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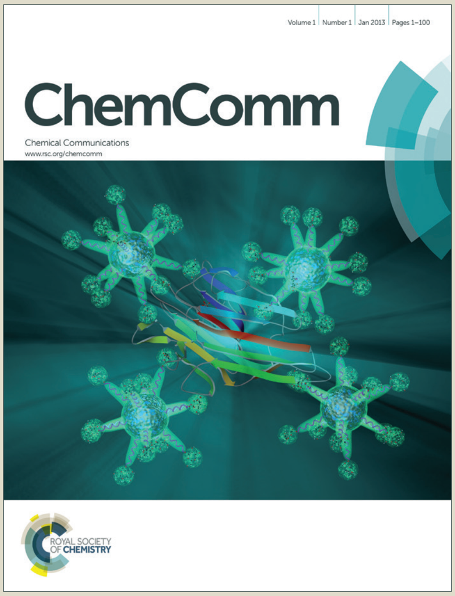

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Dimensionality Changes in Solid Phase at Room Temperature: 2D→1D→3D Evolution Induced by Ammonia Sorption/desorption on Zinc Phosphates

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$NH_4Zn_2(PO_4)(HPO_4)$ (1) two-dimensional zinc phosphate, *via* ammonia vapor interaction at room temperature, transforms to $NH_4Zn(NH_3)PO_4$ (2) one-dimensional novel compound. By ammonia desorption (in air at room temperature) 2 transforms to NH_4ZnPO_4 (3) with a well-known ABW-zeolitic topology. The crystal structure of 2 was solved *ab initio* using synchrotron powder X-ray diffraction data (monoclinic, $P2_1/a$, a = 16.5227(2) Å, b = 6.21780(8) Å, c = 5.24317(6) Å, β= 91.000(2)°, Z = 4). The structures of three compounds include extra-framework ammonium cations to the 4-fold coordinated zinc (ZnO_4 tetrahedra for 1 and 3, and ZnO_3N tetrahedra for 2) and phosphorus (PO_4 tetrahedra) with bi-, mono- or three-dimensional linkages, respectively for 1, 2 or 3. To our knowledge, the process described here constitutes the first example of dimensionality change in solid phase promoted by a solid-gas interaction at room temperature in metal phosphates.

In the past years, a great variety of metal phosphates with fascinating structures of different dimensionalities have been synthesized and characterized. The relationship among the structures of different dimensionalities is considered an aspect of great relevance in understanding the formation of these fascinating architectures. Four-membered ring metal phosphates, which we can consider to be zero-dimensional (0D) monomers, have also been isolated,[1] and there is reason to believe that 0D or 1D structures act as the basic units (SBU) in the building up process.[2,3] Among the hierarchy of metal phosphates, zinc phosphates occupy an apical position. Thus, zinc phosphates with zero-, one-, two-, and three-dimensional structures have been prepared and characterized.[4-7] The transformations of zinc phosphates from low to high dimensional structures have been studied extensively.[1,7-9] Thus, careful studies show that the 0D monomers transform to 1D, 2D, and 3D structures. The 1D ladder structures transform to 2D and 3D structures, while the 2D structures transform to 3D structures but also to 1D. This last fact appears that the transformation of 2D layers to 3D structures is a complex process, quite possibly involving the formation of 1D intermediate. Therefore, it was of great importance to study whether the 2D layers transform to 3D structures.[9] All these transformations take place under hydrothermal conditions in the presence of organic amines, suggesting that the 4-membered rings play the role of a SBU in the building up process. In order to investigate further these structural changes, Rao *et al.*[10] studied the transformation of a 4-memebered ring zinc phosphate to a sodalite-related-3D structure through a linear chain structure at relatively low-temperatures under non-hydrothermal conditions, showing that the 1D to 3D transformation takes place in solid-state, although dissolution (involving hydrolysis) and recrystallization occur during the process.

$NH_4Zn_2(PO_4)(HPO_4)$ (**1**) has been previously obtained as a sub-product from hydrothermal synthesis.[11] The structure of compound **1** is layered with respect to zinc-phosphorus-oxygen connectivity (Figure 1a). Both Zn and P atoms adopt tetrahedral coordination. Six of the eight unique O atoms form bicoordinate Zn–O–P bridges, one O atom is trigonally coordinated, and the remaining O atom forms part of the terminal P–OH bond. The polyhedral connectivity of the tetrahedral units results in corrugated anionic layers of stoichiometry $[Zn_2(PO_4)(HPO_4)]^-$. Extra-layer NH_4^+ cations complete the crystal structure of **1**.

