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STUDIES OF UNUSUAL PACKING AND OF POLYMORPHISM IN TWO CRYSTAL SYSTEMS

Xiang Hao

University of Kentucky

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STUDIES OF UNUSUAL PACKING AND OF POLYMORPHISM IN TWO CRYSTAL SYSTEMS

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Arts and Sciences at the University of Kentucky

By
Xiang Hao
Lexington, Kentucky

Director: Dr. Carolyn P. Brock, Professor of Chemistry
Lexington, Kentucky

2005

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ABSTRACT OF DISSERTATION

STUDIES OF UNUSUAL PACKING AND OF POLYMORPHISM IN TWO CRYSTAL SYSTEMS

Crystal structures of anhydrous pinacol, the hexagonal pinacol, pinacol monohydrate, and pinacol hexahydrate were studied. In all the structures crystal packing is unusual and complicated. The origin of the complexity may be the difficulty in filling space densely and while also satisfying the H-bonding requirements when the molecule has few internal degrees of freedom.

Five 15-crown-5 complexes of M(NO₃)₂ (M = Cu, Zn, Mg, Co, Mn) were synthesized and characterized using X-ray diffraction and differential scanning calorimetry. The system is rich in polymorphs. Nine definite solid-state phases were identified. More phases probably exist in the solid state at temperatures slightly above the room temperature. Most phase transformations in this system take place in single crystals without the loss of crystallinity. The nine phases crystallize in five crystal structures. The crown ether ligands have very similar conformation in all the structures. The asymmetric units in all the structures are complicated and pseudosymmetric, which is the consequence of the presence of the packing problem. The origin of the packing problem that leads to the complicated phase behavior is the odd number of -CH₂-O-CH₂- units in the crown ether ligand.

KEYWORDS: Pinacol, 15-Crown-5, Crystal Packing, H-Bonding, Polymorphism

Xiang Hao

February 11, 2005
STUDIES OF UNUSUAL PACKING AND OF POLYMORPHISM IN TWO CRYSTAL SYSTEMS

By

Xiang Hao

Dr. Carolyn P. Brock
Director of Dissertation
Dr. Mark S. Meier
Director of Graduate Studies
March 24, 2005
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Chapter One
Introduction

Overview

The development of X-ray crystallography as a science in its own right has been greatly facilitated by electronic computers and automated computer-controlled instrumentation. Nevertheless, crystallography’s full potential was not appreciated until the advent of automated four-circle diffractometers controlled by minicomputers in the 1960s. Computer programs for crystal structure solution, refinement and visualization also came into widespread use at this time. By the early 1970s a small-molecule crystal structure could be determined in a reasonably routine way in a few weeks or months. Between 1970 and 1990 there were few major changes in instrumentation in small-molecule crystallography. As computers became faster and more powerful, however, many programs for crystallography were upgraded or rewritten, and many new programs, computational techniques and algorithms were developed. A particularly great achievement, beginning in the 1950s, was the development of direct methods for the determination of crystal structures, which ultimately led to the Nobel Prize in chemistry in 1985 for Herbert Hauptman and Jerome Karle. Indeed, X-ray crystallography and the sciences closely related to it have brought forth an impressive history of recognition by the Nobel committee (see Table 1.1). The advances in computer programs and the use of direct methods have served to make structure determination less difficult and less time-consuming. By 1990 the calculations for routine structures could be done in a few hours or days. The rate-limiting step was often data collection, which could take days or even weeks depending on the number of independent atoms. The reason for the time required was primarily that most four-circle diffractometers were equipped with point detectors, which could only measure diffraction intensities in a serial manner, i.e. one at a time.
Table 1.1 The Nobel Prize in sciences closely related to X-ray crystallography.

<table>
<thead>
<tr>
<th>Year</th>
<th>Subject</th>
<th>Laureates</th>
<th>Achievement</th>
</tr>
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<tbody>
<tr>
<td>1901</td>
<td>Physics</td>
<td>Wilhelm Röntgen</td>
<td>The discovery of the X-ray.</td>
</tr>
<tr>
<td>1914</td>
<td>Physics</td>
<td>Max von Laue</td>
<td>The discovery of the diffraction of X-rays by crystals.</td>
</tr>
<tr>
<td>1915</td>
<td>Physics</td>
<td>William Henry Bragg,</td>
<td>The analysis of crystal structures by using X-ray diffraction.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>William Lawrence Bragg</td>
<td></td>
</tr>
<tr>
<td>1936</td>
<td>Chemistry</td>
<td>Peter Debye</td>
<td>The investigations on dipole moments and on the diffraction of X-rays and</td>
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<td></td>
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<td>electrons in gases.</td>
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<tr>
<td>1954</td>
<td>Chemistry</td>
<td>Linus Pauling</td>
<td>The nature of the chemical bond and its application to the elucidation of</td>
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<td></td>
<td></td>
<td></td>
<td>the structure of complex substances.</td>
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<tr>
<td>1962</td>
<td>Chemistry</td>
<td>Max Perutz, John Kendrew</td>
<td>The studies of the structures of globular proteins.</td>
</tr>
<tr>
<td>1962</td>
<td>Physiology or</td>
<td>Francis Crick, James Watson,</td>
<td>The discoveries concerning the molecular structure of nucleic acids and</td>
</tr>
<tr>
<td></td>
<td>Medicine</td>
<td>Maurice Wilkins</td>
<td>its significance for information transfer in living material.</td>
</tr>
<tr>
<td>1964</td>
<td>Chemistry</td>
<td>Dorothy Crowfoot Hodgkin</td>
<td>The determinations of the structures of important biochemical substances.</td>
</tr>
<tr>
<td>Year</td>
<td>Subject</td>
<td>Laureates</td>
<td>Achievement</td>
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<tr>
<td>1982</td>
<td>Chemistry</td>
<td>Aaron Klug</td>
<td>The development of crystallographic electron microscopy and the structural elucidation of biologically important nucleic acid-protein complexes.</td>
</tr>
<tr>
<td>1985</td>
<td>Chemistry</td>
<td>Herbert Hauptman, Jerome Karle</td>
<td>The development of direct methods for the determination of crystal structures.</td>
</tr>
<tr>
<td>1988</td>
<td>Chemistry</td>
<td>Johann Deisenhofer, Robert Huber, Hartmut Michel</td>
<td>The determination of the three-dimensional structure of a photosynthetic reaction center.</td>
</tr>
<tr>
<td>1994</td>
<td>Physics</td>
<td>Bertram Brockhouse, Clifford Shull</td>
<td>The pioneering contributions to the development of neutron scattering techniques for studies of condensed matter; and for the development of neutron spectroscopy.</td>
</tr>
</tbody>
</table>
High-resolution diffractometers with area detectors were first used in protein crystallography because the large number of diffraction spots made serial measurements impractical. Area detectors for small-molecule work, however, including image-plate and especially CCD detectors began to become available in the early 1990s. CCD detectors revolutionized data collection. First, data could be collected very fast, and the time required for data collection was no longer so closely related to the number of independent atoms in the structure. One consequence of area-detector data collection is that it is much easier to obtain a highly ‘redundant’ dataset, i.e. the same or symmetry-equivalent intensities are measured several times and in different parts of reciprocal space. These ‘redundant’ measurements can be used to correct for some unavoidable experimental errors, including absorption. The redundancy of a dataset is specified before the data collection begins. The higher the redundancy, the more time the data collection requires. Due to the statistical benefits of data merging, a dataset with a higher redundancy has a better signal-to-noise ratio. Another advantage of area detectors is that weak intensities are much more likely to be found and measured. Third, non-Bragg (diffuse) scattering can be observed, measured and analyzed. Diffuse scattering is observed between Bragg reflections. The information contained in such diffuse scattering had been largely ignored since four-circle diffractometers with point detectors supplanted the older X-ray cameras using photographic films because any diffuse scattering present was usually not even seen. Indeed, the electronic area detector shares many characteristics of film but is much more versatile. For example, the Nonius program PRECESSION, which became available in 1999, reconstructs undistorted views of plane-sections of the reciprocal lattice from the raw diffraction frames. These reconstructed precession planes are invaluable for the identification of several crystallographic problems, such as twinning, pseudosymmetry, and diffuse scattering. In the past, precession planes were recorded on photographic film with a Buerger precession camera.

The Cambridge Structural Database (hereafter the CSD; Allen et al., 1983; Allen et al., 1987; Allen, 2002; Orpen et al., 1989), started in 1965, has now become the standard database of crystal structures for organic and metallo-organic compounds. The search engine ConQuest and crystal-structure visualizer Mercury are two programs (Bruno et al., 2002) that make the use of the CSD easy. Currently the CSD contains data for more than 300,000 small-molecule crystal structures. In 2000 there were 17,866 crystal structures added to the CSD, that number increases
every year. The major reason for the rapid growth of the CSD is that current instruments, computers and software are so well developed that many crystal structure determinations of small molecules are routine. It is not unusual for a simple structure to be completed in a few hours. As a result, and because so many structures are being determined by non-experts, automated validation of structures has become a major concern. Error-checking routines such as those built in to *PLATON* (Spek, 2005) have been developed. The IUCr (International Union of Crystallography) CIF-checking program *checkCIF* uses the same algorithms as those in *PLATON*.

Given the wealth of accumulated knowledge on molecular geometry, there may be little new to be learned about bond lengths and angles in individual molecules. Beyond the traditional, routine world of molecular structure determination, X-ray diffraction is also used to study other details of the crystalline state, including charge-density distributions (Coppens, 1997) and the interactions between molecules as a result of their packing, *i.e.* supramolecular chemistry (Lehn, 1995). Pseudosymmetry, modulated superstructures, twinning, disorder, short-range ordering, and solid-solid phase transformations are all intimately related to crystal packing. Many such problems could not be studied well in the past, and were abandoned. However, the advances in both instrumentation and software have made it less difficult to tackle these problems though it is still not easy.

One approach to the studies of crystal packing is to statistically investigate a large number of crystal structures in the CSD (Allen & Motherwell, 2002; Orpen, 2002). For example, Brock and Dunitz performed a study of the space group frequency distributions in the CSD in order to establish a “grammar” of crystal packing (Brock & Dunitz, 1994). Some general rules were deduced regarding molecular crystal packing. These rules could be useful as guides to crystal engineering (Desiraju, 1989) and crystal structure prediction (Lommerse *et al*., 2000; Motherwell *et al*., 2002). Such rules can also aid in space group assignment during the initial stage of structure determination.

Crystal nucleation and growth is also a very important area for future research (Bernstein *et al*., 1999). Polymorphism (Bernstein, 2002) is closely related to this area. If a substance can exist in
more than one crystalline state, the substance is said to be polymorphic. Although the control of polymorphs is extremely important to the pharmaceutical and chemical industries (Byrn et al., 1999), it is still not well understood. Crystal structure prediction is another promising area though current prediction algorithms are not yet successful (Lommerse et al., 2000; Motherwell et al., 2002). It should be pointed out that routine structure determinations are not all that this field can offer.

**Structures with \( Z' > 1 \)**

Of the many numerical quantities associated with crystal structures, there are two, \( Z \) and \( Z' \), which are of essential importance to the interpretation of crystal packing. \( Z \) is the number of formula units in the unit cell, while \( Z' \) is the number of formula units in the asymmetric unit. The asymmetric unit is only part of the unit cell, the symmetry-independent part. The entire unit cell can be generated by applying symmetry operations to the asymmetric unit. The quantity \( Z' \) is given by \( Z' = Z/n \), where \( n \) is the order of the space group. For example, a structure in space group \( P\bar{1} \) (\( n = 2 \)) with four molecules in the unit cell has \( Z = 4 \). The asymmetric unit in this case is only one half of the unit cell because the other half can be generated by an inversion center. As a result, \( Z' = 2 \), which means that there are two independent molecules in the asymmetric unit. To determine such a structure it is necessary to find the coordinates and displacement parameters of each atom in each of the two independent molecules. Generally speaking, to determine a structure is to define the structure of the asymmetric unit.

Studies show that a simpler asymmetric unit (\( Z' \leq 1 \)) tends to be preferred in crystal packing (Brock & Dunitz, 1994). Structures with more than one formula unit in the asymmetric unit (\( Z' > 1 \)) constitute only about 8% of the structures in the CSD. For structures with \( Z' > 1 \) packing problems can usually be identified (Brock, 1999). Studies also indicate that such structures occur more frequently for certain types of molecules, such as those with irregular, non-self complementary shapes, as these molecules often have problems achieving simple packing (Steed, 2003; Steiner, 2000). To partially circumvent the packing problems the molecules construct a more complicated asymmetric unit. Monoalcohols (Brock & Duncan, 1994) and vicinal diols (Brock, 2002b) also are likely to crystallize with \( Z' > 1 \), probably because of the specific H-
bonding requirements of these molecules. Many structures with \( Z' > 1 \) are pseudosymmetric, exceptions are relatively few (Lehmler et al., 2002).

**Pseudosymmetry**

When the asymmetric unit is pseudosymmetric, the atomic coordinates and displacement parameters of the related atoms will be correlated so that refinement difficulties are inevitable. The correlation coefficients can be obtained from the variance-covariance matrix. Significant correlation coefficients are indications of the presence of pseudosymmetry. In an extreme case, for example, if true symmetries are present but have been overlooked, the absolute values of the correlation coefficients will be close to unity. On the other hand, if pseudosymmetries are mistaken as true symmetries, the asymmetric unit will be reduced, and the independent molecules will be averaged by the pseudosymmetry. The consequence of the averaging is that atoms that are less affected by the pseudosymmetry will deviate more from the averaged model. The deviations will be absorbed into the displacement parameters so that the ellipsoids in the averaged model will look eccentric, *i.e.* the ratio of the maximum to the minimum semi-axial lengths of an ellipsoid will be greater than about three. For example, if an atom on a pseudo mirror plane is treated as if it is on a true mirror plane, the ellipsoid of this atom will be elongated along the normal of the mirror plane. In any event, pseudosymmetries will always make structure determinations less routine, and sometimes very difficult.

A very common pseudosymmetry element is a pseudo-inversion center. It is not unusual for a truly centrosymmetric structure to be mistakenly refined in a non-centrosymmetric space group, which means that the true inversion centers have been overlooked. Many non-centrosymmetric structures in the CSD have been found to be better described by a centrosymmetric model (Marsh, 1999; Marsh & Spek, 2001). However, there are some cases in which a pseudo-inversion center is so close to being a true inversion center that it is impossible to distinguish between the two possibilities without special methods. Marsh has pointed out that “for typical molecular compounds, standard crystal-structure techniques may be unable to distinguish between \( P1 \) and \( P\overline{1} \) if the r.m.s. deviation from centrosymmetry is less than ~ 0.1 Å” (Marsh, 1999).
Pseudosymmetry may be identified by the presence of significant correlation coefficients. Nevertheless, it can be difficult to determine whether the symmetry is approximate or true simply based upon the correlation coefficients. Symmetry-checking software is not always correct. A more reliable approach to the identification of pseudosymmetry and missing symmetry is the analysis of diffraction patterns. Until recently, however, it was not possible to examine the diffraction pattern measured with a diffractometer in a systematic way.

