

# Crystallization of Ammonium Nitrate from Nonaqueous Solvents<sup>1</sup>

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Although ammonium nitrate is at best sparingly soluble in typical organic solvents, it may be readily solubilized through the addition of chelating agents such as crown ethers and polyethylene glycols. With suitable choice of solvent and chelating agent, addition of a precipitating solvent leads to the crystallization of uncomplexed ammonium nitrate from such solutions. Crystalline ammonium nitrate obtained through this process of “complexation-mediated crystallization” displays a variety of morphologies, with the crystal form dependent on the nature of both the solvent and the chelating agent.

## Introduction

Ammonium nitrate is the most important commercial ammonium salt, with worldwide production on the order of 50–75 million metric tons per year.<sup>2</sup> Although used primarily as an agricultural fertilizer, a significant proportion is also used in the production of nonmilitary explosives used, for example, in coal and other mining and in quarrying and highway construction.<sup>3</sup> Recently, ammonium nitrate has also received attention as a potentially effective oxidizer for rocket and missile propulsion systems.<sup>4,5</sup> Despite the large-scale utilization of ammonium nitrate, this salt exhibits a number of undesirable properties. Its extremely high solubility in water generally precludes preparation through simple crystallization as a viable option, and most commercial processes resort to prilling<sup>6</sup> or related granulation processes,<sup>7–9</sup> requiring subsequent drying and/or processing steps. Recrystallized ammonium nitrate displays poor crystal form, and even a special vacuum crystallization process<sup>10</sup> was not competitive with prilling techniques due to its formation of only small crystals. In addition, although no discrete hydrates of ammonium nitrate are known, the salt is highly hygroscopic, compromising its effectiveness as an explosive and leading to agglomeration of particles.<sup>3</sup> Finally, five crystalline polymorphs of ammonium nitrate are known (Table 1).<sup>11</sup> The phase transition between phases III and IV is particularly problematic in that it occurs at close to ambient storage temperature (ca. 32 °C). Because significant solid-state reorganization occurs in the course of this phase transition, repeated cycling between phases III and IV leads to degradation of the physical state of ammonium nitrate, a process ultimately leading to “sugaring” (powdering).<sup>2,3</sup>

Since the serendipitous discovery that cyclic polyethers can serve as effective agents for the solubilization of salts in nonaqueous solvents,<sup>12</sup> the preparation and crystallization of countless crown ether complexes has been reported.<sup>13–15</sup> Seldom reported, however, are those cases in which attempted crystallization results in precipitation of the uncomplexed salt. This potentiality, first noted by Pedersen in his pioneering accounts,<sup>12,16</sup> is particularly problematic in the case of salts with high lattice energy (e.g., carbonates, fluorides). Rather than

**Table 1. Ambient Pressure Phases of Ammonium Nitrate<sup>a</sup>**

phase designation	range of stability (°C)	crystal system	space group
I	125.2–169.6	cubic	Pm3m
II	84.2–125.2	tetragonal	P42 <sub>1</sub> m
III	32.2–84.2	orthorhombic	Pnma
IV	–18 to 32.2	orthorhombic	Pmmn
V	less than –18	orthorhombic	Pccn

<sup>a</sup> From data provided in refs 2, 3, and 45.

viewing this as a problem, however, we view it as an opportunity to explore the recrystallization of salts from solvents in which they would ordinarily be insoluble. It is well-known that the nature of the crystallization solvent can and often does exert a dramatic influence on the crystal form of organic compounds.<sup>17,18</sup> Thus, we anticipate comparably dramatic effects on the crystal form of salts crystallized from unusual solvents through the intermediacy of soluble complexes, a process we have termed complexation-mediated crystallization.<sup>19,20</sup> As we report herein, we have successfully crystallized ammonium nitrate from a variety of organic solvents by this technique, with the nature of the crystalline salt indeed very much dependent on the nature of the crystallization solvent.

## Experimental Section

**Reagents.** All reagents were used as received from the following sources: ammonium nitrate, J. T. Baker (New Jersey), 18-crown-6, Acros Organics (New Jersey), and 15-crown-5 and polyethylene glycol derivatives, Aldrich Chemical Co. (Milwaukee, WI).

