

# Ionic bonding driven unusual crystal growth of tubular organic nitrate salts†

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**We report the unusual crystal growth of 10–15 cm long tubular anilinium nitrate salts. The tubes resemble the bamboo structure, in which each shoot is 100–200  $\mu\text{m}$  in length and around 10  $\mu\text{m}$  in diameter. This growth is observed after mixing aniline and aluminium nitrate  $[\text{Al}(\text{NO}_3)_3]$  in methanol.**

Inorganic nitrate salts are commonly used in agriculture and high energy materials research. These compounds are well studied in the literature for their ferroelectric behaviour and phase transitions. Surprisingly, organic nitrate salts are scarcely reported. The standard method of nitration is to treat the compound with concentrated or dilute nitric acid. Here, we report the use of a milder synthetic route for nitration, that is the use of aluminium nitrate  $[\text{Al}(\text{NO}_3)_3]$ . When aniline is treated with  $\text{Al}(\text{NO}_3)_3$  in methanol, a translucent gel is obtained. The gel, on standing for a few hours in an open atmosphere, gave unusual white hair-like crystal growth of 10–15 cm. Even though the formation of aluminium hydroxide is expected during the reaction of  $\text{Al}(\text{NO}_3)_3$  and the base, the observed growth was found to be anilinium nitrate ( $\text{AnHNO}_3$ ). The white hair crystals show bamboo-like growth. This process also yielded rosette shaped alumina from starting aluminium nitrate. We present a detailed investigation of this growth using solid-state NMR, DSC, powder X-ray diffraction and SEM techniques.

Recently, studies on polymorphism<sup>1</sup> and different structural modifications of the same chemical compound, have generated a lot of interest in applied as well as basic research. The occurrence of polymorphic modification in the compounds is manifested not just as a consequence of minimum free energy of the crystalline phases but also by crystal nucleation and growth.<sup>2</sup> On the other hand, alumina has been a subject of interest due to its potential applications in catalysis,<sup>3</sup> adsorptive/separation materials,<sup>4</sup> and optical applications.<sup>5</sup>

The motivation of the present work lies in our attempts to grow crystals in porous solids, especially for layered organic–inorganic hybrid compounds for multiferroic behaviour.<sup>6</sup> The literature has shown that mesoporous/nanoporous alumina can be synthesized using a gel of  $\text{Al}(\text{NO}_3)_3$  or  $\text{AlCl}_3$  in the presence of a proton acceptor.<sup>7</sup> We thought aniline could act as a good proton acceptor source. Therefore, aniline was added directly into the methanolic solution of  $\text{Al}(\text{NO}_3)_3$  (3 : 1 molar ratio). This yielded a translucent gel. The gel was filtered and kept aside. To our surprise, white, hair-like crystals developed from it after 1 h, growing up to 10–15 cm long in about 8–10 h, as shown in Fig. 1. This growth is observed only using  $\text{Al}(\text{NO}_3)_3$  as a substrate<sup>8</sup> and not for  $\text{AlCl}_3$  or other simple salts of