**Reconstructed Precession Planes**

The basis vectors, \( \mathbf{a}, \mathbf{b}, \mathbf{c} \), in direct space, and the mutual angles, \( \alpha, \beta, \gamma \) are shown in Figure 1.1. If \( a, b, c \) represent the magnitudes of \( \mathbf{a}, \mathbf{b}, \mathbf{c} \), then \( a, b, c, \alpha, \beta, \gamma \) are the unit-cell dimensions. In conventional nomenclature, \([uvw]\) is used to represent a crystallographic direction in direct space. For example, \([211]\) corresponds to the direction of \( 2\mathbf{a} + \mathbf{b} + \mathbf{c} \). Also by convention, \( hkl \) and \((hkl)\) are used to represent a reflection and a crystallographic plane. The \( h, k, \) and \( l \) are the Miller indices, which refer to the reciprocal axes.
Figure 1.1 The basis vectors, \( \mathbf{a}, \mathbf{b}, \mathbf{c} \), in direct space. The mutual angles are \( \alpha \) (between \( \mathbf{b} \) and \( \mathbf{c} \)), \( \beta \) (between \( \mathbf{c} \) and \( \mathbf{a} \)), and \( \gamma \) (between \( \mathbf{a} \) and \( \mathbf{b} \)).
Equation 1.1 shows how the basis vectors in reciprocal space are derived mathematically from those in direct space.

$$a^* = \frac{b \times c}{V}, \quad b^* = \frac{c \times a}{V}, \quad c^* = \frac{a \times b}{V}; \quad V = a \cdot b \times c$$

(1.1)

Where \( a, b, c \) are basis vectors in direct space, \( V \) is the volume of the unit cell, and \( a^*, b^*, c^* \) are the basis vectors in reciprocal space.

A reflection with \( hkl \) corresponds to a lattice point in reciprocal space. The coordinates of this lattice point referred to the \( a^*, b^*, c^* \) axes are \( h, k, l \). A precession plane (this terminology goes back to the time when reciprocal-lattice planes were recorded on photographic film with a Buerger precession camera) is the cross section of the reciprocal lattice in a definite direction. For example, precession plane \( hk1 \) is perpendicular to \( c^* \), and contains the set of all reflections with indices \( hk1 \). Figure 1.2 shows an example of a reconstructed precession plane.
Figure 1.2 Reconstructed precession plane \(hk1\) of a room-temperature dataset of the compound [Co(15-crown-5)(H\(_2\)O)\(_2\)](NO\(_3\))\(_2\). The black spots represent reflections. All reflections in this picture have indices of \(hk1\) with \(h\) and \(k\) variable. The graduations of \(h\) and \(k\) are shown in the picture as well.
Careful examination of this picture indicates that reflections with $h + k = \text{odd}$ are systematically weaker than those with $h + k = \text{even}$, especially at low scattering angles, which means that the lattice is approximately $C$-centered (see also Figure 1.3 in the next section). If the reflections with $h + k = \text{odd}$ are systematically absent, then the lattice will be truly $C$-centered. However, the reconstructed precession plane indicates unambiguously that although the reflections with $h + k = \text{odd}$ are very weak, they are present. As a result, the actual lattice is not $C$-centered. Whenever there is an ambiguity about the lattice type or systematic absences, reconstructed precession planes should always be made and examined. A recent study showed that modern software could select the wrong space group due to the presence of pseudosymmetry, while the correct space group could be obtained by the analysis of the diffraction pattern (Guzei et al., 2002).

Besides the identification of pseudosymmetry, reconstructed precession planes can also be used to identify several crystallographic problems, such as disorder, twinning, modulated superstructures, and diffuse scattering. The Atlas of Optical Transforms (Harburn et al., 1975) is a very useful reference book listing almost all kinds of diffraction patterns. Comparison of reconstructed precession planes with similar optical transforms can provide additional insights.

A phenomenon similar to pseudosymmetry has been described by several authors (Freer & Kraut, 1965; Yufit et al., 2002), and is worth mentioning in this context. It concerns a “single” crystal that is actually comprised of two similar phases, giving the crystal a composite nature. This phenomenon is very unusual in molecular organic crystals since one single crystal usually contains one single phase. After the precession planes were carefully examined, the authors could interpret the diffraction pattern as a result of the overlapping of two lattices.

**Separate Wilson Plots**

Visual assessment of precession planes is a qualitative way to study the intensity distributions. A quantitative way involves the generation of reflection-class specific Wilson plots, which have been named “separate Wilson Plots” (Xia et al., 2001; Xia et al., 2002).

A Wilson plot is based on Equation 1.2 (e.g., Giacovazzo et al., 1992):
\[
\ln \left( \frac{\langle |F_{\text{obs}}|^2 \rangle}{\sum_s} \right) = \ln K' - 2B\langle \sin^2 \theta / \lambda^2 \rangle
\] (1.2)

Where the symbol \( \langle p \rangle \) stands for the mean value of \( p \), where \( \sum_s = \sum_{j=1}^{N} f_j^2 \) can be calculated by using the tabulated values of atomic scattering factors (Cowley, 1992) for isolated atoms at \( (\sin \theta / \lambda) = \sqrt{\langle \sin^2 \theta / \lambda^2 \rangle} \), where \( K' \) is the scale factor, and where \( B \) is overall isotropic temperature factor.

The idea of the Wilson plot is to divide the reciprocal lattice into several small shells of increasing resolution. In each shell there are certain number of reflections, over which \( |F_{\text{obs}}|^2 \) and \( \sin^2 \theta / \lambda^2 \) are averaged so that \( \langle |F_{\text{obs}}|^2 \rangle \) and \( \langle \sin^2 \theta / \lambda^2 \rangle \) can be obtained. This averaging removes many of the effects of the specific arrangement of the atoms. Given a dataset and unit-cell dimensions, \( \sin^2 \theta / \lambda^2 \) can be calculated based upon Equation 1.3:

\[
\sin^2 \theta / \lambda^2 = (1/4)(h \ k \ l)G^* G\begin{bmatrix} h \\ k \\ l \end{bmatrix} = \begin{bmatrix} a^* \bullet a^* & a^* \bullet b^* & a^* \bullet c^* \\ b^* \bullet a^* & b^* \bullet b^* & b^* \bullet c^* \\ c^* \bullet a^* & c^* \bullet b^* & c^* \bullet c^* \end{bmatrix}
\] (1.3)

Where \( (h \ k \ l) \) is the vector in the reciprocal lattice, \( \begin{bmatrix} h \\ k \\ l \end{bmatrix} \) is the transpose vector, \( G^* \) is called the inverse (or reciprocal) metric tensor, and \( a^*, b^*, c^* \) are the basis vectors in reciprocal space.

If a linear regression is made for \( \ln \left( \frac{\langle |F_{\text{obs}}|^2 \rangle}{\sum_s} \right) \) vs. \( \langle \sin^2 \theta / \lambda^2 \rangle \), then an approximate scale factor, \( K' \), can be calculated from the intercept at the ordinate axis, and an approximate overall isotropic temperature factor, \( B \), can be calculated from the slope.
In the presence of pseudosymmetry, some reflections are systematically weaker than others, so the reflections can be divided into different groups. Some groups consist of the weak reflections, while the other groups consist of the strong reflections. Making separate Wilson plots for the individual groups will give rise to several separate curves. An example of separate Wilson Plots is shown in Figure 1.3, in which the reflections with \( h + k = \text{even} \) are systematically stronger than those with \( h + k = \text{odd} \).
Figure 1.3 Separate Wilson plots of a room-temperature dataset of the compound [Co(15-crown-5)(H₂O)₂][NO₃]₂. Reflections are divided into two groups: \( h + k = \) even and \( h + k = \) odd. The intensities in the former group are systematically stronger than those in the latter group. The straight lines are generated from the linear regression. The linking lines through the data points are guides to the eye.
Another important feature of separate Wilson plots is that the slopes show how thermal motions affect the intensities as a function of the resolution. Usually the intensity differences between the strong and weak reflection classes are greater in the lower resolution region \((i.e. \text{ smaller } \sin^2 \theta / \lambda^2)\) because pseudosymmetry appears more like true symmetry when the resolution is low. As the resolution increases, the differences between the pseudosymmetrically related atoms become more important so that the intensity differences between the classes of reflections become smaller. For this reason, the curves in separate Wilson plots tend to be farther apart in the lower resolution region, but to converge in the higher resolution region. This observation implies that the intensities of the weaker reflections decrease less rapidly than the intensities of the stronger reflections with increasing resolution. In principle, the intensities of the weaker reflections can even rise with increasing resolution, but this is not often seen. The reason is that although the geometric factor tends to increase the intensities of the weaker reflections in the higher resolution region, the thermal motion (and possibly disorder) tends to decrease the intensities through the entire resolution region. In most cases the thermal motion dominates, and prevents the slope from becoming positive. For this reason, all curves in separate Wilson plots usually have slopes that are negative.

In summary, making reconstructed precession planes and separate Wilson plots are two approaches to the analysis of the intensity distributions. The former is qualitative, while the latter is quantitative. Both of them are extremely useful for the identification of pseudosymmetry, modulated superstructures, twinning, disorder, diffuse scattering, etc.

**Superstructures**

A crystal is a regular, repeating stack of structural building blocks (unit cells) arranged periodically in three-dimensional space, which gives rise to a basic long-range periodicity. A superstructure has additional periodic distortions within each unit cell, which can modulate the basic long-range periodicity. If the modulations are commensurate with the basic periodicity, the superstructure is called a commensurately modulated structure (CMS); otherwise it is called an incommensurately modulated structure (IMS). In mathematical formalism, CMSs can be described in three-dimensional space, while IMSs cannot. Instead, an IMS should be described in
a higher-dimensional (greater than three-dimensional) space (e.g., Giacovazzo et al., 1992). All superstructures in this work belong to the category of CMSs. Incommensurate modulations will not be mentioned further.

Superstructures all have more than one crystallographically independent formula unit \((Z' > 1)\) related by pseudo-crystallographic symmetry operations, which are usually translations. The true (superstructure) unit cell is called the supercell. If the pseudo translations are treated as if they are true translations, the volume of the supercell will be reduced, and this smaller unit cell is called the pseudocell or subcell. The pseudocell, which is generated by averaging of the small distortions, is just an approximation of the true unit cell. An example of a superstructure (Xia et al., 2001; Xia et al., 2002) is illustrated in Figure 1.4.
Figure 1.4 An example of a superstructure (Xia et al., 2001; Xia et al., 2002). The top picture shows the two independent molecules in the supercell (the true unit cell), and the bottom picture shows one independent molecule in the pseudocell. The ellipsoids are drawn at 50% probability. The silicon atoms are labeled: SiA and SiB in the supercell; Si in the pseudocell. The unlabeled ones are all carbon atoms. The hydrogen atoms are omitted for clarity.
In Figure 1.4, the top picture shows the two independent molecules in the supercell (the true unit cell), and the bottom picture shows one independent molecule in the pseudocell. In the supercell the two independent molecules are related by a pseudo translation. The coordinates of a pair of related atoms in the supercell, e.g. SiA and SiB, have the relationship defined in Equation 1.4.

\[(x_b, y_b, z_b) = (x_a, y_a, z_a) + (1/n_x, 1/n_y, 1/n_z) + (\Delta x, \Delta y, \Delta z)\]  

(1.4)

In Equation 1.4, 1/n_x, 1/n_y, and 1/n_z correspond to the translation distances along the a, b, and c directions. For CMSs, n_x, n_y, and n_z are all integers, which represent the orders of the modulations along the a, b, and c directions. In other words the structure is n_x-fold modulated along the a direction, and so on. If one of the n_i is not an integer, for example n_y, then the basic long-range periodicity in the b direction will be broken and the structure will be an IMS. Since the two atoms are related by pseudo translations, none of the \(\Delta x\), \(\Delta y\), or \(\Delta z\) is zero, but they are all expected to be small. As a result, \((1/n_x, 1/n_y, 1/n_z) + (\Delta x, \Delta y, \Delta z)\) are the additional periodic distortions that relate adjacent pseudocells within the true unit cell. Such distortions modulate the basic long-range periodicity, and cause difficulties in the solving and refining of superstructures. However, if the small distortions are ignored, then the pseudo translations will become true translations. Such an approximation will result in a new basic long-range periodicity with a shorter period, i.e. the supercell (the true unit cell) will be reduced to a new smaller unit cell, the pseudocell. The solving and refining of a superstructure in the pseudocell are less difficult than in the supercell because the small distortions are ignored in the pseudocell. The molecular structure in the pseudocell is an average structure of all the independent molecular structures in the supercell. As expected, the results are only approximate. The small distortions will be absorbed into the displacement parameters. As a result, the ellipsoids from the pseudocell refinement might look eccentric. In Figure 1.4, not all the ellipsoids from the pseudocell refinement look eccentric, which implies that the distortions are significant for only some of the atoms in the supercell. The averaging of the larger distortions in the supercell will lead to eccentric ellipsoids in the pseudocell, but the averaging of the smaller distortions will not. As a result, the eccentricity of the ellipsoids from the pseudocell refinement can provide information about which atoms are affected by the modulations and to what extent. It is this information that makes the pseudocell refinement important.
The identification of superstructures critically depends on the analysis of reconstructed precession planes and separate Wilson plots. The presence of systematically weak reflections is a typical symptom of superstructures. These systematically weak reflections are usually called superstructure reflections. They are observed between the stronger reflections. The stronger reflections are called primary or main reflections. The ratios of the intensities of the primary reflections over those of the superstructure reflections determine whether or not a structure should be viewed as a superstructure. It is not appropriate to give a single number as a cut-off ratio since there are many factors that can affect the intensities. Previous experiences show that a ratio of two or more might be a reasonable estimate.

There are two approaches to the indexing of a superstructure: the supercell indexing and the pseudocell indexing. In the case of the supercell indexing, the primary and superstructure reflections are indexed in the same way, i.e. the superstructure is treated as if it is a regular, non-modulated structure. As a result, all indices are necessarily integers. Supercell indexing is applicable to the cases when many of the superstructure reflections are observable and resolvable by the detector. However, if most of the superstructure reflections cannot be measured, then pseudocell indexing is likely to be more convenient. Superstructures of this type usually have weak modulations and large modulation numbers, i.e. the distortions ($\Delta x$, $\Delta y$, $\Delta z$) are very small and at least one of the $n_x$, $n_y$, $n_z$ is a large integer. The very few observable superstructure reflections in these structures are often called satellite reflections. Pseudocell indexing will give rise to integral indices for the primary reflections and fractional indices for the superstructure or satellite reflections.

