2) of 45° and its homologous in the same complex of 31°, presumably induced by the hydrogen bonds and the crystal packing forces.

When single crystals of **1a** are placed under vacuum (0.1 Torr) for 2 h a new metastable crystal phase (**1b**) was observed *via* single-crystal X-ray crystallography, Fig. 2.[17b] The formulation of this crystal phase is *trans*-[Ag(NPI)$_2$](NO$_3$), which lacks solvent and the channels that once held the methanol molecules are closed, apparently, *via* an orchestrated rearrangement of alternate layers of the Ag-complex that rotate counter-clockwise by 63° towards the *a*-direction. Unlike **1a**, pairs of Ag-complexes in **1b** interact *via* two complementary N–H(amide)···O=C(amide) hydrogen bonds that have an average distance of 2.91 Å. Additionally, the nitrate ions bridge adjacent pairs of Ag-complexes *via* hydrogen bonds with N–H(amide)···O(nitrate) average distance 2.94 Å, and their average distances to Ag centers are 2.80 and 2.68 Å. Interestingly, there are no significant changes in the torsion angles of the NPI moieties (<2°), but the bond angle of N(1)–Ag–N(3) changed to 173°. In addition, face-edge interactions between phenyl moieties of NPI are observed. The crystal phase **1b** may be described as a metastable pseudo-polymorph of **1a**.[20]

The phase transition of **1a** → **1b** was examined with DSC and an endothermic ΔH value of 7.3 ± 0.2 kJ mol^{-1} was obtained at

---

[a] *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, 560012, India*
[b] *Department of Chemistry, University of Texas at El Paso, El Paso, TX, 79968-0513, USA. E-mail: jcnoveron@utep.edu; Fax: (915)747-5748; Tel: (915) 747-7572*
[c] *Department of Chemistry, University of Utah, Salt Lake City, UT, 87764, USA*

† Electronic supplementary information (ESI) available: Crystallographic data of **1a–c** and detailed experimental preparations. See DOI: 10.1039/b616502h

Published on 30 January 2007. Downloaded by University of Chicago on 25/10/2014 05:22:17.

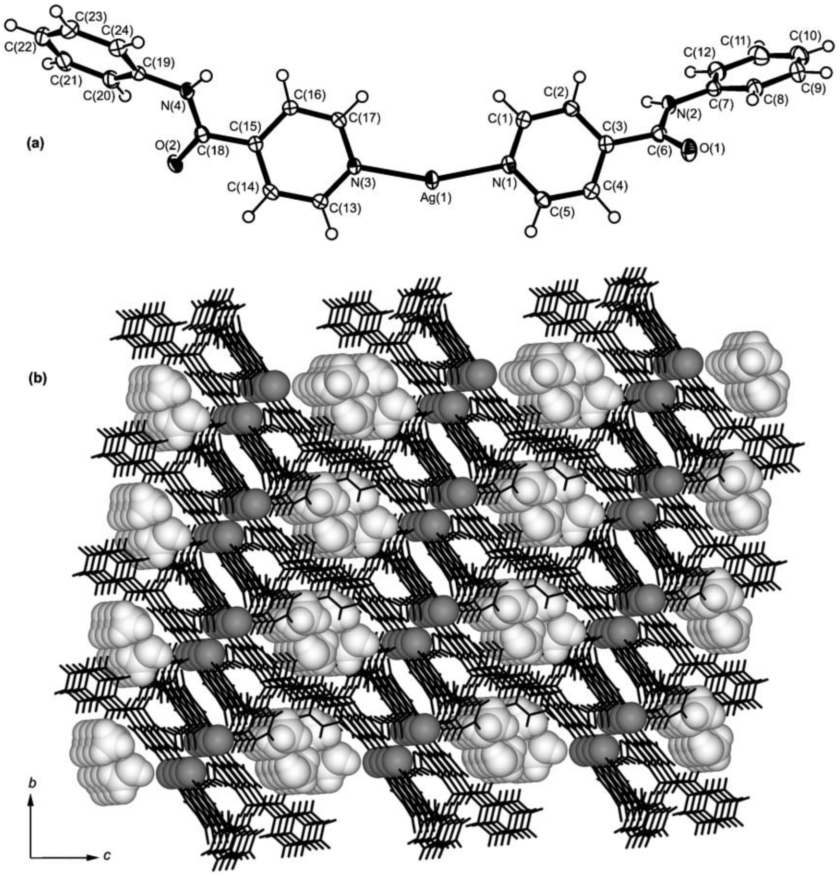


Fig. 1 (a) Thermal ellipsoid plot (probability level 50%) of $[Ag(NPI)_2]^-$. (b) Expanded unit cell of **1a** as viewed from the *a*-direction. Methanol and Ag shown as CPK.