**18-Crown-6-Mediated Crystallization of Ammonium Nitrate.** Ammonium nitrate (0.040 g, 0.5 mmol) and 18-crown-6 (0.13 g, 0.5 mmol) were suspended in 6 mL of the desired solvent (see text for discussion) in a glass test tube and ultrasonicated in a standard laboratory ultrasonic cleaning bath until dissolution appeared complete. Any undissolved solid was removed by filtration. Crystallization was effected by either layering the precipitating solvent (see text for discussion) carefully onto the surface of this solution or by vapor diffusion of the precipitating solvent into the solution, effected by sealing an open vial containing the solution into a bottle containing a comparable volume of the precipitating solvent. When crystallization appeared complete, the product was isolated by filtration.

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**15-Crown-5-Mediated Crystallization of Ammonium Nitrate.** Crystallization was carried out as described above, using 1.0 mmol of ammonium nitrate and up to 2 equiv of 15-crown-5 in 10 mL of solvent.

**Polyethylene Glycol-Mediated Crystallization of Ammonium Nitrate.** Crystallization was carried out as described above, using the following quantities of ammonium nitrate, PEG-300, and solvent: 1.17 mmol of  $\text{NH}_4\text{NO}_3$ , 11.7 equiv of PEG-300, 10 mL of nitrobenzene (decanting from some undissolved  $\text{NH}_4\text{NO}_3$ ); 0.50 mmol of  $\text{NH}_4\text{NO}_3$ , 10.1 equiv of PEG-300, 5 mL of  $\text{CH}_3\text{CN}$ ; 0.50 mmol of  $\text{NH}_4\text{NO}_3$ , 20.6 equiv of PEG-300, 5 mL of  $\text{CH}_2\text{Cl}_2$  (decanting from some undissolved  $\text{NH}_4\text{NO}_3$ ); 0.50 mmol of  $\text{NH}_4\text{NO}_3$ , 10.3 equiv of PEG-300, 5 mL of acetone; 0.50 mmol of  $\text{NH}_4\text{NO}_3$ , 19.4 equiv of PEG-300, 5 mL of  $\text{CHCl}_3$  (decanting from some undissolved  $\text{NH}_4\text{NO}_3$ ).

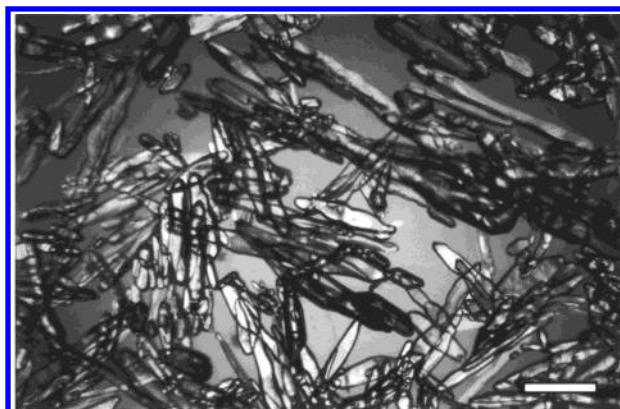
**Analysis.** Samples were ground to powders and analyzed by X-ray powder diffraction, using a Scintag XDS 2000 diffractometer ( $\text{Cu K}\alpha$  source). Selected samples were analyzed by differential scanning calorimetry using a TA Instruments TA9000 calorimeter equipped with a 910DSC cell.

## Results and Discussion

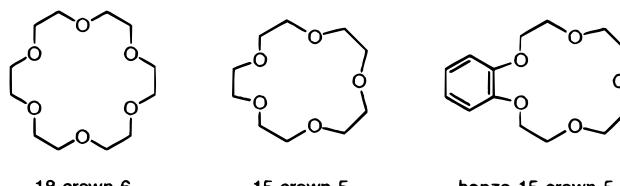
Simple macrocyclic polyethers ("crown ethers") such as 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) can form rather stable complexes with ammonium salts,<sup>21</sup> with reported formation constants up to ca.  $10^4$  for 18-crown-6 in methanol.<sup>22</sup> Substituted ammonium salts (e.g., monoalkylammonium salts) are also complexed efficiently by crown ethers and other related macrocyclic chelating agents, and given the central role such ammonium salt–crown ether complexes have played in numerous molecular recognition studies, the structural details of these complexes have received considerable attention.<sup>23–25</sup> In this vein, we have recently reported the synthesis and structural analysis of a series of ammonium nitrate complexes of 18-crown-6 and related crown ethers.<sup>26</sup> In the course of these studies, however, we found that certain solvent combinations resulted in crystallization not of ammonium nitrate complexes but of phase IV ammonium nitrate itself. This led us to examine the recrystallization of ammonium nitrate from a variety of nonaqueous solvents, mediated by the formation of soluble complexes, with the goal of gaining control over the crystal form of this important commodity salt.