An important concept in superstructures is the $\mathbf{q}$-vector. Figure 1.5 shows the geometric relationship of the reciprocal vectors, $\mathbf{H}$ and $\mathbf{H}'$, and the $\mathbf{q}$-vector.
Figure 1.5 The geometric relationship of the reciprocal vectors, \( \mathbf{H} \) and \( \mathbf{H}' \), and the \( \mathbf{q} \)-vector. The circle represents the Ewald sphere. The bigger solid spots correspond to the primary reflections, and the smaller ones correspond to the superstructure reflections.
For a regular non-modulated structure, the reciprocal vector $\mathbf{H}$ is defined in Equation 1.5.

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

(1.5)

For a modulated superstructure, the reciprocal vector $\mathbf{H}'$ is defined in Equation 1.6.

$$\mathbf{H}' = \mathbf{H} + m\mathbf{q}, \mathbf{q} = q_1\mathbf{a}^* + q_2\mathbf{b}^* + q_3\mathbf{c}^*$$

(1.6)

Where $\mathbf{H}$ has the same meaning as in Equation 1.5.

A $\mathbf{q}$-vector is the vector from a primary reflection to one of its adjacent superstructure reflections. The $q_1$, $q_2$, and $q_3$ are components in the $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ directions. For a CMS, $q_1$, $q_2$, and $q_3$ are fractional numbers, but for an IMS, at least one of them is an irrational number. As shown in Equation 1.6, $m = 0$ corresponds to the primary reflection, and $m = 1, 2, etc.$ correspond to 1$^{st}$, 2$^{nd}$, etc. superstructure reflections.

A superstructure might be solved and refined in the supercell if the superstructure reflections are reasonably strong. The advent of high-resolution diffractometers with CCD detectors has made the measurement of weak reflections more reliable. However, if the superstructure reflections are weak, but still observable by the detectors, solving the structure with direct methods might be problematic. There might be more than one solution having very similar values of the figure-of-merit. In such cases each solution should be tried. It might not be easy to find out which one is the best solution until a stable refinement is obtained. Restraints (or possibly constraints) have to be applied to make the refinement stable. Solving and refining of a superstructure in the pseudocell is an alternative. The small distortions will be absorbed into the displacement parameters. As a result, the ellipsoids from the pseudocell refinement will provide important clues about the distortions in the supercell. If only a few satellite reflections are observed, or if the superstructure turns out to be an IMS, then special programs, such as JANA2000 (Petricek & Dusek, 2000) will be more appropriate.
Twinning

Twinning is a common phenomenon in crystals. A twinned crystal has two or more components joined together in some definite mutual orientation. The twin components have the same crystal structure but their unit-cell vectors do not all point in the same direction.

All crystals should be checked carefully under a polarizing microscope for possible twinning. If the twin components can be separated from each other, this should be attempted before the data collection is performed. Often this can be done by cutting the twinned crystal with a razor blade under the microscope. However, not all the twin components are separable. Sometimes twinned crystals look just like perfect single crystals without twinning. In such cases data collection will be performed as if the crystal is not twinned, and twinning will usually be discovered at a later stage. Several well-known symptoms and warning signs of possible twinning have been discussed (Herbst-Irmer & Sheldrick, 1998; Herbst-Irmer & Sheldrick, 2002).

A twinned crystal is preferably studied with an area detector. The advances in instrumentation and software now allow a large proportion of twinned crystals to be successfully studied. Certain types of twinning can usually be identified by the examination of precession planes. If the crystal is twinned in a non-merohedral way, i.e. without exact superposition of the unit-cell vectors, then the two sets of reflections from the two twin components will not be superimposed exactly so that many extra reflections will be present in the precession planes. One consequence of having many extra reflections is that the unit-cell dimensions might be wrong. A well-known symptom of having faulty unit-cell dimensions because of twinning is that one axis is considerably longer than the other two. In the case of merohedral twinning, the two sets of reflections from the two twin components will be superimposed exactly so that twinning cannot be identified from precession planes. In the case of pseudo-merohedral twinning, the two sets of reflections from the two twin components will be superimposed approximately. Pseudo-merohedral twinning may or may not be identified from precession planes depending on how well the reflections from the twin components are superimposed. The final judgment often depends on the refinement.
Figure 1.6 shows the reconstructed precession plane hk0 of a crystal structure that is twinned pseudo-merohedrally. The identification of twinning from this precession plane seems ambiguous because the sets of reflections from the individual twin components are superimposed well. If the superposition were a little less good it would have been possible to see that the reflections were split.
Figure 1.6 Reconstructed precession plane hk0 of pinacol monohydrate. The black spots represent reflections. The structure is twinned pseudo-merohedrally.
Merohedral and pseudo-merohedral twinning will make the structure appear to belong to a Laue group with symmetry higher than is correct. This can cause trouble in choosing the correct space group so that the structure can be solved. A safe approach is to solve the structure in the space group with lower symmetry. If this lower-symmetry space group is discovered to be incorrect during the refinement, then the structure can always be transformed to the correct higher-symmetry space group.

For structures in which one twin component dominates, solving the structure is usually not a problem, but the refinement will not be satisfactory unless the twinning is taken into account. For structures that are twinned severely, solving the structure might be a problem. In such cases, special programs, such as SHELXD (Schneider & Sheldrick, 2002) might be able to provide a reasonable initial solution to initiate refinement.

The most common method of twin refinement was proposed in the early 1970s (Pratt et al., 1971), and has been incorporated into many refinement programs, including SHELXL (Sheldrick, 1997b). In this method, the description of twinning requires two things: the mutual orientation of the twin components, the so-called twin law, and the fractions \( k_i, \sum k_i = 1 \) of each twin component. To refine a twinned structure, it is first necessary to figure out the twin law. Historically this has been done by hand and eye, but in recent years, algorithms have been developed to aid twin-law recognition prior to data collection and reduction, e.g. GEMINI (Sparks, 1999), and after data collection, e.g. PLATON-TwinRotMat and ROTAX (Cooper et al., 2002). Several frequently encountered twin laws are given in the SHELXL manual. A twin law is actually a pseudosymmetry operation that is added to the true symmetry operations of the structure. This is why the metric symmetry of a twinned structure often looks higher than the true Laue symmetry. The metric symmetry can be studied by the analysis of diffraction patterns. Making reconstructed precession planes is very important. Diffractometers with area detectors are more appropriate.

Twinning generally occurs for good structural reasons, and is often caused by packing faults. As such it is closely related to the process of crystallization, which is not yet understood well. Current knowledge of the process of crystallization indicates that at least two stages are
necessary: nucleation and subsequent growth. At which stage are the packing faults that induce twinning made? Why do they occur? Is there any way to systematically control them? The answers are not yet known. Actual observation of crystal growth cannot be accomplished in a fully satisfactory manner yet, but the advent of the Atomic Force Microscope (AFM) and other related direct-imaging techniques holds great promise. Given the importance of crystal growth in industry, and the fact that it is still not well understood, more efforts should be made to understand the underlying physics of crystallization.

**Polymorphism**

Crystallization is one of the most popular methods for purifying solid compounds. But the process is far beyond our control because our knowledge of nucleation and growth in crystals is still poor. Often, synthetic chemists are surprised when a compound can be crystallized in more than one crystal structure, *i.e.* when the compound gives polymorphs or solvates. In the case of pure elements, polymorphism is usually called allotropism, *e.g.* diamond and graphite are allotropes of carbon. Polymorphism is frequently encountered in mineral crystals. For example, zinc sulfide, ZnS has two known polymorphs: wurtzite and zinc blende. In molecular crystals, polymorphism appears to be less common. Nonetheless, it has been argued that polymorphism should be more likely in molecular crystals (McCrone, 1965). Unlike the nomenclature in mineral polymorphs, organic polymorphs are usually not given special names. They are more often referred to by Roman numerals (I, II, III, *etc.*) or Greek letters (α, β, γ, *etc.*). Different polymorphs can have different physical properties, such as crystal habit, melting point, solubility, optical properties, *etc.* If one polymorph has the desired properties, while the others do not, then a fixed procedure must be followed so that the growth of the other polymorphs will be suppressed. In the pharmaceutical industry polymorphism is very important because different polymorphs of a drug may have different bioavailabilities, and because governmental approval for one polymorph does not extend to other polymorphs.

Polymorphism can often be recognized by careful examination of crystals under the microscope. Different polymorphs usually have different crystal habits, but this is not necessarily true. There are examples, in which different-looking crystals turn out to be same, while similar-looking
crystals can turn out to be different. Determination of melting point is another useful method for the identification of different polymorphs, but if the differences in melting points are within the acceptable range, the existence of other polymorphs may be missed. The final judgment usually comes down to crystal structure determination, which is certainly the most reliable method.

Polymorphism is closely related to the process of crystallization. One critical nucleus ranging from a few tens of molecules to a few million molecules will be able to direct the subsequent growth of a crystal. It follows then that different polymorphs are likely seeded and grown from different nuclei. Nucleation is believed to be under the kinetic control rather than the thermodynamic control, and this provides an intuitive explanation for why the first polymorph seen for a new system may be less stable thermodynamically than polymorphs discovered later. There are examples, in which the less stable polymorph could no longer be prepared once the more stable polymorph was obtained. It was speculated that the presence of the nuclei of the more stable polymorph can suppress the formation of the nuclei of the less stable polymorph (Dunitz & Bernstein, 1995). There are also examples where crystals of different polymorphs were grown concomitantly (Bernstein et al., 1999). It is of no surprise that concomitant polymorphs have very similar lattice energies. The difference in lattice energies of polymorphs is typically about a few kJ/mol.

Polymorphic systems can be dynamic, and phase transformations between polymorphs are very important. There are two basic types of polymorphic systems: the enantiotropic and the monotropic (McCrone, 1965). Figure 1.7 shows the phase behavior of the two systems.
Figure 1.7 The $P$-$T$ plots for an enantiotropic system (left) and a monotropic system (right). The curve labeled with I/v. or II/v. represents the sublimation curve of polymorphs I or II. The curve labeled with I/v. represents the boiling curve. The broken lines represent regions that are unstable or inaccessible thermodynamically.
In an enantiotropic system, the temperature at which the phase transformation occurs is below the melting points of the two polymorphs. As a result, it should be possible to observe a solid-solid phase transformation from one polymorph to the other. In a monotropic system, however, the two polymorphs cannot undergo a solid-solid phase transformation because melting or dissolution must occur first. If the system is under the thermodynamic control, the phase behavior will follow the solid lines in Figure 1.7, but if the system is under the kinetic control, the phase behavior might possibly follow the broken lines. For example, the less stable polymorph of an enantiotropic system may crystallize out first, followed by a solid-solid phase transformation to the more stable polymorph.

Polymorphs provide good systems for people who work in the field of crystal structure prediction (hereafter, CSP). Although currently no one method of CSP is completely reliable, some encouraging progress has been made (Lommerse et al., 2000; Motherwell et al., 2002). It is still very difficult or impossible for people who study CSP to deal with very flexible molecules, uncommon space groups, and structures with $Z' > 1$. Taking the kinetic factors, such as nucleation and subsequent growth, into account is far beyond current expertise. Current CSP programs predict several plausible polymorphs that need to be confirmed experimentally.
Chapter Two
The Unusual Packing of Anhydrous and Hydrated Pinacol

Introduction

Pinacol (2,3-dimethyl-2,3-butanediol) exists in two stable conformations: gauche and trans (see Figure 2.1), both of which are seen in the solid state.
Figure 2.1 The chemical line drawing of pinacol, and the Newman projections of the two stable conformations: gauche and trans.
The phase diagram of the pinacol-water binary system (see Figure 2.2; Pushin & Glagoleva, 1922) indicates that there are two definite hydrated compounds: pinacol monohydrate (mp = 41.2 °C) and pinacol hexahydrate (mp = 45.4 °C); and two eutectic mixtures: pinacol/water (molar ratio = 1:0.25, mp = 29.4 °C) and pinacol/water (molar ratio = 1:1.6, mp = 40.4 °C).
Figure 2.2 The phase diagram of the pinacol-water binary system (redrawn from Pushin & Glagoleva, 1922).
The crystal structures of anhydrous and hydrated pinacol compounds have been investigated since the 1960s (Dahlqvist & Sillanpää, 2000; Jeffrey & Robbins, 1978; Kim & Jeffrey, 1970; O’Connor, 1969). Crystal data are summarized in Table 2.1.
Table 2.1 Summary of crystal data of anhydrous and hydrated pinacol in the literature.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
<td>Anhydrous pinacol</td>
<td>Hexagonal pinacol</td>
<td>Pinacol monohydrate</td>
<td>Pinacol hexahydrate</td>
</tr>
<tr>
<td><strong>mp (°C)</strong></td>
<td>39-40</td>
<td>27-29</td>
<td>N/A</td>
<td>45</td>
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<td><strong>Data collection temperature (K)</strong></td>
<td>Room temperature</td>
<td>193</td>
<td>N/A</td>
<td>Room temperature</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
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<td>P6_5</td>
<td>P4_2</td>
<td>P4_2/mnm</td>
</tr>
<tr>
<td><strong>Z’</strong></td>
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<td>2</td>
<td>1/2</td>
<td>1/8</td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td>C_6H_{14}O_2</td>
<td>C_6H_{14}O_2</td>
<td>C_6H_{14}O_2·H_2O</td>
<td>C_6H_{14}O_2·6H_2O</td>
</tr>
<tr>
<td><strong>R-factor</strong></td>
<td>0.063</td>
<td>0.079</td>
<td>N/A</td>
<td>0.06</td>
</tr>
</tbody>
</table>
The monoclinic anhydrous pinacol structure (Jeffrey & Robbins, 1978) is one of the very few structures in the CSD that has chemically equivalent molecules located on three different crystallographic sites. One molecule is located on a general position, one is on an inversion center, and one is on a twofold axis. Therefore, the number of the molecules in the asymmetric unit is $Z' = 1 + \frac{1}{2} + \frac{1}{2} = 2$. The molecule on the inversion center is disordered, which is probably because the data were collected at room temperature. Disorder always complicates crystal structure determinations, but is often alleviated when crystals are kept very cold. As a result, it was decided to collect data at low temperature and to re-determine the structure.

