

## Complexation-mediated crystallization

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**Abstract.** Crown ether complexation solubilizes organic and inorganic salts in nonpolar media. Induction of crystallization from such solutions can result in crystallization of the free salt rather than the complex. This affords the opportunity to examine solvent effects on the crystallization of salts and other polar materials, leading to the modification of crystal shape and lattice. This approach, which we term complexation-mediated crystallization, has been applied to the crystallization of simple organic salts and to the formation of metal sulfides. The resulting crystal morphologies and structures are presented, as are the structures of an unusual potassium complex of 18-crown-6 and crown ether complexes of lead (II) acetate, hexaquo zinc(II), and aquo(trichloro)zinc(II).

### INTRODUCTION

Interest in the process of crystallization, and in the alteration of the shapes and structures of crystals, dates back to the beginnings of chemistry (ref. 1, 2). Such phenomena continue to be of considerable importance for a great number of reasons, including the generation of nonlinear optical solid-state materials (e.g., crystallographic asymmetry is required to observe second order nonlinear effects), the preparation of inorganic composite materials of increased structural integrity, the achievement of improved solid flow characteristics (e.g., cubic or roughly spherical crystals flow more smoothly than long thin crystals), and the formation of commercially important solid materials less prone to caking upon prolonged storage (e.g., tabular crystals tend to adhere to one another more strongly than roughly spherical or needle-shaped crystals). In addition, studies in this area promise to add to our basic store of knowledge regarding the fundamental phenomena involved in the process of crystallization.

Alteration of the shape or crystal lattice of crystals has traditionally been achieved either through the use of additives (ref. 3, 4) or through variation of the crystallization solvent (including crystallization from the gas phase). Additive effects are in many cases dramatic; the alteration of the crystal form of sodium chloride from cubic to octahedral in the presence of traces of urea provides perhaps the best known example (ref. 1, 5). Variation of crystallization solvent can also provide for interesting crystal habit alterations, although this technique is in many regards limited by the need to dissolve the material in question. For example, very polar materials typically must be crystallized from very polar solvents, as they are insoluble in less polar media. Similarly, formation of typical electronic and optical materials (e.g., metal chalcogenides), through precipitation upon admixture of precursor salt solutions, also requires very polar media in order to dissolve these precursor salts.

### COMPLEXATION-MEDIATED CRYSTALLIZATION

Salts such as potassium chloride, while freely soluble in water, are insoluble in nonpolar media. Solvent effects on the alteration of crystal growth of such salts have thus not been explored to any great extent, for the simple reason that one must dissolve a compound before one can crystallize it from solution. Crown ether complexation provides a convenient method of solubilizing salts, in the form of their complexes, in nonpolar solvents, and the literature is rife with examples of crown ether complexes crystallized from such media (ref. 6). Not infrequently, however, attempted crystallization of a crown ether complex results instead in precipitation of the free (uncomplexed) salt. Indeed, this phenomenon was first reported by Pedersen in his first paper reporting the preparation of crown ethers and their complexes (ref. 7). While seemingly universally viewed as a problem to be avoided, we have focused on this phenomenon as an important approach to the exploitation of solvent effects for the alteration of crystal habit or morphology of polar materials. We have introduced the concept of "complexation-mediated crystallization," whereby we

examine the crystallization of organic and inorganic materials from *nonsolvents* through the intermediacy of soluble complexes (ref. 8). Addition of complexation agents, such as the crown ethers, solubilizes materials in solvents in which they would normally be completely insoluble. Initiation of crystallization then provides the opportunity to observe crystal growth under solvation conditions drastically different from those of "normal" growth conditions. This method provides a simple yet potentially powerful approach to the alteration of crystal shape and lattice.

### CRYSTALLIZATION OF ORGANIC SALTS

Sodium acetate is completely insoluble in hydrocarbon media, but may be readily solubilized in the form of its crown ether complexes. Thus, shaking a solution of 15-crown-5 in dichloromethane with solid anhydrous sodium acetate affords a solution of the corresponding complex. This solution, when diluted with cyclohexane and allowed to evaporate slowly, precipitates free sodium acetate trihydrate in crystalline form, with the hydrates apparently resulting from exposure to atmospheric moisture. Crystallization in this manner affords long, slender needles, contrasting sharply with the hexagonal plates obtained via traditional crystallization from aqueous solution (Fig. 1).