Recrystallization of ammonium nitrate by slow evaporation of aqueous solutions affords poorly formed needles (Figure 1). This material displays appreciable hygroscopicity and tends to clump together upon exposure to ambient temperatures and humidity. In marked contrast, crystallization from ethanolic solutions containing a stoichiometric amount of 18-crown-6 (Figure 2) through the addition of diethyl ether as a precipitating solvent rapidly affords long (up to ca. 2.5 cm or greater) and well-formed needles (Figure 3). Presumably as a result of the higher crystal quality, this material displays negligible hygroscopicity, visibly remaining dry, and undergoing no degradation of crystal quality or clumping even after many months of exposure to ambient laboratory conditions.

Given the critical role of the near-ambient temperature IV–III phase change in the deterioration of solid ammonium nitrate upon prolonged storage, a variety of studies aimed at kinetically delaying its onset have



**Figure 1.** Photomicrograph of ammonium nitrate recrystallized from water. Bar = 500  $\mu\text{m}$ .



**Figure 2.** Chelating agents used for solubilization of ammonium nitrate in nonaqueous solvents.



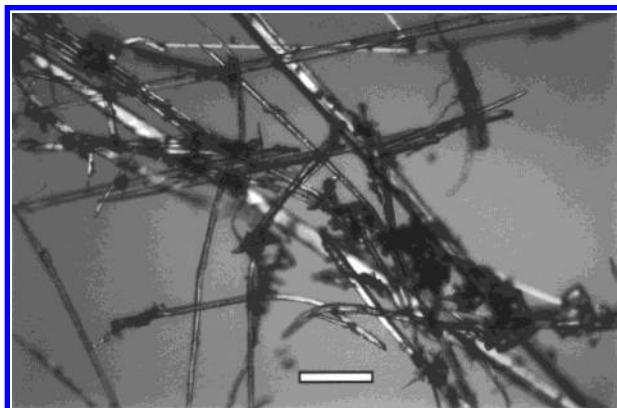
**Figure 3.** Photomicrograph of ammonium nitrate recrystallized from EtOH/18-crown-6/Et<sub>2</sub>O. Crystal length = ca. 2 cm.

been reported. Incorporation of additives, including magnesium nitrate,<sup>27</sup> nitric acid,<sup>28</sup> aluminum(III) salts,<sup>27,29</sup> or a variety of proprietary additives,<sup>30</sup> can provide some measure of kinetic stabilization of phase IV. The thermal interconversions of the various phases of ammonium nitrate, particularly phases II, III, and IV, are also well-known to be quite dependent on water content.<sup>31–33</sup> It has been shown that the IV–III phase change is kinetically sluggish in anhydrous ammonium nitrate, so that routine thermal analysis frequently displays only the IV–II transition.<sup>34</sup> Introduction of increasing amounts of water kinetically reintroduces the IV–III phase change, with the temperature of its onset dependent on the extent of hydration. Importantly, and in accord with these earlier observations regarding the role of water in kinetically controlling the phase transitions of ammonium nitrate, differential scanning calorimetric (DSC) analysis of the ammonium nitrate crystallized from ethanol/diethyl ether reveals a significant delay of the IV–III phase transition, to ca. 40–45 °C.