The hexagonal pinacol structure (Dahlqvist & Sillanpää, 2000), which was claimed to be a new polymorph, was discovered only recently. The needle-shaped crystals were obtained from a 0.1 M cyclohexane solution at 8-10 °C after a long period of time. The crystal structure determination is suspicious. The $R$-factor is high (see Table 2.1). When the structure from the CSD was checked with PLATON, several potentially serious problems were found. First of all, missing symmetry was found by the PLATON-ADDSYM algorithm. The space group was strongly suggested to be $P6_{5}22$ (or $P6_{1}22$) rather than the reported $P6_{5}$. Second, there are solvent-accessible voids in the crystal structure that were analyzed by PLATON-VOID. A packing coefficient was calculated as 0.55, which is even outside the low end of the expected range (0.65-0.80; Kitaigorodskii, 1961; Dunitz et al., 2000). This means that the packing is very loose and is therefore unlikely to be preferred energetically. Third, in the crystal structure the pinacol molecules form empty channels that run parallel to the $c$ axis (see Figure 2.3). The diameter of these channels is about 5 Å. Such large empty channels are very unlikely to be stable in molecular crystals. It is therefore highly likely that some suitably small molecules (e.g. water) might be loosely stacked within the channels. In any event, these channels seemed to be overlooked by Dahlqvist and co-workers in their original investigation.
Figure 2.3 The space-filling model of the reported hexagonal pinacol structure (Dahlqvist & Sillanpää, 2000) looking down the c direction. Carbon, oxygen, and hydrogen atoms are colored in gray, red, and white. The diameter of the empty channels is about 5 Å.
The existence of pinacol monohydrate was established about eighty years ago (Pushin & Glagoleva, 1922), but the crystal structure is not reported in the CSD. O’Connor et al. had tried to tackle this crystal structure before, but the results were not satisfactory (O’Connor, 1969). The proposed space group was $P4_2$ with two formula units in the unit cell. In 1969, the instruments and software were far less advanced than nowadays. With modern equipment and techniques, it seemed feasible and worthwhile to identify the problems and to solve them.

The crystal structure of pinacol hexahydrate (Kim & Jeffrey, 1970) is also worthy of re-determination. The pinacol molecule itself is totally disordered in the structure, and the reported space group, $P4_2/mmm$ is only rarely encountered in the CSD (Brock & Dunitz, 1994). Furthermore, it is common for merohedral twinning to cause a crystal with $4/m$ Laue group symmetry to appear to have higher Laue group symmetry, $4/mmm$. This structure was determined more than thirty years ago using a serial diffractometer. At that time, people worried much less about twinning than they do nowadays. Indeed, the importance of twinning in routine crystal structures was not truly appreciated until the advent of reliable, high-quality area detectors. The advances in instrumentation and computer programs have greatly improved the ability to identify and solve twinned structures. Furthermore, their data were collected at room temperature. With a more advanced diffractometer and a low-temperature system, the quality of the data can certainly be greatly improved.

**Experimental**

**Crystal Growth**

Crystals of monoclinic anhydrous pinacol (see Figure 2.4) were grown by sublimation from a closed vial at room temperature.
Figure 2.4 A photograph of single crystals of anhydrous pinacol.
The hexagonal pinacol does not crystallize at all well at room temperature. Only one needle-shaped crystal (see Figure 2.5) was found in the vial; the rest of the crystals all appear to be the monoclinic pinacol crystals. The hexagonal pinacol crystal is colorless. The colors on the crystal in Figure 2.5 are interference colors due to the presence of the polarizer attached to the microscope. Attempts to grow better crystals of hexagonal pinacol in cyclohexane at lower temperature (~ 5 °C) were not successful because the crystals grew too fast as very small needles. If the temperature can be carefully controlled in a programmed way, perhaps bigger crystals might be obtained over an extended period of time.
Figure 2.5 A photograph of one single crystal of hexagonal pinacol. The crystal is actually colorless. The color on the crystal is an artifact of the polarizer of the microscope.
Crystals of pinacol monohydrate (see Figure 2.6) were grown at room temperature from a closed vial containing excess pinacol and a little water.
Figure 2.6 A photograph of single crystals of pinacol monohydrate.
Crystals of pinacol hexahydrate (see Figure 2.7) were grown from a saturated pinacol-water solution at room temperature.
Figure 2.7 A photograph of single crystals of pinacol hexahydrate.
X-Ray Diffraction

All data collection was performed on a Nonius KappaCCD diffractometer with graphite-monochromated sealed-tube Mo Kα radiation (\(\lambda = 0.71073 \, \text{Å}\)) under the control of the program \textit{COLLECT} (Nonius, 1998). Data reduction was done with \textit{DENZO-SMN} (Otwinowski & Minor, 1997). No extra experiment (e.g., an azimuthal scan) was done for absorption correction, but absorption for small, light atom crystals using Mo Kα radiation is expected to be small in any case. However, since all of the datasets have an average redundancy of at least 3, the scaling algorithm, \textit{SCALEPACK}, which is a part of the data-reduction program, compares the intensities of equivalent reflections, and corrects for anisotropic absorption. This process is usually referred to as \textit{multi-scan}. The structures were solved with \textit{SHELXS97} (Sheldrick, 1997a) or \textit{SHELXD} (Schneider & Sheldrick, 2002) and refined with \textit{SHELXL97} (Sheldrick, 1997b). Molecular and packing diagrams were generated with \textit{XP} (Bruker, 1997) and \textit{Mercury} (Bruno et al., 2002). Publication tables were prepared with \textit{XCIF} (Bruker, 1997). Other experimental details are given in Appendix A. Crystal data, atomic coordinates, displacement parameters, bond lengths and angles, and torsion angles are given in Appendix B.

The diffractometer is equipped with a low-temperature system from CRYO Industries of America, which generates a steady nitrogen gas stream from below 90 K up to around 320 K by boil-off of liquid nitrogen. Programmed cooling or warming at a specified rate is also feasible. All data in this chapter were collected at low temperature by using flash cooling, \textit{i.e.} crystals were cooled to the low temperature in less than a second. Table 2.2 lists the local data code and data collection temperature for each compound. The anhydrous pinacol and the hexagonal pinacol were studied in 2001 before a new, more advanced low-temperature device was installed. The most convenient operating temperature of the old device was 173 K, and represented a trade off between liquid nitrogen consumption and low temperature. After the installation of the new low-temperature device, pinacol monohydrate and pinacol hexahydrate were studied. The normal operating temperature is 90 K on the new device, but temperatures as low as 80 K are possible with increased liquid nitrogen consumption. Anhydrou pinacol was re-studied at 90 K by using the new low-temperature device. Since suitable crystals of hexagonal pinacol could not be obtained again, this compound could not be re-studied at 90 K.
Table 2.2 The local data code in X-Ray Lab of Chemistry Department at University of Kentucky, and data collection temperature of five pinacol structures.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Local data code</th>
<th>Data collection temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous pinacol</td>
<td>k03278</td>
<td>90</td>
</tr>
<tr>
<td>Anhydrous pinacol</td>
<td>k01154</td>
<td>173</td>
</tr>
<tr>
<td>Hexagonal pinacol</td>
<td>k01235</td>
<td>173</td>
</tr>
<tr>
<td>Pinacol monohydrate</td>
<td>k03227</td>
<td>90</td>
</tr>
<tr>
<td>Pinacol hexahydrate</td>
<td>k03226</td>
<td>90</td>
</tr>
</tbody>
</table>
Anhydrous Pinacol

In the reported RT (room-temperature) structure (Jeffrey & Robbins, 1978), molecules on the inversion centers are disordered. The ratio of occupancies for the two disorder parts is 0.75:0.25. The two parts seem to be related by a pseudo mirror plane (see Figure 2.8).
Figure 2.8 A disordered pinacol molecule on an inversion center in the reported RT anhydrous pinacol structure (redrawn from Jeffrey & Robbins, 1978). Carbon and oxygen atoms are colored in black and red. Hydrogen atoms are omitted for clarity. The major disorder part depicted with solid lines has occupancy of 0.75; the minor disorder part with open lines has occupancy of 0.25. The two parts seem to be related by a pseudo mirror plane.
Data in this work were collected at two LTs (low temperatures): 173 and 90 K. There is no disorder at all in either of the two LT structures. The space group is \( C2/c \). Structure solution and refinement were routine. The two LT structures and the reported RT structure are almost the same except for the disorder. In this case the advantages for collecting data at low temperatures are to eliminate the disorder and to get a better refinement.

Figure 2.9 shows the ellipsoid plots for the two LT structures. Molecule 1 is on a twofold axis; molecule 2 is on a general position; and molecule 3 is on an inversion center. As a result, the number of the independent molecules is \( Z' = \frac{1}{2} + 1 + \frac{1}{2} = 2 \). Molecules 1 and 2 are in the gauche conformation; and molecule 3 is required by the centrosymmetry to be in the trans conformation.
Figure 2.9 The two (one full and two halves) symmetry-independent molecules in the two LT (173 and 90 K) structures of anhydrous pinacol. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 50% probability. Molecule 1 is on a twofold axis (half independent); molecule 2 is on a general position (fully independent); and molecule 3 is on an inversion center (half independent).
The hydrogen atoms of the methyl groups were put in calculated positions (AFIX 137) with isotropic displacement parameters of 1.5 times $U_{eq}$ of the attached parent carbon atoms. The hydrogen atoms of the hydroxyl groups were located from a difference map and refined using isotropic displacement parameters.

The crystal consists of two-dimensional H-bonded layers stacked along the b direction (see Figure 2.10). Inside each layer there are two types of H-bonded motifs: one is an $R_{2}^{2}(10)$ dimer, and the other is an $R_{4}^{4}(8)$ tetramer. Graph-set symbols, such as $R_{2}^{2}(10)$, are described in Bernstein’s book (Bernstein, 2002). An $R_{2}^{2}(10)$ dimer consists of two gauche conformers (see the molecules colored in blue in Figure 2.11). A gauche conformer has $C_{2}$ symmetry, hence is chiral. Both of the two gauche conformers of a dimer lie on general positions, but only one conformer is crystallographically independent because the two conformers are related by an inversion center. It means that the $R_{2}^{2}(10)$ dimer is centrosymmetric, and consists of an enantiomeric pair of the gauche conformers. An $R_{4}^{4}(8)$ tetramer consists of one $R_{2}^{2}(10)$ dimer, one gauche conformer (this gauche conformer lies on a twofold axis, and is colored in green in Figure 2.11), and one trans conformer (it lies on an inversion center, and is colored in red in Figure 2.11). The H-bonding in the c direction shows the pattern of $\cdots R_{2}^{2}(10) R_{4}^{4}(8) R_{4}^{4}(8) R_{2}^{2}(10) R_{4}^{4}(8) R_{4}^{4}(8) \cdots$. The two adjacent $R_{4}^{4}(8)$ tetramers are related by an inversion center because they are connected to each other by sharing a trans conformer. The two $R_{4}^{4}(8)$ tetramers that are separated by an $R_{2}^{2}(10)$ dimer are also related by an inversion center because the dimer lies on an inversion center. The H-bonding in the [1 0 1] direction shows the same pattern as in the c direction except that the two adjacent $R_{4}^{4}(8)$ tetramers are related by a twofold axis because they are connected to each other by sharing a gauche conformer that lies on a twofold axis.
Figure 2.10 Three H-bonded layers stacked along the $b$ direction in the crystal structure of anhydrous pinacol. Molecules in green are on twofold axes; molecules in blue are on general positions; molecules in red are on inversion centers. Hydrogen atoms are omitted for clarity. H bonds are represented by black dotted lines.
Figure 2.11 One H-bonded layer looking down the $b$ direction in the crystal structure of anhydrous pinacol. Molecules in green are on twofold axes; molecules in blue are on general positions; molecules in red are on inversion centers. Hydrogen atoms are omitted for clarity. H bonds are represented by black dotted lines.
Hexagonal Pinacol

As mentioned previously, the reported hexagonal "anhydrous" pinacol structure (Dahlqvist & Sillanpää, 2000) has clear and identifiable flaws. The structure has empty channels in it (see Figure 2.3). If solvent molecules exist in the "empty" channels, then technically the hexagonal phase is not a polymorph of the monoclinic anhydrous pinacol, but a solvate. Based on our data, this hexagonal pinacol is probably pinacol hemihydrate. During our refinement, a reasonably high peak of electron density (0.90 e/Å³) was located within the channel in a difference map. The peak was assigned to be an oxygen atom of a water molecule. The occupancy of the water O atom appeared to be a little less than 0.5. In order to make the refinement stable, the occupancy of this water O atom was fixed at 0.5.

The space group should be $P6_522$ or $P6_122$ rather than the reported $P6_5$. The ambiguity in the handedness of the screw axis exists because it is impossible to determine the absolute structure with Mo radiation for purely light-atom structures such as pinacol. The reported structure has $Z' = 2$. Because the order of the space group here is twice that of the reported space group, the structure here has $Z' = 1$, i.e. one formula unit ($C_6H_{14}O_2\cdot0.5H_2O$) in the asymmetric unit (see Figure 2.12). The pinacol molecule is in the gauche conformation.
Figure 2.12 One pinacol molecule and half water molecule in the asymmetric unit of the hexagonal pinacol structure (173 K). The ellipsoids are drawn at 50% probability. The hydrogen atoms of the methyl groups are omitted for clarity. The hydrogen atom in each hydroxyl group is disordered equally over two positions. The hydrogen atoms of the water molecule were not included in the refinement.
The hydrogen atoms of the methyl groups were put in calculated positions \textit{(AFIX 137)} with isotropic displacement parameters of 1.5 times $U_{eq}$ of the preceding parent carbon atoms. The hydrogen atoms of the hydroxyl groups were located from a difference map, and in each hydroxyl group the hydrogen atom is disordered equally over two positions (H1OA and H1OB in –O1H; H2OA and H2OB in –O2H; see Figure 2.12). The isotropic displacement parameters of the four disordered hydrogen atoms were fixed at 0.12 Å$^2$; and the four O-H distances were all made equal to a single refinable parameter (a “free variable”, or $FVAR$ in the program \textit{SHELXL}), which refined to 0.87(5) Å. The displacement parameters for the water O atom (O1W, see Figure 2.12) are very large; therefore, it is impossible to find any hydrogen atom attached to it.