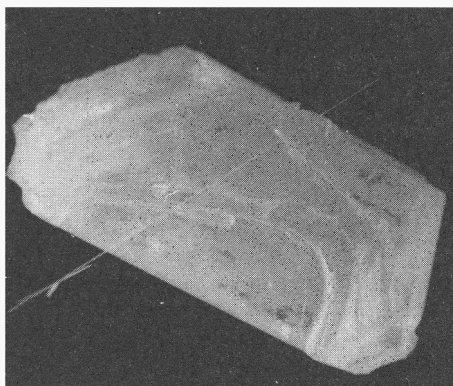


Fig. 1. Crystal form of sodium acetate trihydrate crystallized from aqueous solution (block) and from methylene chloride/cyclohexane (needle). (Longest dimension of each crystal is ca. 1.5 cm.)

X-ray diffraction analysis demonstrates an identical crystal lattice to that of the hexagonal form (ref. 9). Consideration of this crystal lattice allows a simple rationalization of the alteration of crystal habit. The needle axis is comparatively polar, being built up of alternating layers of sodium ions, waters, and acetate carboxylates. In contrast, the plate plane, to which the needle axis is perpendicular, is relatively non-polar; van der Waals contacts between methyl groups of the acetates appear to dominate. In a polar solvent like water, selective solvation of the more polar faces of the growing crystal leads to slowing of growth in these directions; a platy habit results. In a non-polar solvent like cyclohexane, the more hydrophobic faces are selectively solvated, slowing their growth and leading to elongation along the more polar axis; needles result.

This explanation of the growth alteration of sodium acetate trihydrate is probably overly simplistic, ignoring, for example, both nucleation phenomena and the effects of crown ether coordination. Nevertheless, it provides a useful model, and suggests the study of other organic salts to test the generality of such simplistic solvation rationalizations. In addition, modification of the crystal properties of organic materials is a matter of some technological importance. Thus, we have continued to study the complexation-mediated crystallization of other organic salts. Our work with dipotassium tartrate is suggestive of the types of effects one may find.

Dipotassium tartrate may be solubilized in chlorocarbon solvents in the form of its 18-crown-6 complex. Slow evaporation affords a crystalline potassium complex of 18-crown-6. Curiously, nuclear magnetic resonance and analytical data suggest that tartrate is not present in this complex. Single crystal X-ray diffraction and elemental analysis demonstrate that the counteranion is chloride, not tartrate, and that the complex is a most unusual one, containing a nine-coordinate potassium (bearing three hydrates in addition to the six ethereal oxygen ligands from the crown ether) and an 18-crown-6 moiety in a very asymmetric

conformation (Fig. 2, ref. 10). Chloride, we feel, arises from decomposition of the chloroform/methylene chloride solvent mixture, probably as a result of its deprotonation by the solubilized tartrate, which may act as a much stronger base as a "naked anion" in organic solution than it is in water. Consistent with this, the crystalline complex also contains an additional chloride ion, with the charge apparently balanced by a protonated lattice water molecule.

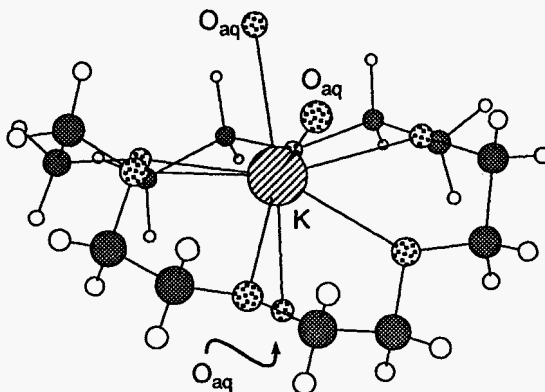


Fig. 2. Molecular structure of 18-crown-6·KCl·3H<sub>2</sub>O (noncoordinated lattice hydrates and chloride ions omitted for clarity).