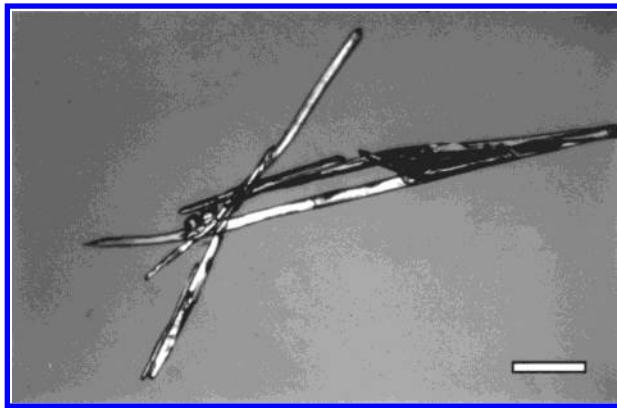
The amount of 18-crown-6 used to facilitate the dissolution of ammonium nitrate in ethanol must be



**Figure 4.** Photomicrograph of ammonium nitrate recrystallized from acetonitrile/15-crown-5//benzene. Bar = 100  $\mu\text{m}$ .

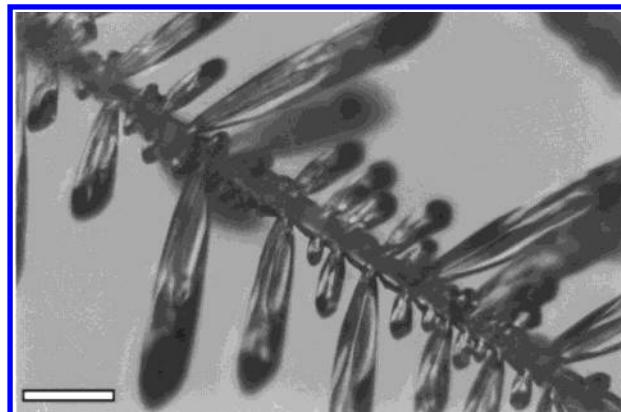


**Figure 5.** Photomicrograph of ammonium nitrate recrystallized from acetonitrile/PEG-300//toluene. Bar = 500  $\mu\text{m}$ .

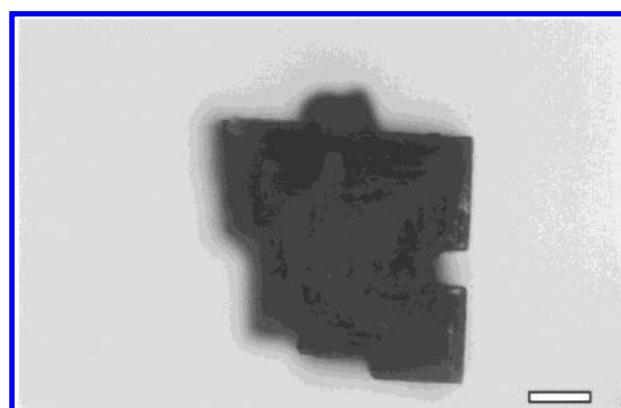


**Figure 6.** Photomicrograph of ammonium nitrate recrystallized from dichloromethane/PEG-300//toluene. Bar = 500  $\mu\text{m}$ .

controlled carefully to avoid formation of crystalline complexes of 1:1 stoichiometry, the nature of which are discussed elsewhere. Thus, whereas use of 0.3 equiv of 18-crown-6 allows the successful recrystallization of ammonium nitrate, use of 0.5 equiv affords a mixture of ammonium nitrate and a complex with 18-crown-6. Not surprisingly, use of 1 or more equiv of the crown ether results in the clean formation of the complex.<sup>26</sup> Crystallization of 18-crown-6 complexes rather than simple ammonium nitrate is observed from a wide variety of other solvent mixtures as well, and indeed the ethanol/diethyl ether mixture appears to be unique in providing the opportunity to avoid complex crystallization when using 18-crown-6. Pedersen and others have long noted the propensity of salts of high lattice energy (e.g., carbonates, halides) to be reprecipitated



**Figure 7.** Photomicrograph of ammonium nitrate recrystallized from nitrobenzene/PEG-300//trichloroethylene. Bar = 100  $\mu\text{m}$ .