Although the mistakes in the reported structure have been corrected, the refinement here is still not satisfactory partially because of the limited resolution (the crystal diffracted only up to ~ 45° in 2θ). Attempts to grow better crystals in cyclohexane at lower temperature (~ 5 °C) were not successful. The crystals always grew too quickly and produced bundles of small needles. Shortly after the new diffractometer was installed (Bruker-Nonius Kappa goniometer with an FR591 Cu rotating anode and SMART 6K CCD detector), a small needle-shaped crystal was examined. The results were still not satisfactory because the crystal still diffracted poorly at high scattering angles. This is probably due to the presence of disordered molecules in the channels in the crystal. Although it is likely that there is water in the channels (see Figure 2.13), the electron density found within the channels was very diffuse, which implies that water molecules must stack very loosely within the channels.
Figure 2.13 The space-filling model of the hexagonal pinacol structure looking down the c direction. Carbon, oxygen, and hydrogen atoms are colored in gray, red, and white. The hydrogen atoms of the water molecules are not shown.
In the crystal structure, two adjacent pinacol molecules form an H-bonded $R_2^2(10)$ dimer. The common feature of the dimer here and the dimer in the anhydrous pinacol structure is that both dimers consist of two gauche conformers. The difference is that the dimer here lies on a twofold axis, whereas the dimer in the anhydrous pinacol structure lies on an inversion center (see Figure 2.14). The centrosymmetric dimer consists of an enantiomeric pair of the gauche conformers, and the four oxygen atoms are almost co-planar. The $C_2$ dimer, however, consists of two enantiomerically pure gauche conformers, and the four oxygen atoms are not co-planar. In structures of vic-diols, centrosymmetric $R_2^2(10)$ dimers are very likely to be encountered; enantiomerically pure crystals are less likely than racemic crystals to contain dimers (Brock, 2002b). Hexagonal pinacol crystallizes in $P6_122$ or $P6_522$ with $Z' = 1$. Therefore, the crystal studied consists of enantiomerically pure gauche conformers.
Figure 2.14 Two types of H-bonded dimers seen in two pinacol structures. Carbon and oxygen atoms are colored in gray and red. Hydrogen atoms are omitted for clarity. H bonds are represented by black dotted lines. Plot 1 shows a dimer on an inversion center (seen in the anhydrous pinacol structure). Plot 2 shows a dimer on a twofold axis (seen in the hexagonal pinacol structure).
Two $\text{R}_{2}^{2}(10)$ dimers are H-bonded and form an $\text{R}_{4}^{4}(8)$ tetramer (see Figure 2.15). The dimers pack along the $3_1$ (or $3_2$) screw axes to form ribbons that twist into a helix having three dimers per turn. The alternation pattern of the helix, $\cdots \text{R}_{2}^{2}(10) \text{R}_{4}^{4}(8) \text{R}_{2}^{2}(10) \text{R}_{4}^{4}(8) \cdots$, is characteristic of vic-diols, but the twisting seems to be surprising because a packing pattern in which the ribbons are approximately planar would have been expected (Brock, 2002b). The threefold helix here is reminiscent of the fivefold helix in the structure of $N''$-cyano-$N,N$-diisopropylguanidine (Hao et al., 2005). Inside each helix all the hydroxyl groups point inwards, which leads to hydrophobic outer surfaces formed by the methyl groups. The helices pack along the $6_1$ (or $6_5$) screw axes and form channels that could accommodate water molecules, and possibly other small molecules as well, such as $\text{N}_2$ or $\text{O}_2$. The channels have hydrophobic inner surfaces, which prevent the water molecules from interacting with the hydroxyl groups. Therefore, water molecules are H-bonded to themselves and form helical chains along the $6_1$ (or $6_5$) screw axes. Ideally, water molecules should form H bonds in the tetrahedral geometry (e.g., as in ice) because of the H-bonding requirements (two donors; two-acceptors). However, such desirable geometry is difficult to achieve in a narrow hydrophobic channel. Similar H-bonded chain-like water structure has been discovered in other systems, such as single-walled carbon nanotubes (Kolesnikov et al., 2004) and some transmembrane proteins (Kong & Ma, 2001; Pomes & Roux, 2002).
Figure 2.15 Packing of the hexagonal pinacol structure looking down the \( c \) direction (the top plot). Carbon and oxygen atoms are colored in gray and red. Hydrogen atoms are omitted for clarity. H bonds are represented by black dotted lines. The bottom plot shows only part of the structure in the top plot and is viewed from a different direction.
Pinacol Monohydrate

The crystal structure was determined in 1969 (O’Connor, 1969). The proposed space group was $P4_2$ with two formula units in the unit cell. The results were not satisfactory. Data in this work were collected at 90 K. The structure determination was not routine. The diffraction patterns look unusual (see Figure 2.16). All diffraction spots tend to have similar intensities, and the spots also look very big. These are the symptoms of twinning; twinning was later confirmed by the structure solution and refinement.
Figure 2.16 Reconstructed precession plane 2kl of the pinacol monohydrate structure (90 K).
The space group determination was difficult. The unit cell in this work is eight times bigger than the cell reported by O’Connor (O’Connor, 1969). The cell dimensions [14.688(3), 14.727(3), 15.244(3) Å and 90.00(2), 90.03(3), 90.00(2)°] are consistent with an orthorhombic space group. The program *XPREP* (Bruker, 1997) suggested three options: *I*-centered tetragonal, *I*-centered orthorhombic, and *I*-centered monoclinic. The agreement factors ($R_{\text{sym}}$) of the three options were 0.193, 0.117 and 0.098. Since the third option had the lowest $R_{\text{sym}}$, it was probably the right one; that choice was later confirmed by the structure solution and refinement in space group $I2/a$ (an alternate setting of $C2/c$). The number of the independent formula unit ($C_6H_{14}O_2\cdot H_2O$) is $Z = 2$, which means that there are two pinacol and two water molecules in the asymmetric unit (see Figure 2.17). Both pinacol molecules are in the *trans* conformation.
Figure 2.17 The asymmetric unit of the pinacol monohydrate structure (90 K). O5 and O6 are oxygen atoms of water molecules. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 50% probability.
The structure could not be solved with direct methods, which are the methods used to solve most small-molecule structures. It is not surprising that direct methods failed since the $E$-values are biased due to twinning. The Patterson method is also not a good choice due to the absence of heavy atoms in the compound. Eventually the structure was solved in space group $I2/a$ using a program called *SHELXD* (*XM* in Bruker’s *SHELXTL* software suite). *SHELXD* uses a different algorithm for structure solution, called dual space recycling. This solution was then used as a starting model to initiate refinement. The structure was refined using a twin model with four twin components in the crystal (For simplicity, the word “twin” will be used here, even though there are four, rather than two, orientations of diffracting domains).

It is reasonable to assume that in the crystal the four twin components are orientated in a pseudo-merohedral way such that the $c$ axis is nearly a fourfold axis. Such an assumption is consistent with the unit-cell dimensions: the edges $a$ and $b$ are very similar, and the angle $\beta$ is almost 90°. The assumption explains why the program *XPREP* gave an option of $I$-centered tetragonal structure. The assumption is also supported by the observation that the reflections are not split (see Figure 2.16), which implies that reflections from the four twin components overlap well.

In order to refine such a twin structure, the overlapped reflections must be separated out. Since each reflection includes contributions from all four twin components, each reflection of $hkl$ has to be split into four reflections, the indices of which are $hkl$, $h-k-l$, $kh-l$, and $k-hl$. These indices were worked out by assuming the $c$ axis is a pseudo fourfold axis. Data were merged in $I2/a$ before the splitting to avoid introducing incorrect standard uncertainties (Herbst-Irmer & Sheldrick, 2002). A new file of data, which consists of the split reflections, was then prepared according to the “HKLF 5” option in program *SHELXL*. In order to define the fractional contribution of each twin component to any given intensity, three parameters (*BASF* parameters in program *SHELXL*) are required (the fourth fraction is known because the contribution of all four must sum to unity). The refined values [0.287(2), 0.186(2), and 0.179(2)] have small standard uncertainties, which is good evidence that the twin model is correct.

Although twinning was taken into account, the refinement was still neither straightforward nor totally satisfactory. The correlation coefficients were still very high (0.8 ~ 0.7), which means that
there must be some unrecognized symmetry or pseudosymmetry. Careful examination revealed a surprisingly good inversion center at the center of each pinacol molecule, which explains the large intra-molecular correlations. Hence the atoms in the two related parts of each pinacol molecule were required (EADP) to have the same displacement parameters, and chemically equivalent distances were restrained (SADI) to be the same. The restraint “SAME” was also used to make the two independent pinacol molecules have similar geometry. The approximate positions of the two pseudo inversion centers are (0.5, 0.25, 0.5) and (0.25, 0.5, 0.25). Since these are special positions, they give rise to additional pseudosymmetry, which is a pseudo translation of $\frac{1}{2}$ along the b direction. Such a pseudo translation causes further high correlation between the two water molecules (The absolute values of the correlation coefficients are 0.8 ~ 0.7). Hence, EADP was used to make the two water O atoms have the same displacement parameters.

It is possible that the pseudosymmetry found is actually true symmetry, but this possibility is not easily tested because of the orientation of the twin operators relative to the cell axes of the possible smaller, higher symmetry unit cell. In any event the constraints and restraints used in the refinement would substitute for the true symmetry conditions. The rest of the discussion will assume that the correct space group is the pseudosymmetric $I2/a$ described above.

The hydrogen atoms of the methyl groups were put in calculated positions (AFIX 137) with isotropic displacement parameters of 1.5 times $U_{\text{eq}}$ of the preceding parent carbon atoms. The hydrogen atoms of the hydroxyl groups were put in calculated positions (AFIX 87) with isotropic displacement parameters of 1.5 times $U_{\text{eq}}$ of the preceding parent oxygen atoms. The hydrogen atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.94(2) Å. The H-O-H angles were restrained to be 104.5º. The isotropic displacement parameters were set to 1.5 times $U_{\text{eq}}$ of the bonded oxygen atoms.

In the crystal structure, all the pinacol molecules are in the trans conformation; therefore, an $R_2^2(10)$ dimer that is limited to the gauche conformer cannot be formed. Actually pinacol and water form infinite H-bonded chains in the structure. The basic building block of the chain is an
$R_4^4(8)$ ring, which consists of two pinacol molecules and two water molecules. There are two types of $R_4^4(8)$ rings: rings of Type I lie on inversion centers; and rings of Type II lie on twofold axes (parallel to the $b$ direction). The chain extended in the $b$ direction consists of rings of Type I (see plot 1 of Figure 2.18). The chain extended in the $a$ direction consists of rings of Type II (see plot 2 of Figure 2.18). The chain extended in the $c$ direction consists of the alternations of rings of Types I and II (see plot 3 of Figure 2.18).
Figure 2.18 The H-bonding of the pinacol monohydrate structure. Hydrogen atoms are omitted for clarity. H bonds are shown in black dotted lines. The two independent pinacol molecules are colored in blue and green. The two independent water molecules are colored in red and yellow. Plot 1 shows an H-bonded chain lies on inversion centers, and is extended in the \( b \) direction. Plot 2 shows an H-bonded chain lies on twofold axes (parallel to the \( b \) direction), and is extended in the \( a \) direction. Plot 3 shows an H-bonded chain that is extended in the \( c \) direction.
Figures 2.19, 2.20, and 2.21 show the three-dimensional H-bonding network from the \textbf{b}, \textbf{a}, and \textbf{c} directions. The structure is a superstructure with twofold modulations in the \textbf{b} direction, \textit{i.e.} there are pseudo translations of ½ along the \textbf{b} direction (see Figure 2.19). Furthermore, both of the two independent pinacol molecules are located on pseudo inversion centers. These pseudosymmetric relationships caused some refinement difficulties during the structure determination. These pseudosymmetric relationships might be real, but the constraints and restraints in the refinement have substituted for the missing symmetry relationships.
Figure 2.19 The three-dimensional H-bonding network of the pinacol monohydrate structure looking down the b direction (the top plot). The bottom plot shows the same structure rotated by a few degrees about the c axis. The color schemes and atom types are defined in Figure 2.18.
Figure 2.20 The three-dimensional H-bonding network of the pinacol monohydrate structure looking down the a direction. The color schemes and atom types are defined in Figure 2.18.
Figure 2.21 The three-dimensional H-bonding network of the pinacol monohydrate structure looking down the c direction. The color schemes and atom types are defined in Figure 2.18.
Pinacol Hexahydrate

The structure was determined at room temperature in 1970 (Kim & Jeffrey, 1970). It is suspected that the structure may be twinned because the space group, $P4_2/mnm$, is rare in the CSD. In order to obtain a more convincing structural model, data were collected at 90 K. Indeed, the LT structure could be solved and refined reasonably well using the reported space group, $P4_2/mnm$. However, when the crystals were examined by using a polarized microscope, the extinction condition (see Appendix E for further reading) did not seem to be quite perfect, as it should be for tetragonal crystals, which indicated that the actual crystal system was probably not tetragonal. It was then proposed that the actual structure is orthorhombic, but twinned pseudo-merohedrally. It is the twinning that makes the $c$ axis appear to be an approximate fourfold axis, therefore the twin law is ($0 1 0 / 1 0 0 / 0 0 -1$).

Such an assumption is consistent with the microscopic behavior of the crystal. The reason that the crystal nearly extinguishes is because the domain sizes of the twin components are small enough that the visible light is only barely affected. The X-rays, on the other hand, have a much shorter wavelength, therefore, they are more significantly affected. When the domain size gets down to a certain size, the diffraction becomes much less sharp and hence more diffuse. Thus the observation of the diffuse scattering (see Figure 2.22) by using X-rays supports such an assumption. A quantitative treatment of diffuse scattering is beyond the scope of this work. The occurrence of the diffuse scattering was not reported in the original work (Kim & Jeffrey, 1970), but there are good reasons that Kim and co-workers could not observe the diffuse scattering even if they did try to look for it. First, the reconstructed precession plane shown in Figure 2.22 was generated from the raw diffraction frames collected with a CCD detector. In 1970, such a precession plane had to be recorded on photographic film with a Buerger precession camera. The weak diffuse scattering would be very difficult to observe on film. Second, the data in this work were collected at 90 K, while the old data were collected at room temperature. Collecting data at low temperature undoubtedly increased the chance to observe the weak diffuse scattering.
Figure 2.22 Reconstructed precession plane hk0 of the pinacol hexahydrate structure (90 K). The diffuse scattering is indicated by the presence of the weak streaks between the Bragg reflections.
In order to test the assumption further, the LT structure in space group $P4_2/mnm$ was transformed to an orthorhombic space group. The only possible orthorhombic space group with the same systematic absences is $Pnmn$. The refinement in $Pnmn$ turned out to be as satisfactory as in $P4_2/mnm$. In both models, there are two formula units (C$_6$H$_{14}$O$_2$·6H$_2$O) in the unit cell; and pinacol has to be in the trans conformation because it sits on an inversion center and a mirror plane. In $P4_2/mnm$ pinacol is also located on a second mirror plane with the normal direction of $\mathbf{a} - \mathbf{b}$ (see Figure 2.23). It is this second mirror plane that causes pinacol to be disordered. The ratio of occupancies for the two disorder parts is required by the reflection symmetry to be 0.5:0.5. In $Pnmn$, however, such a second mirror plane does not exist, but pinacol is still disordered in the same way, which causes large correlations between the two disorder parts during the least-squares refinement. As a result, several restraints (SAME, SADI, ISOR, DELU, SIMU, commands in program SHELXL) were used to make the refinement stable. The ratio of occupancies for the two disorder parts in $Pnmn$ refined to 0.428(4):0.572(4), which is different enough from 0.5:0.5 to add credence to the $Pnmn$ assignment. As mentioned previously, the $Pnmn$ structure is also twinned pseudo-merohedrally. The twin fraction (“batch-scale factor”, or BASF in SHELXL) refined to 0.32(2), which means that the “single” crystal consists of twin domains with fractional ratio of 0.68(2):0.32(2). If the structure is actually tetragonal, then this ratio should be 0.5:0.5. Again, the refinement seems to support the twinned orthorhombic model with space group $Pnmn$. 
Figure 2.23 The asymmetric unit in the two structural models of pinacol hexahydrate (90 K); only the independent atoms are labeled. The ellipsoids are drawn at 50% probability. O2 and O3 are oxygen atoms of water molecules. Hydrogen atoms are omitted for clarity. Pinacol is disordered in both models. The chemical bonds in the two disorder parts are shown in solid and open lines. The directions of the unit-cell vectors are the same in both models.
In both models, the hydrogen atoms of the methyl groups were put in calculated positions (AFIX 137) with isotropic displacement parameters of 1.5 times $U_{eq}$ of the preceding parent carbon atoms. The hydrogen atoms of the hydroxyl groups were located from a difference map, and were freely refined with isotropic displacement parameters set to 1.5 times $U_{eq}$ of the bonded oxygen atoms. In $P4_{2}/mnm$ the hydrogen atoms of the water molecules were treated the same way as the hydroxyl groups. In $Pnnm$ the O-H distances in water molecules were all made equal to a free variable, which refined to 0.84(1) Å. The H-O-H angles were restrained to be 104.5°. The isotropic displacement parameters of the hydrogen atoms in water molecules were set to 1.5 times $U_{eq}$ of the bonded O atoms.