Similar deprotonation chemistry is observed in a two-phase approach to the complexation-mediated crystallization of dipotassium tartrate. In this approach, an aqueous solution of dipotassium tartrate is layered above a solution of 18-crown-6 in methylene chloride. Upon prolonged contact of these two solutions, single crystals appear at the interface. Infrared, nuclear magnetic resonance, and solubility data suggest that this is neither a crown ether complex nor dipotassium tartrate, but rather potassium hydrogen tartrate, and this is confirmed by single crystal X-ray diffraction analysis. In contrast, recrystallization of dipotassium tartrate from water proceeds uneventfully; potassium hydrogen tartrate is not formed. Again, then, solubilization of tartrate in the methylene chloride solvent, where it behaves as a stronger base, may be responsible for the formation of the monoprotonated salt. Interestingly, the crystal form displayed by the potassium hydrogen tartrate formed in this two-phase complexation-mediated approach is distinct from that of the same salt crystallized from water (Fig. 3), suggesting that even this simple approach to crystal property modification has promise (ref. 11).

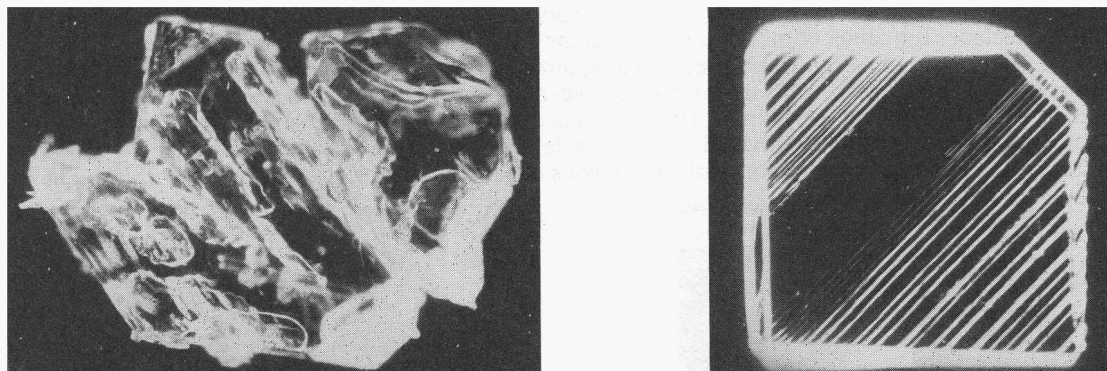


Fig. 3. Crystal form of potassium hydrogen tartrate crystallized from methylene chloride/18-crown-6/water (left) and from aqueous solution (right) (Each crystal ca. 1 mm in longest dimension.)

Armed with these results, suggesting that interesting effects, both anticipated and unanticipated, may be observed, we are continuing to examine the complexation-mediated crystallization of organic materials. In addition, we have expanded our studies to include the crystallization of inorganic materials, as we discuss in the following section.

### CRYSTALLIZATION OF INORGANIC MATERIALS

We have focused our attention on the crystallization of metal sulfides, materials displaying a number of interesting technological applications while providing a convenient forum for an assessment of the fundamental effects under investigation. Here, of course, we don't expect to solubilize monomeric metal sulfides as a prelude to their crystallization, but rather their precursors, i.e., metal halides or pseudohalides and alkali metal sulfides. Use of such ionic precursors represents an age-old approach to the metal sulfides (ref. 12). However, such salt elimination reactions have always been carried out in aqueous media, as water is required to dissolve these ionic precursors. Thus, significant solvent effects on the crystallization of metal sulfides have not previously been observed. By applying our technique of complexation-mediated crystallization to this problem, we have been able to exert influence over both the crystal shape and lattice of metal sulfides formed from these simple salt precursors.

Dibenzo-18-crown-6 was chosen as an inexpensive, commercially available crown ether displaying somewhat enhanced lipophilicity compared to the parent 18-crown-6. Despite this enhanced lipophilicity, the heavy metal salt complexes of dibenzo-18-crown-6 display only limited solubility in common organic solvents. For example, the mercuric chloride complex precipitates even from boiling n-butanol. The lead (II) acetate complex is somewhat more soluble and may be recrystallized from n-butanol. As comparatively few lead complexes of crown ethers have been structurally characterized, we performed a single crystal X-ray diffraction analysis of this complex (Fig. 4, ref. 13). The beautifully symmetrical complex displays a rather unusual coordination geometry, with the six oxygens of the crown ether joining the two bidentate acetate ligands to provide overall ten-coordination about the lead center.