Later, our group reports the synthesis of compound **1** as a single-phase product and its evolution during the reaction with *n*-alkylamine vapors to obtain $(C_nH_{2n+1}NH_3)ZnPO_4{\cdot}xH_2O$ (n = 1–6) compounds.[12] However, when ammonia is used, the hypothetical $NH_4ZnPO_4{\cdot}xH_2O$ layered compound is not obtained.

In this paper, we describe the transformation of compound **1** to a novel one-dimensional compound $NH_4Zn(NH_3)PO_4$ (**2**) in presence of ammonia vapors at room temperature (see Supporting Information). The crystal structure of **2** was solved *ab initio* using synchrotron powder X-ray diffraction data (see Supporting Information). Its structure (Figure 1c) is characterized by zinc phosphate chains of composition $[Zn(NH_3)PO_4]^-$. The charge comp-

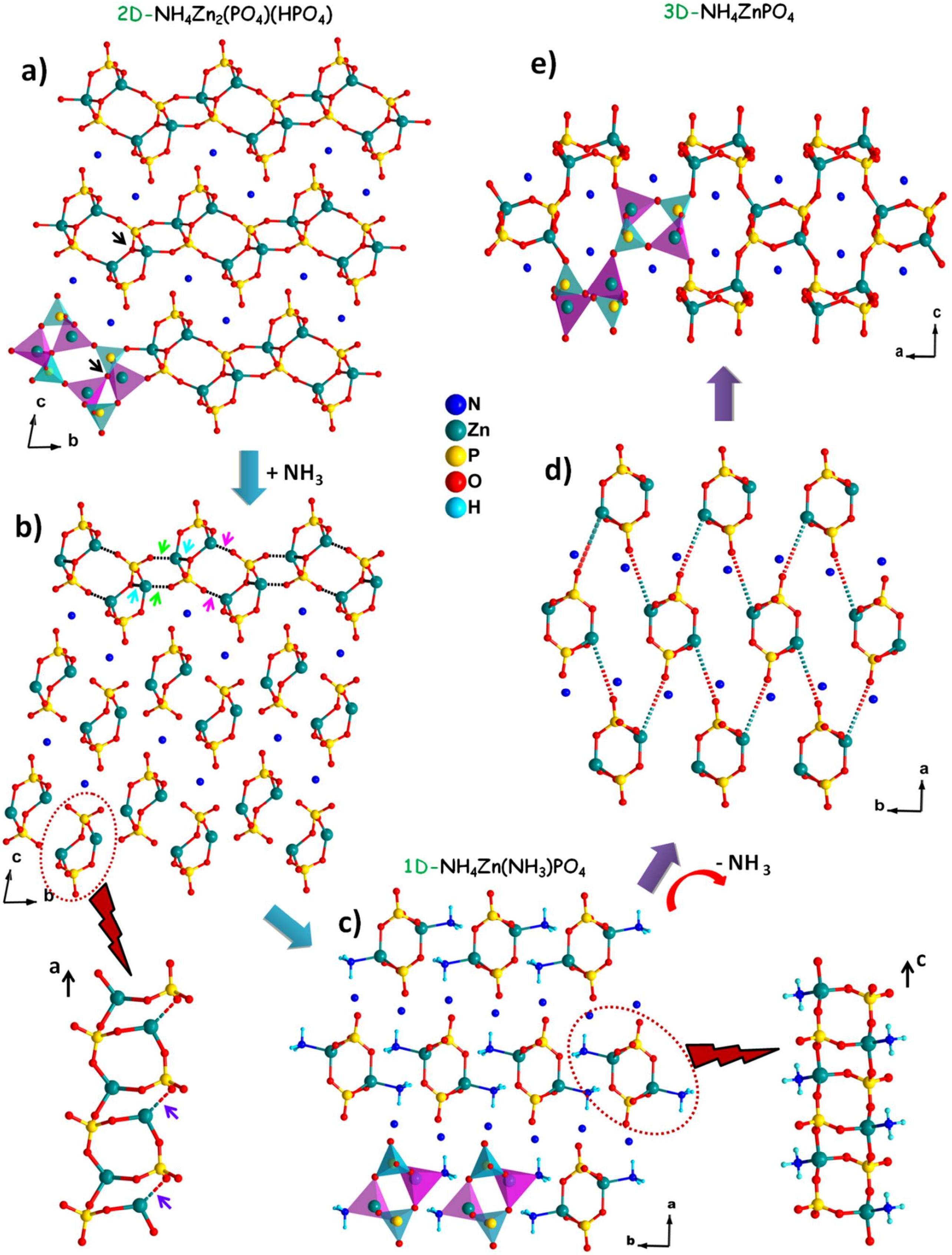
2D-$NH_4Zn_2(PO_4)(HPO_4)$
3D-NH_4ZnPO_4
a)
e)
c
b
c
a
N
Zn
P
O
H
+ NH_3
b)
d)
c
b
a
b
a
1D-$NH_4Zn(NH_3)PO_4$
- NH_3
c)
c
a
b