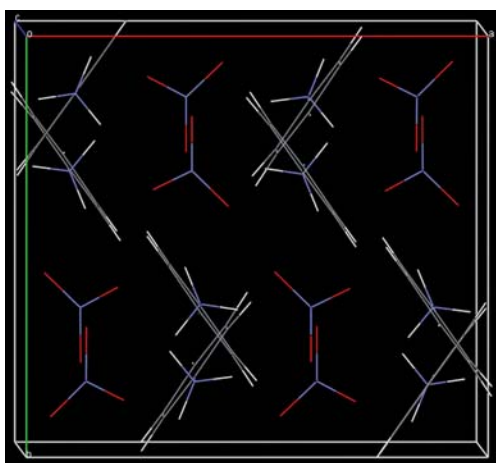
aluminium. The observed crystals showed a signature of presence of anilinium nitrate ( $\text{AnHNO}_3$ -I) by liquid state NMR, and FT-IR spectroscopy. Unfortunately,  $\text{AnHNO}_3$ -I crystals were too thin for single-crystal X-ray analysis. That means that in this system,  $\text{Al}(\text{NO}_3)_3$  is acting as a source of nitrate anion, an environmentally friendly nitrating reagent. Normally, concentrate or diluted  $\text{HNO}_3$  is used to make nitrate salts. Thus, anilinium nitrate was synthesized by treating aniline with concentrated  $\text{HNO}_3$ . In the latter case, we obtained very good quality sugar-like crystals ( $\text{AnHNO}_3$ -II). Single-crystal X-ray analysis of  $\text{AnHNO}_3$ -II at room temperature, shows that it crystallizes in orthorhombic system having space group *Pbca* (no. 61),  $Z = 8$ ,  $a = 10.158(2)$ ,  $b = 9.277(2)$ ,  $c = 16.177(3)$  Å.<sup>9</sup> The primitive unit cell contains eight molecules of anilinium nitrate. Mono-protonated anilinium cation interacts through weak hydrogen bonds with three neighbouring nitrate anions. There are six  $\text{N}\cdots\text{O}$  hydrogen bonds, which, can be divided in two groups. One group of three bonds with similar lengths equal to 2.81, 2.86 and 2.88 Å, gives average value equals 2.85 Å. Three other hydrogen bonds with lengths 3.13, 3.17 and 3.20 Å constitute the second group with average value of lengths equal to 3.17 Å. These two groups of  $\text{N}\cdots\text{O}$  hydrogen bond distances corresponds to essentially linear or bent  $\text{N}\cdots\text{O}$  interactions, respectively. These  $\text{N}\cdots\text{O}$  hydrogen bonds helps alternately stacked and mutually perpendicular anilinium cations to form a chain along the crystallographic *c* axis, as shown in Fig. 2. The calculated powder X-ray pattern of  $\text{AnHNO}_3$ -II from powder crystal X-ray diffraction data matches well with the  $\text{AnHNO}_3$ -I see Fig. 3. Both these compounds have largely similar powder X-ray diffraction patterns. Powder X-ray diffraction data, obtained from single-crystal X-ray data, show that  $\text{AnHNO}_3$ -II has one major peak at  $22.1^\circ 2\theta$ , which was indexed to the 212 plane. The corresponding plane is also observed in  $\text{AnHNO}_3$ -I. Apart from this very strong peaks at  $19$  and  $28^\circ 2\theta$  were observed for  $\text{AnHNO}_3$ -I, which were indexed for the 020 and 302 planes. Even though latter peaks were present in  $\text{AnHNO}_3$ -II, their intensities were quite less. Apart from this, the major differences in both the compounds are the presence of 301 plane and absence of 204, 023, and 114 planes for  $\text{AnHNO}_3$ -I. The small difference in the indexed cell parameters for



Fig. 1 Crystal growth of  $\text{AnHNO}_3$ -I from the gel on filter paper after 8 h.

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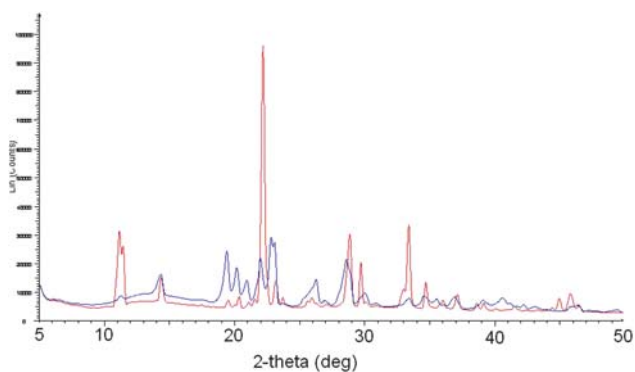
† Electronic supplementary information (ESI) available: Solid-state NMR, powder X-ray data, single-crystal X-ray data and SEM images. See DOI: 10.1039/b920059b