In the crystal structure ($Pnnm$ model), there are two independent water molecules (see Figure 2.23). The O2-water molecule (the oxygen atom of this water molecule is labeled as O2) is on a general position. The O3-water molecule (the oxygen atom of this water molecule is labeled as O3) is on a twofold axis (parallel to the c direction). Pinacol molecules are all in the trans conformation, and each of them is H-bonded to four O2-water molecules. Water molecules form H bonds in approximately tetrahedral geometry. The O2-water molecule forms H bonds with one pinacol molecule, another O2-water molecule, and two O3-water molecules. The O3-water molecule forms H bonds with four O2-water molecules. Pinacol molecules and O2-water molecules form H-bonded chains in the $a + b$ and $a - b$ directions. The basic building block of the chain is a $R_{2}^{2}(12)$ ring, which consists of two pinacol molecules and four O2-water molecules (see Figure 2.24). The chains are H-bonded through O3-water molecules (see Figures 2.25 and 2.26). The H-bonding is three-dimensional (see Figures 2.27 and 2.28).
Figure 2.24 An H-bonded chain in the pinacol hexahydrate structure. Hydrogen atoms are omitted for clarity. H bonds are shown in black dotted lines. Pinacol molecules (colored in green) are on inversion centers and mirror planes (perpendicular to the c direction). The minor disorder part of the pinacol molecule is omitted for clarity. The water molecules on general positions are colored in blue. The water molecules on twofold axes (parallel to the c direction) are colored in red (not shown in this figure).
Figure 2.25 Two H-bonded chains that are extended in the same direction in the pinacol hexahydrate structure. The color schemes and atom types are defined in Figure 2.24. The two chains are H-bonded to each other through water molecules that are on twofold axes. Plot 2 shows the same structure as in plot 1 viewed from a different direction.
Figure 2.26 Two H-bonded chains that are extended in different directions in the pinacol hexahydrate structure. The color schemes and atom types are defined in Figure 2.24. The two chains are H-bonded to each other through water molecules that are on twofold axes. Plot 2 shows the same structure as in plot 1 viewed from a different direction.
Figure 2.27 The three-dimensional H-bonding network of the pinacol hexahydrate structure looking down the $c$ direction. The color schemes and atom types are defined in Figure 2.24.
Figure 2.28 The three-dimensional H-bonding network of the pinacol hexahydrate structure looking down the $a - b$ direction. The color schemes and atom types are defined in Figure 2.24.
Summary and Discussion

The obvious question is, why does a simple molecule like pinacol produce a series of structures that are so unusual and so crystallographically perverse? The answer seems to be that the molecule is small and undeformable, and that it should participate in four O-H⋯O bonds.

Since the van der Waals surfaces of methyl groups are roughly spherical (with a few bumps) and since conformations that have no torsion angles near 60° are unfavorable, the overall shape of pinacol is more or less fixed. The molecular shape cannot adjust much to improve the packing density.

The H-bonding requires that the two hydroxyl groups participate in two H bonds with certain orientations. It is not surprising that hydrates are formed since the H-bonding requirements of pinacol and water are actually the same (two donors; two acceptors).

Table 2.3 summarizes the crystal data of anhydrous and hydrated pinacol. None of these structures is especially densely packed. The anhydrous and monohydrate structures have similar densities and melting points. The hexahydrate structure is the most densely packed, whereas the hexagonal structure is the least densely packed. A packing coefficient was calculated as well for each structure by using PLATON-VOID. The expected range of packing coefficients for typical molecular crystals is 0.65-0.80 (Kitaigorodskii, 1961; Dunitz et al., 2000). The packing coefficients for the structures here are all very low, which suggests that the packing is loose.
Table 2.3 Summary of crystal data of anhydrous and hydrated pinacol in this work.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Anhydrous pinacol</th>
<th>Hexagonal pinacol</th>
<th>Pinacol monohydrate</th>
<th>Pinacol hexahydrate</th>
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<tr>
<td><strong>mp (ºC)</strong></td>
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<td>27-29</td>
<td>41.2</td>
<td>45.4</td>
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<td><strong>Data collection</strong></td>
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<td>173</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>temperature (K)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
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<td>P6₁22 or P6₅22</td>
<td>I2/a</td>
<td>Pnnm</td>
</tr>
<tr>
<td><strong>Z’</strong></td>
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<td>1</td>
<td>2</td>
<td>1/4</td>
</tr>
<tr>
<td><strong>Formula</strong></td>
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<td>C₆H₁₄O₂·0.5H₂O</td>
<td>C₆H₁₄O₂·H₂O</td>
<td>C₆H₁₄O₂·6H₂O</td>
</tr>
<tr>
<td><strong>R-factor</strong></td>
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<td>0.073</td>
<td>0.053</td>
<td>0.036</td>
</tr>
<tr>
<td><strong>Conformer(s) in the crystal</strong></td>
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<td>Only the gauche conformer</td>
<td>Only the trans conformer</td>
<td>Only the trans conformer</td>
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<tr>
<td><strong>Density (g/cm³)</strong></td>
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<td>0.990</td>
<td>1.097</td>
<td>1.196</td>
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<tr>
<td><strong>Packing coefficient</strong></td>
<td>0.66 (90 K), 0.65 (173 K)</td>
<td>0.59</td>
<td>0.65</td>
<td>0.69</td>
</tr>
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</table>

* The melting points of anhydrous pinacol, pinacol monohydrate, and pinacol hexahydrate are taken from (Pushin & Glagoleva, 1922). The melting point of hexagonal pinacol is taken from (Dahlqvist & Sillanpää, 2000).
Anhydrous Phase

The complexity of the anhydrous pinacol structure suggests that the packing is not especially favorable. It seems to be a rule of crystal packing that the size of the asymmetric unit should be minimized (Brock & Dunitz, 1994). Furthermore, structures containing more than one conformer are rare, although less rare for vic-diols (Brock, 2002b). If \( Z' > 1 \) there is usually an identifiable reason that can be traced to packing problem (Duncan et al., 2002; Hao et al., 2005; Koutentis et al., 2001; Lehmler et al., 2002; Lehmler et al., 2004), especially if the crystal has not been cooled for data collection. In the case of pinacol the packing problem is the conflict between needing to fill space densely and needing to satisfy the H-bond donors and acceptors. This conflict is compounded by the relative inflexibility of the molecule.

The disorder seen by Jeffrey & Robbins (Jeffrey & Robbins, 1978) in the room-temperature structure of anhydrous pinacol suggests loose packing. That disorder, which is limited to the \textit{trans} conformer, is reminiscent of the disorder found in the hexahydrate structure. If the disorder is a symptom of loose packing, and if there is a low-energy pathway linking the two sites, then the structure might be expected to order as the unit cell contracts. Indeed at low temperature, where the packing is denser by \( 3.1\% \) (173 K) and \( 4.0\% \) (90 K) than at room temperature, the structure is fully ordered.

Hexagonal Phase

This phase, although difficult to produce and frustrating to study, is in some ways the most normal. The H-bonded dimer ribbons, with their alternating \( R_2^1(10) \) and \( R_4^4(8) \) rings, are characteristic of vic-diols (Brock, 2002b). It is easy to imagine fragments of these ribbons existing in solution. The surprise is the twisting of the ribbons around the \( 3_1 \) (or \( 3_2 \)) screw axes, because a packing pattern in which the ribbons are approximately planar would have been expected (Brock, 2002b).

The density of this phase is very low. “Empty” channels are formed around the \( 6_1 \) (or \( 6_5 \)) screw axes. Water molecules pack loosely in the channels and form helical water chains. Even if the hexagonal phase contains enough water to be the monohydrate (which is doubtful), the density (1.060 g/cm\(^3\)) is still 2.0\% less dense at 173 K than the anhydrous phase. The fineness of the
needle-like crystals indicates that growth perpendicular to the hexagonal axis is slow relative to growth along the axis. The existence of this obviously unfavorable structure again suggests that pinacol has difficulty finding a satisfactory crystal packing arrangement.

**Monohydrate**

Apparently O’Connor *et al.* had difficulties in growing single crystals of this compound (O’Connor, 1969). In this work, however, it is certainly not the case. The well-developed single crystals (see Figure 2.6) are easy to grow at room temperature (about 21 °C). The trick is to close the vial to avoid evaporation and sublimation. What is certain is that no anhydrous pinacol crystal can be obtained from solutions having $X_{\text{pinacol}} < 0.80$ (Pushin & Glagoleva, 1922; see Figure 2.2).

The melting points (Pushin & Glagoleva, 1922) of the monohydrate (41.2 °C) and of anhydrous pinacol (41.0 °C) are essentially the same, but a comparison of the temperatures is problematic because the two phases melt to give different liquids. The similar density and packing coefficient to the anhydrous phase indicate that the packing of the monohydrate phase is loose as well.

The monoclinic crystal is doubly twinned pseudo-merohedrally such that the $c$ axis is nearly a fourfold axis. The striking pseudosymmetry in this structure seems to be a consequence of the symmetry of the molecules and of the H-bonding pattern's being simple in a way that is inconsistent with allowed space-group symmetries.

**Hexahydrate**

The existence of the hexahydrate, with a melting point 4.4 °C above that of the anhydrous phase (Pushin & Glagoleva, 1922), is another indication that the anhydrous phase of pinacol (as well as the pure phase of water) is not an especially favorable structure, especially since the extensive disorder (about 57% in the crystal studied) of the pinacol molecule in the hexahydrate is again an indication of loose packing.
The orthorhombic crystal is twinned pseudo-merohedrally so that the crystal system appears to be tetragonal. The occurrence of diffuse scattering in the $a^* \pm b^*$ directions implies that the long-range periodicity is not perfect, especially in those two directions.

**Conclusion**

While it might seem that simple molecules should be expected to have simple crystal structures, molecules that are small and simple, especially those that should participate in H bonds, may in fact be likely to give unusual and relatively complicated structures. The origin of the complexity may be the difficulty in filling space densely and while also satisfying donors and acceptors when the molecule has few internal degrees of freedom.
Chapter Three

Polymorphism of 15-Crown-5 Complexes of M(NO₃)₂, M = Cu, Zn, Mg, Co, Mn

Introduction

Previously Brock et al. had seen two compounds, of which “single” crystals actually contained two similar phases related by a small modulation (Brock & Patrick, 2002; Duncan et al., 2002; Xia et al., 2001; Xia et al., 2002). The problem is surprising to people who study molecular crystals, but the compounds in the papers listed above are difficult to synthesize. In another context Brock came across two room-temperature structures (Dejehet et al., 1987b; Rogers & Song, 1995) in the CSD that seem to be polymorphs related by some modulations. The compound is [Cu(15-crown-5)(H₂O)₂](NO₃)₂. Figure 3.1 shows the chemical line drawing of the compound. The synthesis of this compound is very simple and inexpensive. Therefore it seemed as if it might be a good system to study.
Figure 3.1 The chemical line drawing of \([\text{Cu}(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2\).
As shown in Table 3.1, one structure has a unit cell ten times as large as the other one. The one with the bigger unit cell has ten formula units (ten cations and twenty nitrates) in the asymmetric unit. It is a modulated superstructure, but the pseudosymmetry seems to have been overlooked by Dejehet and co-workers. The modulations are twofold and fivefold along the \( \mathbf{a} \) and \( \mathbf{c} \) directions when the structure is transformed from the \( \text{Pc} \) setting to \( \text{Pn} \) (see Figure 3.2). The other structure, with the smaller unit cell, is not modulated, but must be disordered since the cation is located on an inversion center (see Figure 3.3).
Table 3.1 Data collection temperature, space group and unit-cell dimensions of the two reported crystal structures of the compound \([\text{Cu}(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2\).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Dejehet \textit{et al.}, 1987b</th>
<th>Rogers &amp; Song, 1995</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Data collection Temperature (K)</strong></td>
<td>295</td>
<td>293</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>(Pc)</td>
<td>(Pn)</td>
</tr>
<tr>
<td>(a / \text{Å})</td>
<td>14.758(5)</td>
<td>14.758</td>
</tr>
<tr>
<td>(b / \text{Å})</td>
<td>13.978(4)</td>
<td>13.978</td>
</tr>
<tr>
<td>(c / \text{Å})</td>
<td>43.914(13)</td>
<td>43.273</td>
</tr>
<tr>
<td>(\beta / ^\circ)</td>
<td>102.19(3)</td>
<td>97.28</td>
</tr>
<tr>
<td>(V / \text{Å}^3)</td>
<td>8855(5)</td>
<td>885.3</td>
</tr>
<tr>
<td>(Z)</td>
<td>20</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 3.2 The asymmetric unit (transformed from the \( P_\text{c} \) setting to \( Pn \)) of the first reported crystal structure of \([\text{Cu}(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2\) (redrawn from Dejehet \textit{et al.}, 1987b). Ten independent cations are modulated twofold along the \( a \) direction and fivefold along \( c \). The cations are colored in red and blue, which correspond to two conformational enantiomers. Hydrogen atoms, the coordinated water molecules, and nitrate anions are omitted for clarity.
Figure 3.3 The disordered cation in the second reported crystal structure of [Cu(15-crown-5)(H₂O)₂](NO₃)₂ (redrawn from Rogers & Song, 1995). The red and blue cations correspond to two conformational enantiomers. Hydrogen atoms and the coordinated water molecules are omitted for clarity.
The relationship of the two reported structures is even clearer if the unit cell of the modulated structure is transformed from the \( P_c \) setting to \( P_n \). The transformation matrix is shown in Table 3.1. The smaller \( P2_1/c \) unit cell can be transformed to the bigger \( P_n \) unit cell by doubling \( a \) and multiplying \( c \) by five. It should be easy to distinguish the two structures by the examination of diffraction patterns. Figure 3.4 shows the schematic drawing of the diffraction patterns of the two structures. In the left-side picture there is one weak reflection between every two adjacent strong reflections along \( a^* \), and four weak reflections between every two adjacent strong reflections along \( c^* \). The strong reflections are primary reflections, while the interleaving weak reflections are superstructure reflections. Indexing of the reflections gives rise to two classes: \( h = 2n, l = 5n \) (primary reflections, strong) and \( h \neq 2n \) and/or \( l \neq 5n \) (superstructure reflections, weak). The diffraction pattern that is on the left side of Figure 3.4 is consistent with the modulations of the superstructure (see Figure 3.2). The right-side picture in Figure 3.4 is much simpler. Only primary reflections are present. This diffraction pattern corresponds to the simpler structure with the smaller unit cell. There is no modulation at all in the simpler structure since the weak interleaving reflections are absent. The simpler diffraction pattern (the right-side picture in Figure 3.4) is what Rogers & Song had claimed in their paper (Rogers & Song, 1995).
Figure 3.4 Schematic drawing of the precession planes of the two reported structures of [Cu(15-crown-5)(H₂O)₂](NO₃)₂ looking down the b* direction. The left-side picture corresponds to the modulated superstructure with the bigger unit cell. The bigger solid spots represent primary reflections, and the smaller solid spots represent superstructure reflections. The right-side picture corresponds to the non-modulated structure with the smaller unit cell.
In summary, the crystal structures of the two reported polymorphs of \([\text{Cu}(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2\) are closely related. One of them is modulated twofold along the \(a\) direction, and fivefold along the \(c\) direction; while the other one is not modulated at all. The modulations are due to the small distortions of the spacing and orientations of the crown ether ligands. It is well known that some non-modulated structures undergo a phase transformation and become modulated at lower temperature. On the other hand, it might be possible to eliminate modulations at higher temperature. If the crystal of the modulated superstructure is heated up to a higher temperature, then there is a chance that the modulations will disappear and the superstructure will undergo a phase transformation to a non-modulated structure. This research will help to clarify the solid-state phase transformation of the two polymorphs, and to understand the nature of the modulations as well.