305 K. When crystals of **1b** are exposed to methanol, they revert back to phase **1a**, as indicated by X-ray powder diffraction and elemental analysis. Similar solvent-driven reversible transformations have been observed in other systems. Although the crystalline phase of **1b** lacks any imminent porosity, the fact that it can take up methanol to reconstitute **1a** suggests a well-orchestrated mechanism reminiscent of cooperativity dynamics. This behavior is consistent with other recent crystals that lack porosity, but yet they are able to incorporate guest molecules into their lattice *via* cooperativity effects.[14–16]

When crystals of either **1a** or **1b** are heated slowly (5 °C min^{-1}) to higher temperatures, there is a second phase change around 453 K with an endothermic ΔH value of 16.5 ± 0.3 kJ mol^{-1}. This new phase change also occurs with the preservation of the single-crystal quality of the material forming a new crystal phase, **1c**,[17c] with molecular formula *trans*-$[Ag(NPI)_2](NO_3)$, Fig. 3. Single-crystal X-ray crystallography studies on **1c** revealed that the Ag-complexes interact primarily *via* π–π stacking interactions and pack in columns along the *c*-axis. The nitrate ions hydrogen bond

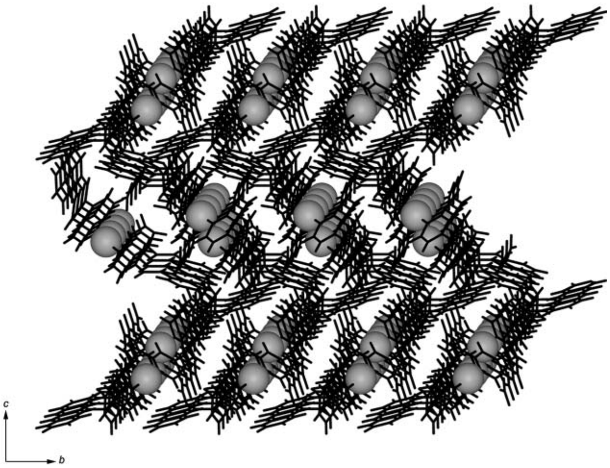


Fig. 2 Expanded unit cell of **1b** as viewed from the *a*-direction.

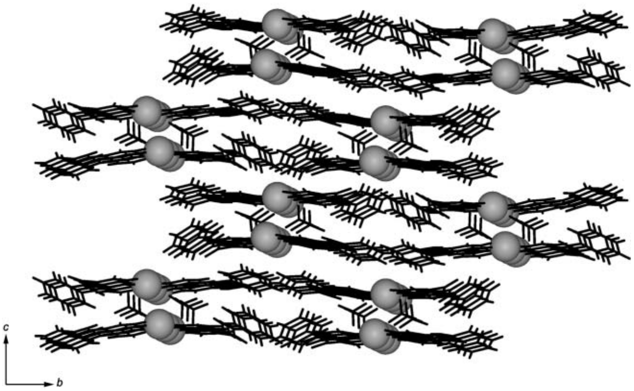


Fig. 3 Expanded unit cell of **1c** as viewed from the *a*-direction.

Published on 30 January 2007. Downloaded by University of Chicago on 25/10/2014 05:22:17.

to the columnar Ag-complexes *via* N–H(amide)···O(nitrate), (2.92 Å). The NPI ligand moieties become more planar on one side of the complex, which exhibits a torsion angle C(16)–C(15)–C(18)–N(4) of 4° (*vs.* 45° in **1a**), while the other side undergoes little change (33°). On the other hand, no significant changes occur in the bond angle of N(1)–Ag–N(3) ($<2°$). In contrast to **1b**, crystalline samples of **1c** do not uptake methanol and with further heating decompose above 270 °C.

In summary, we reported the single-crystal to single-crystal phase transformations of the Ag-complex **1a** to the pseudopolymorphic phases **1b** and **1c**, which were induced by vacuum and by heat, respectively. The results indicated that each phase transition was accompanied by changes in intermolecular hydrogen bonding and π–π stacking interactions, which may have played a role in orchestrating the structural changes in the crystal lattice and maintaining single-crystal quality. The study of phase transformations in designed crystals will eventually lead to practical materials with flexible and dynamic frameworks that can switch their structure upon external stimuli with well-defined molecular motions in the solid state.