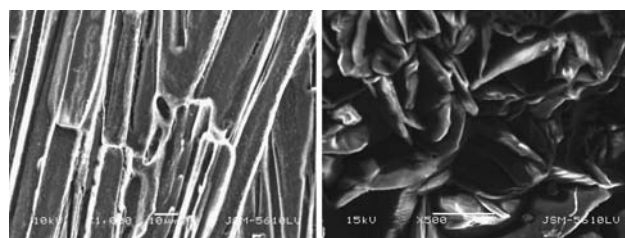
**Fig. 2** Room-temperature structure of AnHNO<sub>3</sub>-II, showing alternately stacked anilinium cations held together by nitrate anions forming mutually penetrating chains.

these two compounds, and large difference in the relative intensities of the peaks, made it difficult to classify them as polymorphs or unusual habits (see ESI)<sup>†</sup> and therefore, we are presently investigating this in more detail. Liquid-state NMR spectra for both the compounds were similar. Therefore solid-state <sup>13</sup>C CP MAS NMR was carried out, which showed three peaks at 130.9, 127, and 122 ppm for AnHNO<sub>3</sub>-II, while an additional shoulder at 130 ppm was observed for AnHNO<sub>3</sub>-I. FT-IR spectra for both the compounds were largely similar, only minor difference were observed at  $\nu_{\text{stretch}}\text{NH}\cdots\text{O}$  band around 2934 cm<sup>-1</sup> and NH $\cdots$ O in-plane deformation mode around 1384 cm<sup>-1</sup>.

An SEM study on AnHNO<sub>3</sub>-I shows that these hair-like crystals are tubes with diameters of *ca.* 10  $\mu\text{m}$ , and lengths of *ca.* 100–200  $\mu\text{m}$ , see Fig. 4 (left). These small tubes resemble bamboo shoots, as they pack above each other to give a total length of 10–15 cm, which looks like a bamboo tree. The presence of pores on the tubes helped us to identify the porous nature and hence the diameter of these tubes. EDAX measurements have shown the presence of nitrogen only on the outer wall of these hollow crystals. That means the inside of the hollow cylinder is hydrophobic. We observed hair-like crystal growth only for *para*-substituted aniline derivatives. That means *meta*- and



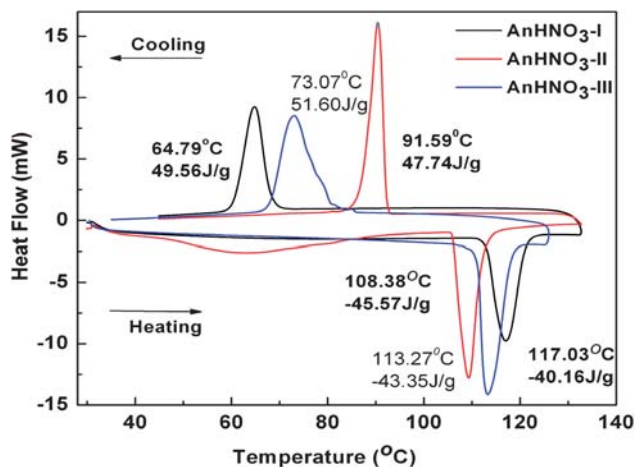
**Fig. 3** Powder X-ray diffraction spectra for AnHNO<sub>3</sub> compounds; red line = II; blue line = I. The powder X-ray pattern (blue line) is calculated from the single-crystal X-ray structure.



**Fig. 4** SEM photograph showing (left) bamboo type structure for AnHNO<sub>3</sub>-I and (right) rosette shaped porous alumina.

*ortho*-substitution makes growth hindered due to steric reasons. The growth was also observed for pyridine derivatives, but not for pyrrole. Surprisingly, in all these compounds only electron donating groups at the *para* position gave hair-like crystal growth. The growth also depends upon the rate of evaporation of the solvent, which indicates a kinetically controlled mechanism. This is why gels prepared with methanol were grown with much higher density than ethanol. Interestingly, gels prepared using water as a solvent gave growth of hair-like crystals (AnHNO<sub>3</sub>-I), sugar-like crystals (AnHNO<sub>3</sub>-II) and thin plates (AnHNO<sub>3</sub>-III), a case similar to concomitant polymorphism.<sup>10</sup> As such, polymorph discovery and formation usually rely on the manipulation of conventional process variables such as solvent, temperature, additives, and crystallization rate, and more recently, substrates that regulate heterogeneous nucleation.<sup>11</sup> All these crystals of anilinium nitrate are monotropic<sup>12</sup> in nature, because AnHNO<sub>3</sub>-I and AnHNO<sub>3</sub>-III convert to AnHNO<sub>3</sub>-II when recrystallized using different solvents.