A survey of similar compounds in the CSD indicated that three other compounds (\(M = \text{Zn}^{2+}, \text{Mg}^{2+}, \text{and Co}^{2+}\)) had the same general chemical formula, \([M(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2\). The Zn structure (Dejehet \textit{et al.}, 1987a) is very similar to the Cu superstructure except that the modulations along the \(c\) direction are threefold rather than fivefold. The reason for the difference is unclear. The Zn structure is a room-temperature structure. Like the Cu superstructure, it was originally described in \(Pc\), a non-centrosymmetric space group. The Mg structure (Junk & Steed, 1999) is a low-temperature (100 K) structure. The unit-cell dimensions are very close to the Zn structure. However, unlike the Zn structure, the space group is \(P2_1/c\), a centrosymmetric space group. The Mg structure was not determined well. Two crown ether ligands in the asymmetric unit must be disordered because they are located on inversion centers. The conventional \(R\)-factor is 0.112, which implies that there must be some serious problems with the structure. The Co structure (Holt \textit{et al.}, 1981) is a room-temperature structure, and was originally described in space group \(P4_12_12_2\). The crown ether ligand was disordered since it was located on a twofold axis. The problem with this structure is that the thermal ellipsoids of some carbon atoms are very eccentric, which makes the structure determination suspicious.

So far four compounds with similar chemical formula but different metal ions have been mentioned. The Cu compound appears to have two polymorphs, while the rest of them have only a single polymorph. It appears that 15-crown-5 structures are prone to disorder and modulation.
It would be interesting to find out why. Therefore it was decided that all the structures should be re-investigated. Other metal ions, such as Mn\(^{2+}\), Fe\(^{2+}\), etc. should be studied as well to make more comparisons. In order to bind to crown ether, the size of the metal ions must match the size of the crown ether cavity. For 15-crown-5 the cavity diameter is 1.7 to 2.2 Å (Holt et al., 1981; Junk & Steed, 1999). It has been reported that 0.75 to 0.90 is the favorable ratio range for the alkali metal ions, in which the ratio is defined as the ionic diameter over the cavity diameter (Christensen et al., 1971). Table 3.2 lists all the metal ions that can yield well-developed single crystals in this work, and the ionic diameters (Pauling, 1960) and ratio ranges. It seems reasonable that all these ions can bind to 15-crown-5. Maybe Mg\(^{2+}\) is a little small and Mn\(^{2+}\) is a little big, but the results in this work show that all of the metal ions shown in Table 3.2 fit into the cavity quite well. In terms of the electronic configuration in the \(d\)-orbitals, Cu\(^{2+}\) and Co\(^{2+}\) are partially filled; Zn\(^{2+}\) is fully filled; Mg\(^{2+}\) is empty, and Mn\(^{2+}\) is half-filled. This means that the major types of \(d\)-orbital electronic configuration are all included in current work.
Table 3.2 The ionic diameters (Pauling, 1960), ratio ranges*, and number of electrons in $d$-orbitals for the five metal ions.

<table>
<thead>
<tr>
<th>$M^{2+}$ ion</th>
<th>Ionic diameter (Å)</th>
<th>Ratio range</th>
<th>Number of electrons in $d$-orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>1.40</td>
<td>0.64 ~ 0.82</td>
<td>9</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>1.48</td>
<td>0.67 ~ 0.87</td>
<td>10</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1.30</td>
<td>0.59 ~ 0.76</td>
<td>0</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>1.48</td>
<td>0.67 ~ 0.87</td>
<td>7</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>1.60</td>
<td>0.73 ~ 0.94</td>
<td>5</td>
</tr>
</tbody>
</table>

* Ratio = (ionic diameter of the metal ion) / (cavity diameter of 15-crown-5). The cavity diameter of 15-crown-5 is 1.7 to 2.2 Å (Holt et al, 1981; Junk & Steed, 1999).
Experimental

Crystal Growth

The chemical equation 3.1 shows how the compounds were synthesized. The two reactants were mixed in equal molar quantities. In the case of Cu$^{2+}$, $n = 3$; in the case of Mn$^{2+}$, $n = 4$; and for the rest of the metal ions, $n = 6$, where $n$ is the number of water molecules in the chemical formula of the hydrated nitrates. The Cu compound was prepared in different solvents: water, methanol, mixture solvent of methanol and acetonitrile. All of them yielded the same crystal. For the rest of the compounds, the only solvent used was water.

\[
\text{M(NO}_3\text{)}_2 \cdot n\text{H}_2\text{O} + 15\text{-crown-5} \xrightarrow{\text{solvent}} \text{[M(15-crown-5)(H}_2\text{O)}_2\text{](NO}_3\text{)}_2}
\]  

(3.1)

All single crystals were grown by slow evaporation of solvents at room temperature. In the case of the Cu compound, higher temperatures (up to 60 °C) were tried as well, but the crystal structures turned out to be the same. The Mn compound crystallized from aqueous solution first as triclinic crystals. If the triclinic crystals are kept in the solution in which they were grown, the crystal habit will change significantly within one month, and the crystal structure will change to be tetragonal. However, if the triclinic crystals are dried or kept in paratone (an inert oil), the crystal structure does not change. Thus two polymorphs of the Mn compound were discovered at room temperature. The rest of the compounds show only one polymorph at room temperature. Figure 3.5 shows photographs of the single crystals of the five compounds.
Figure 3.5 Photographs of the single crystals of the five compounds. The metal ion of each compound is labeled in the corresponding photograph. The Mn compound has two polymorphs at room temperature.
X-Ray Diffraction

All data collection was performed on a Nonius KappaCCD diffractometer with graphite-monochromated sealed-tube Mo Kα radiation (\(\lambda = 0.71073\) Å) under the control of the program COLLECT (Nonius, 1998). Data reduction was done with DENZO-SMN (Otwinowski & Minor, 1997). No extra experiment (e.g., an azimuthal scan) was done for absorption correction. However, since all of the datasets have an average redundancy of at least 3, the scaling algorithm, SCALEPACK, which is a part of the data-reduction program, compares the intensities of equivalent reflections, and corrects for anisotropic absorption. This process is usually referred to as multi-scan. The structures were solved with SHELXS97 (Sheldrick, 1997a) and refined with SHELXL97 (Sheldrick, 1997b). Molecular and packing diagrams were generated with XP (Bruker, 1997) and Mercury (Bruno et al., 2002). Publication tables were prepared with XCIF (Bruker, 1997). Other experimental details are given in Appendix A. Crystal data, atomic coordinates, displacement parameters, bond lengths and angles, and torsion angles are given in Appendix B.

The diffractometer is equipped with a low-temperature system from CRYO Industries of America, which generates a steady nitrogen gas stream from below 90 K up to around 320 K by boil-off of liquid nitrogen. Programmed cooling or warming at a specified rate is also feasible. Unless otherwise specified, the low-temperature data in this chapter were all collected by using flash cooling, i.e. crystals were cooled to the low temperature in less than a second. Table 3.3 lists the local data code and data collection temperature for each compound. The Cu and Zn compounds were studied at LT (low temperature), RT (room temperature) and HT (high temperature). The Mg and Co compounds were studied at LT and RT. The Mn compound has two RT polymorphs: the triclinic and the tetragonal. Both of them were also studied at LT. The Mn compound also has a third polymorph, the LTP (low temperature phase/polymorph), which is monoclinic. The Mn LTP can only be studied at LT since it is not stable at RT.
Table 3.3 The local data codes in the X-Ray Lab at Chemistry Department of UK, and data collection temperatures for the five compounds \([\text{M}(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2\), \text{M} = \text{Cu}, \text{Zn}, \text{Mg}, \text{Co}, \text{Mn}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Local data code</th>
<th>Data collection temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Cu compound</td>
<td>k02008</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>k02122</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>k03004</td>
<td>320</td>
</tr>
<tr>
<td>The Zn compound</td>
<td>k04160</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>k02168</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>k04134</td>
<td>311</td>
</tr>
<tr>
<td>The Mg compound</td>
<td>k02119</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>k02169</td>
<td>294</td>
</tr>
<tr>
<td>The Co compound</td>
<td>k02099</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>k02155</td>
<td>294</td>
</tr>
<tr>
<td>The Mn compound</td>
<td>k03012 (triclinic)</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>k03125 (triclinic)</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>k03098 (tetragonal)</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>k03100 (tetragonal)</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>k03126 (monoclinic)</td>
<td>90*</td>
</tr>
</tbody>
</table>

* Done by slow cooling from 294 K to 160 K at 0.2 K/min, followed by a little faster cooling from 160 K to 90 K at 5 K/min. The rest of the 90 K data were all done by flash cooling from 294 K to 90 K.
Differential Scanning Calorimetry Measurements

Crystals were washed with water and acetone, and then dried under vacuum. The dried and cleaned crystals were ground into a fine powder. A small amount (5 ~ 20 mg) of sample was hermetically sealed in aluminum pans. All measurements were performed on a 2920 Modulated Differential Scanning Calorimetry (hereafter DSC) apparatus from TA Instruments. Files of DSC measurements are given in Appendix C.

Structure Determination

The Structures of the Cu Compound at 88 K and 294 K

The structures determined at 88 K and 294 K are the same. As mentioned previously, there are two published room-temperature structures. The structure with the bigger unit cell is a modulated superstructure. The modulations are fivefold along c and twofold along a (see Figure 3.2). The structure with the smaller unit cell is not modulated at all, which can be regarded as if the ten cations were averaged to only one, which is why the unit cell is ten times smaller (see Table 3.1). Since the cation exists as two conformational enantiomers, and especially since the cation lies on an inversion center in the simpler non-modulated structure, the averaging of the enantiomers required by the centrosymmetry results in disorder (see Figure 3.3). Ideally, it should not be difficult to distinguish the two structures by the examination of diffraction patterns. The diffraction of the superstructure will give rise to extra weak reflections (known as superstructure reflections) between the strong reflections (known as primary reflections), while that of the non-modulated structure does not (see Figure 3.4).

Crystals were grown in several batches under different conditions: different solvents at room temperature (distilled water, methanol, mixture solvent of methanol and acetonitrile), and from water solution at different temperatures (294 K, ~315 K, and ~338 K). A total of 10 ~ 15 single crystals out of different batches were examined. All of them showed the same diffraction patterns as those of the superstructure. The reconstructed precession planes (see Figure 3.6 for one example) and separate Wilson plots (see Figure 3.7) show clearly that the weak superstructure reflections (h ≠ 2n and l ≠ 5n) are present.
Figure 3.6 Reconstructed Precession plane h1l of the Cu compound at 294 K. Reflections are shown as black spots. The darkness of the spot is proportional to the intensity of the reflection. The darker and bigger spots are primary reflections with $h = 2n$ and $l = 5n$. The less dark and smaller spots are superstructure reflections with $h \neq 2n$ and $l \neq 5n$. 
Figure 3.7 Separate Wilson plots for the Cu compound at 294 K. The reflections are divided into several classes according to their Miller indices, such as $h = 2n$, $l = 5n$, etc. The intensities of the superstructure reflections ($h \neq 2n$ and $l \neq 5n$) are much weaker than those of the primary reflections ($h = 2n$ and $l = 5n$).
The superstructure has a large unit cell. The edge $c$ is about 42 Å, which is remarkably long for a small-molecule crystal. The long axis gave rise to some experimental difficulties. The larger the unit cell, the more reflections are present. The diffractometer used is equipped with Mo radiation, which is the most popular X-ray source for small-molecule crystals. However, in case of a very large unit cell, Mo radiation is no longer so good because more reflections are present in a relatively narrow range of $2\theta$. The possibility of the overlapping of reflections is greatly enhanced, which will result in poorly resolved data. When such a situation arises, Cu radiation is a better choice because reflections are spread out in a relatively wider range of $2\theta$; hence the resolution will be better. This is why Cu radiation is more popular for protein crystals. On the other hand, Cu X-rays are more absorbed than Mo X-rays, especially when there are electron-rich metal atoms or ions in the crystal; hence the intensities of reflections will be reduced and the absorption corrections will become very important. At the time when this study was done there was no Cu radiation available. Furthermore, the crystals contain metal ions ($\text{Cu}^{2+}$). In order to overcome the overlapping among reflections with Mo radiation, the detector had to be put far away from the crystal ($D_x = 80 \sim 90$ mm, $D_x$: detector-to-crystal distance). The data were better resolved by using a large $D_x$. The other problem for superstructures is that there are many systematically weak reflections, but this problem was easily solved by using the highly sensitive CCD detector.