Figure 1. Perspective view of: a) 2D-$(NH_4)Zn_2(PO_4)(HPO_4)$ (**1**), black arrows show the trigonal oxygen atoms; b) Evolution of **1** induced by NH_3 sorption with the formation of isolate chains, dashed lines highlight the break of Zn–O(P) bonds in the *ab*-plane and the formation of new Zn–O(P) bonds along *a*-axis; c) 1D-$NH_4Zn(NH_3)PO_4$ (**2**) highlights the formation of an unusual bond between a NH_3 and zinc atoms; d) Structural transformation of **2** induced by desorption of NH_3, dashed lines highlight the formation of new Zn–O(P) bonds; e) 3D-NH_4ZnPO_4 (**3**). See that the SBU (highlighting 4-membered ring) is preserved in all process.

ensation is achieved by the presence of ammonium cations. The zinc atoms are coordinated by three oxygen atoms from three equivalent phosphate groups, and one nitrogen atom from ammonia to complete its tetrahedral coordination environment. The strictly alternating ZnO_3N and PO_4 tetrahedra by sharing their vertices form four-membered rings, which in turn form double chains by sharing their edges. Compound **2** is a new member of the rare family of solids containing both NH_4^+ cations and coordinated NH_3 molecules,[13-17] where the existence of $ZnO_3(NH_3)$ tetrahedra has only been recently reported in $NH_4Zn_4(NH_3)(PO_4)_3$.[17] By ammonia desorption, compound **2** slowly evolves (in air at room temperature) to NH_4ZnPO_4 (**3**). This process is rapidly completed under vacuum and/or soft heating (see Supporting Information). Compound **3** has a three-dimensional structure with zeolite ABW topology (Figure 1e) being built from negatively charged $[ZnPO_4]^-$ framework balanced by the extra-framework ammonium cations.[18]

The proposed mechanism for structural transformations from **1** to **3** is illustrated in Figure 1. In presence of ammonia vapors, **1** transforms to **2** by causing the break of Zn–O(P) bonds in the *ab*-plane and the formation of new Zn–O(P) bonds along *a*-axis (illustrated by dashed black and red-green bonds, respectively, in Figure 1b). However, similar SBUs (4-membered rings) are maintained like in **1** (Figure 1c). First, the nucleophilic attack by NH_3 into Zn atoms provokes the change in the zinc tetrahedral environment, from ZnO_4 to ZnO_3N, by the break of, among other, Zn–O(P) bond of trigonal oxygen atoms (see cyan and pink arrows in Figure 1b). Later, the break of third Zn–O(P) bond in the *ab*-plane and establishing new Zn–O(P) bond along *a*-axis (see green and violet arrows, respectively, in Figure 1b), leads to the formation of completely isolate infinite chains. Finally, the rearrangement of the isolate infinite chains due the sorption of more ammonia as NH_4^+ cations leads to **2**. Structural transformation from **2** to **3** is induced by desorption of NH_3, in which new Zn–O(P) bonds are established connecting every isolate infinite chain to four neighboring chains (see dashed red-green bonds in Figure 1d) due to the change of zinc environment from ZnO_3N to ZnO_3, Later, the rearrangement of the bonded-chains and NH_4^+ cations leads to **3**, in this case the SBUs are preserved (see Figure 1e).

Thermal evolution of **2** to **3** was monitored by synchrotron radiation X-ray powder diffraction (see Supporting Information). Figure 2 shows the evolution of powder diffraction patterns from room temperature up to 160 ºC. At room temperature, two well defined peaks were observed at 2θ 11.32º and 16.14º which corresponded, respectively, to the (2,0,0) and (1,1,0) reflections of **2**. Also, a very low intensity peak was observed at 2θ 15.20º, which correspond to the (1,0,1) reflection of **3**, shown that **2** slowly decompose in air at room temperature (**2** can be preserved in ammonia atmosphere). At higher temperatures the intensities of the two reflections corresponding to **2** decreased while the reflection of **3** increased as a consequence of the structural change. The maximum intensities of these three Bragg reflections are measured at each temperature. These values are converted to extent of reaction (α), scaled from zero to one, using the relationship $\alpha(t) = [I_{hkl}(t) - I_{hkl}(t{=}0)] / [I_{hkl}(t{=}t_f) - I_{hkl}(t{=}0)]$, where $I_{hkl}(t)$ is the area of a given peak at time t, and $I_{hkl}(t{=}0)$ is the area at the initial time and $I_{hkl}(t{=}t_f)$ is the final area. The results are shown in Figure S2. As can be seen, the conversion of the structural transformation is closed to zero below 90 ºC, later increases exponentially with the temperature.