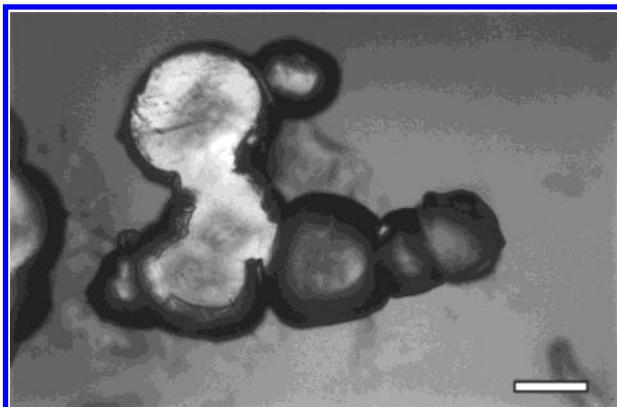
**Figure 8.** Photomicrograph of ammonium nitrate recrystallized from acetonitrile/PEG-300//trichloroethylene. Bar = 100  $\mu\text{m}$ .



**Figure 9.** Photomicrograph of ammonium nitrate recrystallized from acetonitrile/PEG-300//carbon tetrachloride. Bar = 500  $\mu\text{m}$ .

during attempted crystallization of crown ether complexes.<sup>12,16</sup> Unfortunately, the lower lattice energy of ammonium nitrate, together with the efficient complexation of the ammonium ion by 18-crown-6, clearly favor crystallization of the complex rather than salt precipitation.

In an attempt to circumvent this problem, we replaced 18-crown-6 with 1,4,7,10,13-pentaoxacyclopentadecane ("15-crown-5", Figure 2), which typically displays somewhat lower association constants for ammonium salts.<sup>35</sup> In accord with solution<sup>36,37</sup> and solid-state studies<sup>26,38</sup> of ammonium ion complexation by this smaller crown ether, which point to a 2:1 stoichiometry, 2 equiv of 15-crown-5 are needed to solubilize ammonium nitrate in nonaqueous solvents. Provision of this stoichiometry permits the generation of up to ca. 0.04 M solutions of



**Figure 10.** Photomicrograph of ammonium nitrate recrystallized from acetone/PEG-300//hexanes. Bar = 500  $\mu\text{m}$ .

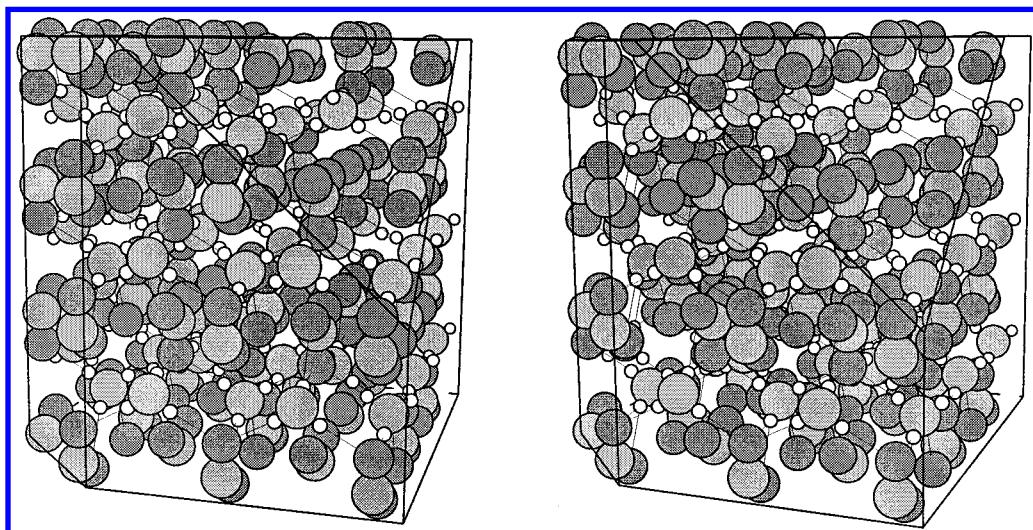
ammonium nitrate, in the form of its crown ether complex, in a variety of organic solvents, including acetone, acetonitrile, dichloromethane, and chloroform. In most cases, induction of crystallization through addition of a precipitating solvent (e.g., benzene, diethyl ether, tetrahydrofuran, ethyl acetate, trichloroethylene, or carbon tetrachloride, in which ammonium nitrate displays at best sparing solubility even in the presence of 2 equiv of 15-crown-5) still results in the formation of a crystalline complex rather than free ammonium nitrate. However, these studies did lead to the discovery of a solvent system, acetonitrile/benzene, from which ammonium nitrate may be successfully recrystallized using 15-crown-5. Interestingly, the crystals obtained from this solvent mixture display a prismatic habit (Figure 4) rather than the needlelike morphology so strongly favored by ammonium nitrate.