DSC measurements on AnHNO<sub>3</sub>-I have shown that it has endothermic transition at 117.03 °C while heating and an exothermic transition at 64.79 °C while cooling, as shown in Fig. 5. It is interesting to note that the hysteresis width for this transition in AnHNO<sub>3</sub>-I is quite large as compared to the other two crystals, as shown in Table 1. The hysteresis study using DSC on the same sample was repeated at least eight times, but no observable change was observed for peak position as well as energy involved. This shows the reversibility of this order–disorder transition. This is in accordance with the powder X-ray diffraction study and TG-DTA study. Powder X-ray diffraction pattern for AnHNO<sub>3</sub>-I, virgin and heated



**Fig. 5** DSC thermogram of AnHNO<sub>3</sub> crystals.

**Table 1** DSC measurements on crystals of AnHNO<sub>3</sub>

Compounds	Scanning rate/°C m <sup>-1</sup>	Peak position/°C (E/J g <sup>-1</sup> )		Hysteresis/°C
		Heating	Cooling	
AnHNO <sub>3</sub> -I	10	117.03 (-40.16)	64.79 (49.56)	52.24
AnHNO <sub>3</sub> -II	10	108.38 (-45.57)	91.59 (47.74)	16.78
AnHNO <sub>3</sub> -III	10	113.27 (-43.35)	73.07 (51.60)	40.20

samples were almost similar but differs from AnHNO<sub>3</sub>-II, as mentioned above (see ESI).† TG-DTA study shows no mass loss until 150 °C, continues small mass change is observed between 150 °C to 220 °C. KNO<sub>3</sub> and NaNO<sub>3</sub> are inorganic analogues of these organic salts, and have shown ferroelectric behaviour. Along with this, DSC studies on these compounds shows that the energy involved in the endothermic transition is much less than the energy released during the exothermic transition, which can make them candidates for phase change materials.

The growth of AnHNO<sub>3</sub> leaves behind hard cocoon shaped (about 1–2 cm long and 0.5 cm thick) particles. An SEM image, (Fig. 4, right) exhibits the surface of these cocoons, resembling rosette minerals. They look like hard, refractory type materials. These cocoons were then washed with methanol and dried at 70 °C. The obtained white crystalline precipitates showed that they have average pore diameters of 2–20 μm using a mercury porosimeter. Powder X-ray diffraction and solid-state <sup>27</sup>Al NMR study on these cocoons showed the signature for alumina. We are presently involved in their detailed study. Since the reaction is kinetically driven,<sup>13</sup> we think that strong Lewis acidity provided by the exposed aluminium ions will be uniform, and can act as an ideal support for heterogeneous catalysis. On this basis, probable mechanism for overall growth can occur in two steps (a) nitrate ion gets attracted toward the anilinium cation formed in the gel by breaking bonding with aluminium cation (competitive ionic bonding), (b) slow crystallization of AnHNO<sub>3</sub> (in bamboo type growth of ~10 μm) due to aerial evaporation leaving rosette alumina at the bottom with average pore size of 2–20 μm). Thus, on this basis, formation of rosette shaped alumina and bamboo type structures of AnHNO<sub>3</sub> can be correlated.

Thus, we have demonstrated a novel route for forming nitrate salts of organic compounds in an environmentally friendly procedure. The salts show unusual crystal growth patterns, with hollow, bamboo-type tubes forming at 10–15 cm in length. The simplicity, versatility, and reproducibility of this synthetic approach will facilitate the development of newer ways for crystal growth of technologically important organic nitrate salts and probably new types of metal

oxides. The present work also highlights the use of simple gel-mediated generation of different morphologies.

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