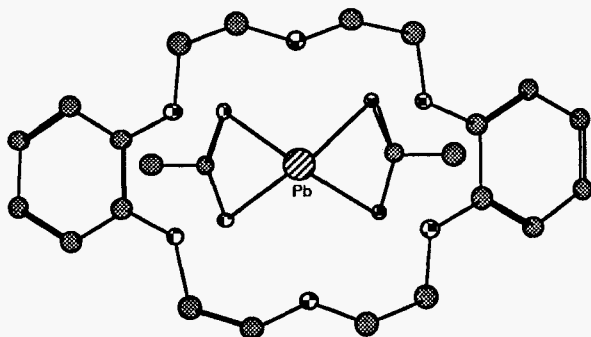


Fig. 4. Molecular structure of dibenzo-18-crown-6•Pb(OAc)<sub>2</sub>.

The sodium sulfide complex of dibenzo-18-crown-6 is also only sparingly soluble in nonpolar organic solvents. These solubility problems preclude simple codiffusion approaches to the precipitation of the metal sulfides. Accordingly, we have adopted a modified approach to the complexation-mediated crystallization of these materials, in which a *catalytic* amount of crown ether is stirred with a suspension of the metal halide and sodium sulfide in the chosen solvent. This approach is nonoptimal in that vigorous stirring precludes formation of macroscopic crystalline products, and in addition, metal sulfides are formed even in the absence of crown ether. Nevertheless, intriguing results have been obtained from these "first generation" experiments which suggest that complexation-mediated crystallization can indeed exert the intended effects. For example, stirring lead (II) acetate with sodium sulfide in aqueous solution affords a black precipitate of very finely divided cubic-phase lead sulfide (galena, as determined by X-ray powder diffraction analysis) which appears nearly amorphous under scanning electron microscopy (SEM, Fig. 5).

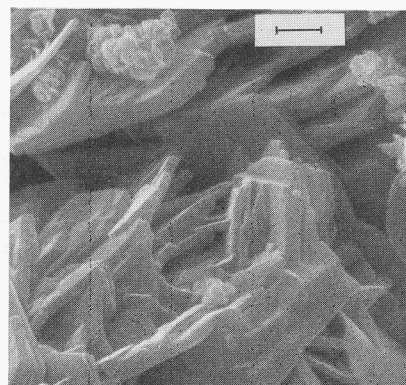
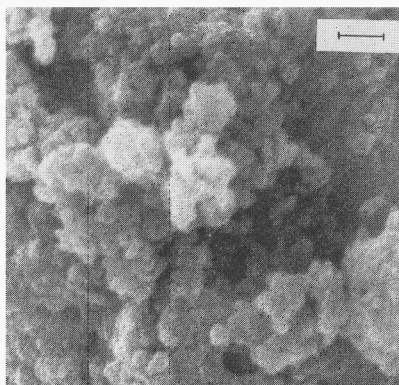


Fig. 5. Scanning electron micrographs of PbS obtained from aqueous solution (left, scale represents 0.5  $\mu$ ) and from anhydrous tetrahydrofuran/dibenzo-18-crown-6 (right, scale represents 1  $\mu$ ).

A stirred suspension of lead (II) acetate and anhydrous sodium sulfide in anhydrous tetrahydrofuran (THF) affords samples of cubic lead sulfide of apparently identical morphology. In contrast, the presence of a catalytic amount of dibenzo-18-crown-6 in the anhydrous THF affords samples of cubic lead sulfide displaying much greater crystallinity (Fig. 5). Similar, albeit less dramatic effects are seen in analogous experiments using anhydrous *N,N*-dimethylformamide or toluene as solvent. Samples from each of these three solvents display distinctive crystal habits, suggesting that solvation effects can indeed play a role in the precipitation of metal sulfides under even these nonideal conditions.

We have also explored alternative approaches to circumvent the insolubility of our metal sulfide precursor complexes. For example, sodium sulfide is solubilized in chlorocarbon solvent (either chloroform or methylene chloride) by addition of dibenzo-18-crown-6. When an aqueous solution of mercuric chloride is layered onto this solution, mercuric sulfide slowly precipitates at the interface between the two reacting solutions. This mercuric sulfide, shown by SEM to be quite coarsely crystalline (Fig. 6), is comprised of roughly equimolar amounts of the cubic (metacinnabar) and hexagonal (cinnabar) phases of mercuric sulfide (as determined by X-ray powder diffraction), whereas the catalytic solubilization procedure described above or precipitation from aqueous solution affords only metacinnabar. Similar results are obtained upon admixture of homogeneous solutions of mercuric iodide and sodium sulfide in dimethylsulfoxide. In the absence of crown ether, only the cubic phase is obtained, while addition of dibenzo-18-crown-6 affords mixtures of the cubic and hexagonal phases.