A benzannelated analogue of 15-crown-5, benzo-15-crown-5 (Figure 2), also forms complexes of 2:1 stoichiometry in solution (as judged by the stoichiometry required to solubilize ammonium nitrate) and the solid state.<sup>26,39</sup> Although formation of a crystalline complex still prevails,<sup>26</sup> two solvent mixtures, acetonitrile/ethyl acetate and acetonitrile/tetrahydrofuran (THF), permit ammonium nitrate recrystallization using this crown ether. The former mixture affords needlelike crystals, while the latter solvent mixture affords nearly amorphous material, supporting our earlier observations that solvent<sup>19,20</sup> and/or crown ether<sup>40</sup> can indeed induce

dramatic alterations of crystal form. In each case, contamination by a crystalline complex is also noted. It is interesting that in the three cases in which 15-crown-5 derivatives permit the recrystallization of ammonium nitrate, acetonitrile is the dissolving solvent. Acetonitrile is well-known to form complexes with crown ethers through a tripod of C–H $\cdots$ O hydrogen bonds.<sup>41</sup> Perhaps the interaction of this solvent with the crown ether, together with the reduced affinity of the smaller crown ether for the ammonium ion, serves to drive the system toward crystallization of the free salt rather than of the ammonium complex.

To further minimize the likelihood of crystallization of complexes, we turned our attention to acyclic analogues of the crown ethers, low molecular weight polyethylene glycol derivatives, as solubilizing agents for ammonium nitrate. With their expected reduced formation constants for ammonium complexes,<sup>42</sup> we anticipated the successful recrystallization of ammonium nitrate from a wider variety of solvents. In addition, a powerful incentive to pursue these studies was provided by the realization that whereas bulk-scale recrystallization requiring stoichiometric amounts of crown ethers is unlikely to be practical for both safety and financial reasons, large-scale use of polyethylene glycol appears to offer no such problems.

Several molecular weight fractions of polyethylene glycol (PEG) were examined. The highest molecular weight fraction used, PEG-1000, tends to form colloids rather than homogeneous solutions with ammonium nitrate in various solvents. Lower molecular weight fractions, PEG-200, PEG-300, and PEG-400, in contrast, afford up to ca. 0.1 M solutions of ammonium nitrate in solvents such as acetone, acetonitrile, and nitrobenzene containing approximately 9 or more equiv of the PEG derivative. Lower, but still significant, concentrations are obtainable in poorer solvents such as chloroform and dichloromethane, again with 9 equiv of the PEG derivative. In the course of solubility testing, a number of ineffective solvents, including benzene, tetrahydrofuran, ethyl acetate, carbon tetrachloride, and trichloroethylene, were also identified, and these were explored as precipitating solvents in recrystallization experiments. Importantly, in all cases, pure ammonium nitrate is obtained as the sole crystalline phase in these PEG-mediated recrystallization experiments.



**Figure 11.** Packing diagram (stereoview) for phase IV ammonium nitrate, viewing from the (100) direction and including (111) and (111) surfaces. Dark shading = nitrogen, light shading = oxygen, white = hydrogen; thin lines = hydrogen bonds.

**Table 2. Summary of Ammonium Nitrate Crystal Morphologies Obtained in PEG-300-Mediated Recrystallizations**

morphology	dissolving solvent <sup>a</sup>	precipitating solvent <sup>a</sup>
acicular <sup>b</sup>	CH <sub>3</sub> CN	Et <sub>2</sub> O, THF, EtOAc, CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , PhH, PhCH <sub>3</sub> , PERC
	CHCl <sub>3</sub>	Et <sub>2</sub> O, PhH
	PhNO <sub>2</sub>	CCl <sub>4</sub> , Et <sub>2</sub> O, THF, EtOAc, PhH
	CH <sub>3</sub> CN	CCl <sub>4</sub> , TCE
prismatic dendritic	CH <sub>3</sub> CN	EtOAc, TCE, CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>
	PhNO <sub>2</sub>	CH <sub>3</sub> CN
	CH <sub>2</sub> Cl <sub>2</sub>	CCl <sub>4</sub>
tabular	CH <sub>3</sub> CN	THF, EtOAc
	CHCl <sub>3</sub>	THF, EtOAc
	acetone	CH <sub>2</sub> Cl <sub>2</sub>
spherical	PhNO <sub>2</sub>	CCl <sub>4</sub>
	acetone	EtOAc