We gratefully acknowledge Prof. Peter J. Stang for helpful discussions and Prof. Charles A. Wight for assistance with the DSC. Financial support for N. L. by the Border Health Research Fund from the University of Texas at El Paso is gratefully acknowledged.

References

1 J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.
2 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311–2327.
3 P. H. Dinolfo and J. T. Hupp, *Chem. Mater.*, 2001, **13**, 3113–3125.
4 S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109–119.
5 B. Moulton and M. J. Zawarotko, *Chem. Rev.*, 2001, **101**, 1629–1658.
6 O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703–706.
7 J. P. Zhang, Y. Y. Lin, W. X. Zhang and X. M. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 14162–14163.
8 T. K. Maji, G. Mostafa, R. Matsuda and S. Kitagawa, *J. Am. Chem. Soc.*, 2005, **127**, 17152–17153.
9 S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.*, 2002, **124**, 2568–2583.
10 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148–1150.
11 C.-H. Hu and U. Englert, *Angew. Chem., Int. Ed.*, 2005, **44**, 2281–2283.
12 L. Iordanidis and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2000, **122**, 8319–8320.
13 M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725–1727.
14 J. L. Atwood, L. J. Barbour, A. Jerga and B. L. Schottel, *Science*, 2002, **298**, 1000–1002.
15 J. C. Noveron, A. M. Arif and P. J. Stang, *Chem. Mater.*, 2003, **15**, 372–374.
16 C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158–5168.
17 (*a*) *Crystal data* for **1a**: C_{26} $H_{28}N_5O_7Ag$, $M_r = 630.40$, colorless plates of dimensions 0.30 × 0.25 × 0.05 mm, triclinic, space group $P\bar{1}$, $a = 8.72340(10)$, $b = 9.6897(3)$, $c = 16.9513(5)$ Å, $\alpha = 74.6602(12)$, $\beta = 76.7586(16)$, $\gamma = 76.8878(16)°$, $V = 1323.80(6)$ Å^3, $Z = 2$, $D_c = 1.582$ Mg m^{-3}. A total of 9546 reflections were measured, of which 5982 were unique. Final residuals were $R1 = 0.0283$ and $wR2 = 0.0614$; (*b*) *Crystal data* for **1b**: $C_{24}H_{20}N_5O_5Ag$, $M_r = 566.32$, colorless plates of dimensions 0.25 × 0.25 × 0.08, monoclinic, space group $P2_1/c$, $a = 12.7187(6)$, $b = 8.4330(2)$, $c = 21.2767(9)$ Å, $\beta = 98.2743(17)°$, $V = 2258.32(15)$ Å^3, $Z = 4$, $D_c = 1.666$ Mg m^{-3}. A total of 9388 reflections were measured, of which 5111 were unique. Final residuals were $R1 = 0.0371$ and $wR2 = 0.0703$; (*c*) *Crystal data* for **1c**: $C_{24}H_{20}N_5O_5Ag$, $M_r = 566.32$, colorless plates of dimensions 0.25 × 0.10 × 0.10, monoclinic, space group $P2_1/c$, $a = 8.8731(10)$, $b = 36.1311(5)$, $c = 13.9696(2)$ Å, $\beta = 93.3705(5)°$, $V = 4470.83(10)$ Å^3, $Z = 8$, $D_c = 1.683$ Mg m^{-3}. A total of 19602 reflections were measured, of which 10777 were unique. Final residuals were $R1 = 0.0414$ and $wR2 = 0.0747$. The data for all structures were collected at 150(1) K on a Nonius Kappa CCD diffractometer equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å). Structure refinements by full-matrix least-squares on F^2 and Fourier Transform techniques and location of hydrogen atoms and their isotropically refinement was done using SHELXTL-97 (Bruker-AXS, Inc. Madison, WI). Further crystallographic data can be obtained from the ESI.† CCDC 627373–627375. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616502h.
18 L. P. Olson, D. R. Whitcomb, M. Rajeswaran, T. N. Blanton and B. J. Stwertka, *Chem. Mater.*, 2006, **18**, 1667–1674.
19 J. C. Noveron, M. S. Lah, R. E. Del Sesto, A. M. Arif, J. S. Miller and P. J. Stang, *J. Am. Chem. Soc.*, 2002, **124**, 6613–6625.
20 J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press/Clarendon Press, New York/Oxford, 2002.