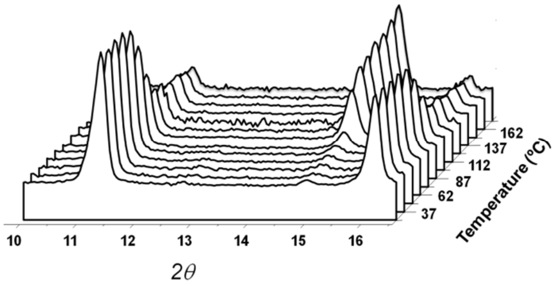

Figure 2. X-ray thermodiffractograms of **2** recorded as a function of temperature.

In conclusion, the trigonally coordinated oxygen atom in the layered structure of compound **1** (see Figure 1a) is the key point. At room temperature, the nucleophilic attack by ammonia into all metal centers provokes the change in the zinc tetrahedral environment, from ZnO_4 to ZnO_3N, and the concomitant transformation from a layered structure to one-dimensional order, with the formation of a unusual bond between ammonia molecules and zinc atoms (Figure 1c) (such M-NH_3 bonding is reported only for other three metal phosphates:[14,17,19] $NH_4VO(NH_3)PO_4$, $Fe(NH_3)PO_4$, and $NH_4Zn_4(NH_3)(PO_4)_3$). Finally, the novel 1D-compound slowly transforms into a zeolite-type material. To our knowledge, the process described here constitutes the first example of dimensionality changes in solid phase promoted by a solid-gas interaction at room temperature in the field of metal phosphates.

Notes

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Electronic Supplementary Information (ESI) available: [Synthesis, experimental procedures, details on the crystal structure of **2**, and cif file of **2**. This material is available free of charge via the Internet at http://pubs.rsc.org/]. See DOI: 10.1039/c000000x/

References

1 C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj, A. A. Ayi, *Acc. Chem. Res*., 2001, **34**, 80.
2 G. Ferey, *Chem. Mater*., 2001, **13**, 3084.
3 R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja, C. N. R. Rao, *Chem. Rev*., 2008, **108**, 3549.
4 C. N. R. Rao, S. Natarajan, S. Neeraj, *J. Solid State Chem*., 2000, **152**, 302.
5 S. Natarajan, S. *Solid State Sci*., 2005, **7**, 1542.
6 S. Mandal, S. Natarajan, *Inorg. Chim. Acta,* 2004, **357**, 1437.
7 A. Choudhury, S. Natarajan, C. N. R. Rao, *Inorg. Chem.,* 2000, **39**, 4295.
8 A. J. Norquist, D. O'Hare, *J. Am. Chem. Soc*., 2004, **126**, 6673-6679.
9 A. Choudhury, S. Neeraj, S. Natarajan, C. N. R. Rao, *J. Mater. Chem.,* 2002, **12**, 1044.
10 M. Dan, D. Udayakumar, C. N. R. Rao, *Chem. Comm*., 2003, **2212**.
11 Z. Bircsak, W. T. A. Harrison, *Acta Crystallogr*., 1998, **C54**, 1383.
12 B. Ramajo, A. Espina, S. A. Khainakov, J. R. García, *J. Incl. Phenom. Macro*., 2004, **49**, 241.
13 M. Harel, C. Knobler, J. D. McCullough, *Inorg. Chem.,* 1969, **8**, 11.
14 B. M. Gatehouse, L. W. Guddat, *Acta Crystallogr.,* 1987, **C43**, 1445.
15 H. Headlam, M. A. Hitchman, H. Stratemeier, J. M. M. Smits, P. T. Beurskens, E. de Boer, G. Janssen, B. M. Gatehouse, G. B. Deacon, G. N. Ward, M. J. Riley, D. Wang, *Inorg. Chem.,* 1995, **34**, 5516.
16 D. Fratzky, H. Worzala, T. Goetze, M. Meisel, *Acta Crystallogr.* 1999, **C55**, 156.
17 L. Karanovic, D. Poleti, T. Dordevic, S. Sutovic, *J. Solid State Chem.* 2011, **184** , 2506.
18 X. H. Bu, P. Y. Feng, T. E. Gier, G. D. Stucky, *Zeolites* 1997, **19**, 200.
19 M. A. Salvadó, P. Pertierra, S. García-Granda, A. Espina, C. Trobajo, J. R. García, *Inorg. Chem.* 1999, **38**, 5944.