<sup>a</sup> Abbreviations: THF = tetrahydrofuran, TCE = trichloroethylene, PERC = tetrachloroethylene. <sup>b</sup> Needlelike, i.e., very slender prisms.

To reduce the number of experimental variables, PEG-300 was chosen as the solubilizing agent for each recrystallization experiment. The propensity of ammonium nitrate to crystallize in acicular (needlelike) forms remains evident in these PEG-mediated crystallizations, with this form obtained from a wide variety of solvent combinations, including acetonitrile/benzene, acetonitrile/toluene (Figure 5), and dichloromethane/toluene (Figure 6). However, a number of solvent combinations allow the successful habit modification of ammonium nitrate. Nitrobenzene solutions generally afford acicular crystals, often as dendritic aggregates, regardless of the precipitating solvent used; material obtained from nitrobenzene/trichloroethylene is typical (Figure 7). Acetonitrile mixtures, in contrast, generally afford more prismatic forms, best illustrated by the intergrown pseudocubic forms obtained from acetonitrile/trichloroethylene (Figure 8) and the comparatively large prisms obtained from acetonitrile/carbon tetrachloride (Figure 9). Finally, roughly spherical crystals are obtained from acetone/hexanes (Figure 10). Table 2 provides a summary of solvent systems examined and the crystal form of ammonium nitrate resulting from PEG-300-mediated crystallization.

In our studies of the crystallization of salts of organic acids,<sup>41</sup> simple arguments about selective solvation of and/or chelation to various crystal surfaces have provided an intuitive understanding of the habit modifications observed in complexation-mediated crystallization experiments. Unfortunately, crystalline phase IV ammonium nitrate<sup>43</sup> presents a more complex case for analysis, as the packing diagram in Figure 11 suggests, with multiple sites for hydrogen bonding and/or dipole/dipole interactions provided by virtually any chosen crystal surface. This complexity has precluded development of a detailed understanding of the molecular-level interactions responsible for the observed habit modification. Nonetheless, it is clear that the technique of complexation-mediated crystallization can indeed permit the successful habit modification, into technologically intriguing forms, of inorganic salts such as ammonium nitrate. Particularly significant is the ability to crystallize ammonium nitrate with enhanced kinetic-phase stability toward the annoying IV–III phase transition and in the form of roughly equidimensional prismatic crystals (e.g., Figures 8 and 9).

We have found complexation-mediated crystallization rather routinely offers access to metastable phases of

various inorganic oxides, for which the room-temperature preparation generally allows for kinetic trapping of these phases.<sup>44</sup> However, in no case was evidence obtained for the formation of metastable polymorphs of ammonium nitrate—single-crystal and/or powder X-ray diffraction analyses consistently reveal the formation of phase IV ammonium nitrate. This is not overly surprising, given the generally facile thermal interconversions among the various polymorphs of ammonium nitrate, although the apparent requirement of water to mediate the IV–III phase transition suggests that kinetic trapping of phase III may be possible, and we continue to explore this possibility.

## Summary

Although ammonium nitrate is at best sparingly soluble in typical organic solvents, it may be readily solubilized through the addition of chelating agents such as crown ethers and polyethylene glycols. With suitable choice of solvent and chelating agent, addition of a precipitating solvent leads to the crystallization of uncomplexed ammonium nitrate from such solutions. Crystalline ammonium nitrate obtained through this process of “complexation-mediated crystallization” displays a variety of morphologies, with crystal form dependent on the nature of both the solvent and the chelating agent. Particularly significant is the ability to obtain crystalline ammonium nitrate in the form of blocky prisms, providing lower surface area than the more commonly obtained acicular forms (needles) and thereby potentially reducing undesirable properties such as hygroscopicity and clumping.

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