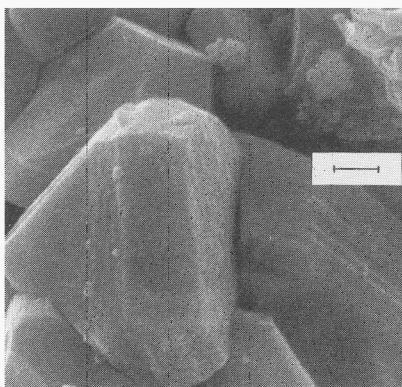


Fig. 6. Scanning electron micrograph of HgS obtained from methylene chloride/dibenzo-18-crown-6/H<sub>2</sub>O (scale represents 1  $\mu$ ).

A similar solvent layering approach was attempted for the preparation of zinc sulfide. In this case, however, another variant is made possible by virtue of the solubility of zinc chloride in ethereal solvents. Layering a diethyl ether solution of zinc chloride onto a solution of 18-crown-6 solubilized sodium sulfide in 2-bromotoluene (the density of which permits facile layering of the ethereal solution) results in rapid formation of large single crystals at the interface between the reacting solutions. However, repetition of the experiment in the absence of sodium sulfide affords the same result, suggesting the crystals are actually a zinc chloride complex of 18-crown-6. This appears to be the case based on qualitative analytical analysis of the solid, but facile loss of solvate results in rapid decomposition of the crystals, thus far precluding single crystal X-ray diffraction analysis. Recrystallization of the putative complex from carbon tetrachloride/acetone affords a stable acetone solvate, not of the anticipated simple addition complex, but rather of an extensively hydrolyzed product, whose structure was determined by single crystal X-ray diffraction analysis (Fig. 7). This complex displays a number of fascinating features, including an

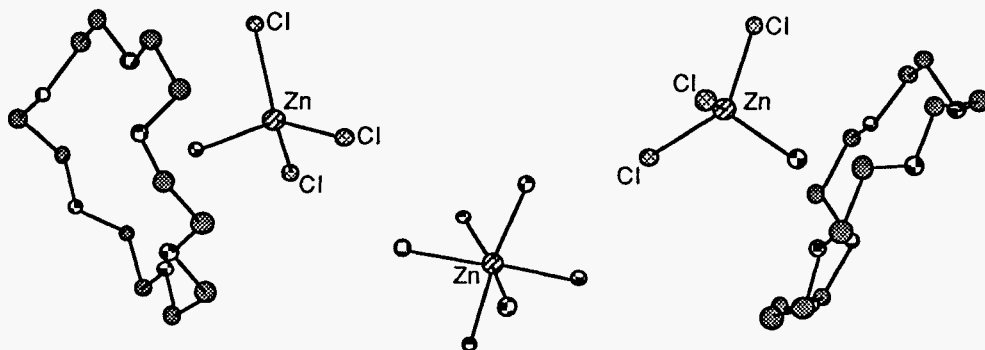


Fig. 7. Molecular structure of (18-crown-6)<sub>2</sub>•[ZnCl<sub>3</sub>(H<sub>2</sub>O)]<sub>2</sub>•Zn(H<sub>2</sub>O)<sub>6</sub>.

extensive three-dimensional network of hydrogen bonds. Interestingly, it is a representative of the class of "complexes of complexes" studied extensively by Stoddart *et al.* for the crown ether complexes of metal amines (ref. 14). Curiously, this complex crystallized in a noncentrosymmetric space group,  $P2_12_12$ , and in fact it displays a molecular asymmetry due to the asymmetric conformation of the 18-crown-6 moiety. The crystal examined displayed only a single enantiomeric form, and structure refinement clearly favored the enantiomer shown.

### SUMMARY

Initial studies of the complexation-mediated crystallization of organic and inorganic salts and solid-state materials have demonstrated that effects of both solvent and crown ether on crystal shape and lattice can indeed be observed and may be dramatic. In the course of these studies, a number of other interesting results have been obtained, including the characterization of an unusual crown ether complex of potassium and two heavy metal crown ether complexes. Prompted by the potential for both predicted and unexpected but no less interesting results, our work in this area continues.

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