As mentioned previously, two separate groups have studied the crystal structure of this compound at room temperature. Both groups used serial detectors (also known as point detectors), which are less sensitive than the CCD detector. The people who found the superstructure used Cu radiation. The X-ray production ($K\alpha$ X-rays) is about twice as efficient for Cu as for Mo. Furthermore, the scattering power for X-rays is proportional to the cube of the wavelength; hence the scattering of Cu X-rays ($\lambda = 1.54178$ Å) is about ten times as efficient as that of Mo X-rays ($\lambda = 0.71073$ Å). The resolution of the data is also better using Cu radiation than using Mo radiation. Although the absorption of Cu X-rays is a problem, and although serial detector used by Dejehet and co-workers (Dejehet et al., 1987b) was less sensitive, their chance to observe and resolve the weak superstructure reflections would still be good. However, the people who claimed to find the simpler polymorph used Mo radiation and a serial detector (Rogers & Song, 1995). It is possible, perhaps even probable, that the weak superstructure
reflections were not included when the orientation matrix was first determined; and that only the strong primary reflections were therefore collected. For this reason, the unit cell found by Rogers and Song was ten times smaller; and the structure was not modulated, but disordered. The disorder originated from the averaging of the modulations. This is why the second polymorph with the smaller unit cell is very suspicious. On the other hand, polymorphism in molecular crystals is still not understood very well. There are documented examples showing that it is possible that a given polymorph can be very difficult to reproduce even though it has been obtained previously. These polymorphs are referred to as “Disappearing Polymorphs” (Dunitz & Bernstein, 1995). As a result, the second polymorph might be actually obtained by Rogers and Song, but could not be reproduced in this work. Does the second polymorph exist or not? The question cannot be answered now. Nevertheless, all the crystals of the Cu compound studied in this work show diffraction patterns of the superstructure.

The reported superstructure (Dejehet et al., 1987b) is described in $Pc$, a non-centrosymmetric space group. Since the crystals in this work show the same diffraction patterns as those of the reported superstructure, the crystal structure in this work was initially solved and refined in $Pc$. Later on the structure was transformed to the $Pn$ setting so that the modulations are along the axial directions (see Figure 3.8).
Figure 3.8 Transformation of the superstructure unit cell of the Cu compound from the $Pc$ to the $Pn$ setting. The viewing direction is the $b$ and $b'$ directions. The $Pc$ cell is colored in black and the $Pn$ cell is colored in green. The unit-cell vectors of the $Pc$ cell are $a$, $b$, and $c$ (colored in black). The unit-cell vectors of the $Pn$ cell are $a'$, $b'$, and $c'$ (colored in green). The transformation matrix is given in the equation. The cations are colored in red and blue to represent the two conformational enantiomers. Hydrogen atoms, the coordinated water molecules, and nitrate anions are omitted for clarity. After the transformation from the $Pc$ to the $Pn$ setting, the structure is modulated along the axial directions.
In $Pn$ there are ten cations and twenty nitrates in the asymmetric unit. The refinement in $Pn$ was problematic. The least-squares calculations had to be highly restrained and constrained; otherwise several atoms would become non-positive-definite. If an atom is non-positive-definite, it means that at least one of the three eigenvalues of the tensor that describes the atomic displacements is negative, or in other words, that the distribution of the atomic displacement from the mean position cannot be described by a Gaussian probability distribution function. Careful examination indicated that the non-positive-definite values were caused by the large correlation (coefficients greater than 0.95) among coordinates and atomic displacement parameters. Such remarkably large correlation implies that very important symmetry must be missing. It turned out that the true space group is $P2_1/n$, which is centrosymmetric. The large correlation in $Pn$ is a consequence of the missing centrosymmetry (see Figure 3.9).
Figure 3.9 Packing of the Cu compound in $Pn$ looking down the $b$ direction. The cations are colored in red and blue to represent the two conformational enantiomers. Hydrogen atoms, the coordinated water molecules, and nitrate anions are omitted for clarity. In $Pn$ the missing inversion centers are shown as green circles. The true unit cell in $P2_1/n$ is shown in purple lines. The number of the independent formula units in $P2_1/n$ is reduced by half, i.e. $Z' = 10/2 = 5$. 

$Pn$

$Z' = 10$

$P2_1/n$

$Z' = 5$

○: inversion center
The number of the independent formula unit in $P2_1/n$ is five, *i.e.* there are five cations and ten nitrate anions in the asymmetric unit. The refinement in $P2_1/n$ is very stable. For the 88 K structure, no restraints and constraints are necessary. Non-positive-definite atoms became normal. For the 294 K structure, constraints ($EADP$) had to be used. Such constraints make the pseudosymmetrically related atoms have the same displacement parameters. The reason for using the constraints for the RT structure is because the weak superstructure reflections of the RT data are less intense compared to those of the LT data; therefore there is no enough information to refine the pseudosymmetric relationships freely. The constraints compensate for the shortcomings of the RT data. The ellipsoids of the independent cations and anions of both LT and RT structures are shown in Figure 3.10.

The H atoms of the methylene groups were put in calculated positions ($AFIX$ 23) with isotropic displacement parameters of 1.2 times $U_{eq}$ of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.77(1) Å for the 88 K structure. The H-O-H angles were constrained to be 104.5º. The displacement parameters of the water H atoms were set to 1.5 times $U_{eq}$ of the bonded O atoms. For the 294 K structure, the H atoms of the water molecules were located from a difference map, and the coordinates of the H atoms were fixed because the coordinates could not be refined in the same way as in the 88 K structure. The displacement parameters of the water H atoms were set to 1.5 times $U_{eq}$ of the bonded O atoms.
Figure 3.10 The ellipsoids (50% probability level) of the independent ions (five cations and ten anions) in the asymmetric unit of the Cu compound structures at 88 K and 294 K. H atoms are omitted for clarity.
The Structure of the Cu Compound at 320 K

The structure is twinned pseudo-merohedrally about the [1 1 2] direction. The space group is $P\overline{1}$; however, twinning makes the metric symmetry appear higher. The space group suggested by the instrument software was $C2/m$, but the structure could not be solved in that group. The structure could be solved in $P\overline{1}$, but the refinement was not satisfactory. Twinning was found by using the program PLATON, and the twin law is (-1 0 0 / 0 -1 0 / 1 1 1). Inclusion of the twin law led to a satisfactory refinement. One of the twin fractions ($BASF$) refined to 0.418(1). The ellipsoids of the independent ions in the asymmetric unit are shown in Figure 3.11.

The H atoms of the methylene groups were put in calculated positions ($AFIX$ 23) with isotropic displacement parameters of 1.2 times $U_{eq}$ of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map, and the coordinates were fixed. The isotropic displacement parameters of the water H atoms were set to 1.5 times $U_{eq}$ of the bonded O atoms.
Figure 3.11 The ellipsoids (50% probability level) of the independent ions (two cations and four anions) in the asymmetric unit of the Cu compound structure at 320 K. H atoms are omitted for clarity.
The Structures of the Zn Compound at 90 K and 294 K

The reported RT structure (Dejehet et al., 1987a) was described in a non-centrosymmetric space group, \(Pc\). It is also a modulated superstructure, which is very similar to the modulated superstructure of the Cu compound at 88 K and 294 K. The difference is that the modulations for the Zn compound are threefold rather than fivefold along the \(c\) direction. Both the Zn and Cu structures were reported by the same research group. The authors certainly overlooked the modulations in the structures, and both structures were described in a non-centrosymmetric space group. As mentioned previously for the Cu structure, the refinement in the non-centrosymmetric space group was problematic. The same problem with correlations was encountered during the refinement of the Zn structure in \(Pc\). The true space group of the Zn structure is \(P2_1/c\), which is centrosymmetric. The refinement is very stable in \(P2_1/c\). No restraints or constraints are necessary for both the LT and RT structures. Structures are the same at LT and RT. The ellipsoids of the independent ions in the asymmetric unit are shown in Figure 3.12.

The H atoms of the methylene groups were put in calculated positions (\(AFIX\ 23\)) with isotropic displacement parameters of 1.2 times \(U_{eq}\) of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.78(1) Å for both the LT and RT structures. The H-O-H angles were constrained to be 104.5 °. The isotropic displacement parameters of the water H atoms were set to 1.5 times \(U_{eq}\) of the bonded O atoms.
Figure 3.12 The ellipsoids (50% probability level) of the independent ions (three cations and six anions) in the asymmetric unit of the Zn compound structures at 90 K and 294 K. H atoms are omitted for clarity.
The Structure of the Zn Compound at 311 K

The structure was solved without problem, but the refinement was not straightforward. The space group is $P2_1$ with $Z' = 8$. The structure is twinned racemically. One of the twin fractions ($BASF$) refined to 0.54(5), which implies that the twinning is almost perfect. The structure is non-centrosymmetric, but the twinning causes the structure to be almost centrosymmetric, which results in refinement difficulties. The structure is also a modulated superstructure. There are systematically weak superstructure reflections. Since the data collection was done at high temperature (17 degrees higher than RT), the weak superstructure reflections are even weaker. Since the weak reflections contain important information about the small distortions among the chemical species, the refinement had to be heavily restrained in order to obtain a relatively stable refinement. The instruction $EADP$ was used to make the displacement parameters the same for atoms related by the pseudosymmetry. The instruction $DELU$ was used to make the components of the displacement parameters similar in the bonding direction for all pairs of bonded atoms. The instruction $SAME$ was used for the eight cations and sixteen anions, which was to make the geometry similar for chemically identical, but crystallographically independent species. The ellipsoids of the independent ions in the asymmetric unit are shown in Figure 3.13.

The H atoms of the methylene groups were put in calculated positions ($AFIX$ 23) with isotropic displacement parameters of 1.2 times $U_{eq}$ of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map, and the coordinates were fixed. The isotropic displacement parameters of the water H atoms were set to 1.5 times $U_{eq}$ of the bonded O atoms.
Figure 3.13 The ellipsoids (50% probability level) of the independent ions (eight cations and sixteen anions) in the asymmetric unit of the Zn compound structure at 311 K. H atoms are omitted for clarity.
Although the refinement is heavily restrained, the refinement is still not satisfactory. The $R$-factor is high (0.085), and the difference map is not flat. The residual peaks of the electron density are high (range from 1.17 to 0.98 e/Å$^3$). The peaks can be interpreted as the minor disorder of the crown ethers (see Figure 3.14). The disorder can be viewed as if the crown ethers are located on pseudo inversion centers. Still, the basic structure is almost certainly correct.
Figure 3.14 Eight independent cations of the 311 K structure of the Zn compound looking down the \( \mathbf{b} \) direction. The H atoms and anions are omitted for clarity. Zn, C, and O atoms are colored in purple, gray, and red. The residual peaks (colored in blue) from a difference map are located inside two crown ether ligands. The range of the height of these peaks is \( 1.17 \sim 0.98 \text{ e/Å}^3 \).
The Structures of the Mg Compound at 90 K and 294 K

The structures at LT and RT are the same. They are also isostructures of the Zn LT and RT structures. The space group is $P2_1/c$. When solving the structure with SHELXS, two equally good solutions (same $CFOM$ and $NQUAL$ values) were obtained, but only one of them could be the right solution. So the question is which one is right. The way to differentiate the two solutions is to refine the two models and see which one gives better results. For solution I there are three cations and six nitrates in the asymmetric unit. The ions are all on general positions. For solution II there are four independent cations in the asymmetric unit, but two of the cations are on inversion centers; hence they are disordered. Solution II is the reported structure (Junk & Steed, 1999). As mentioned previously, the reported structure is problematic. So solution I seemed likely to be the right one, which was later confirmed by a satisfactory refinement. The reason why Junk and Steed picked the wrong solution is that the structure is a modulated superstructure; hence there is significant pseudosymmetry in the structure, in other words some reflections are systematically weak. Solving pseudosymmetric structures with direct methods can be problematic. The reason is that direct methods are based on the assumption of randomly distributed atoms, which means that there is no important pseudosymmetry. However, in this structure there is pseudosymmetry, which means that the assumption is invalid. The program SHELXS is based on direct methods. When solving pseudosymmetric structures, it is necessary to modify the $E$-value normalization and check the output diagnostic file. If there is more than one equally good solution, each of them should be tried. Indeed, such suggestions are given in the program manual.

The H atoms of the methylene groups were put in calculated positions ($AFIX$ 23) with isotropic displacement parameters of 1.2 times $U_{eq}$ of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.832(8) and 0.76(1) Å for the LT and RT structures. The H-O-H angles were constrained to be 104.5°. The displacement parameters were set to 1.5 times $U_{eq}$ of the bonded O atoms. The ellipsoids of the independent ions in the asymmetric unit are shown in Figure 3.15.
Figure 3.15 The ellipsoids (50% probability level) of the independent ions (three cations and six anions) in the asymmetric unit of the Mg compound structures at 90 K and 294 K. H atoms are omitted for clarity.
The Structures of the Co Compound at 90 K and 294 K

The LT and RT structures are the same. The reported RT structure (Holt et al., 1981) is not fully correct because the authors missed the systematically weak reflections. Separate Wilson plots were made for both LT and RT structures (see Figure 3.16). The reflections with $h + k = \text{odd}$ are the systematically weak reflections. For the RT structure, these reflections are even weaker.
Figure 3.16 Separate Wilson plots for the LT (90 K, the top plot) and RT (294 K, the bottom plot) structures of the Co compound.
The serial detectors used in the 1980’s were not as sensitive as the CCD detector used in this study, so it is not surprising that the weak reflections were missed. The consequence of missing weak reflections is that the unit cell was smaller and the crown ether was disordered (Holt et al., 1981). Figure 3.17 shows how the smaller pseudo unit cell is generated because of the missing of the weak reflections.
Figure 3.17 The schematic drawing of a precession plane of the Co structure viewed along the c* direction. The blue triangle-shaped spots represent the weak reflections with $h + k =$ odd. The black diamond-shaped spots represent strong reflections with $h + k =$ even. The true cell in reciprocal space is shown in blue lines. If the weak reflections are missing, the pseudo reciprocal cell (in black lines) will be twice as big as the true reciprocal cell. Thus in direct space the pseudo unit cell will be smaller by a factor of two.
Since the weak reflections were observed with the CCD detector, the unit cell here is twice as big as the cell reported by Holt and co-workers. The reported smaller unit cell can be transformed to the larger true cell through the transformation matrix, \((1 \ -1 \ 0 \ / \ 1 \ 1 \ 0 \ / \ 0 \ 0 \ 1)\). The space group should then be \(P4_1\) rather than the reported \(P4_12_12\). There are two independent formula units (two cations and four nitrates) in the asymmetric unit.

Both the LT and RT structure are twinned merohedrally. The twin law is \((0 \ 1 \ 0 \ / \ 1 \ 0 \ 0 \ / \ 0 \ 0 \ -1)\). One of the twin fractions (BASF) refined to 0.183(2) for the LT structure and to 0.562(3) for the RT structure. The fractional ratios are different because two different crystals were used. The crystal studied at LT was twinned less.

The refinement of the LT structure is satisfactory. No restraints and constraints were necessary. The H atoms of the methylene groups were put in calculated positions (AFIX 23) with isotropic displacement parameters of 1.2 times \(U_{eq}\) of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.79(2) Å. The H-O-H angles were constrained to be 104.5°. The displacement parameters were set to 1.5 times \(U_{eq}\) of the bonded O atoms. The ellipsoids of the independent ions in the asymmetric unit are shown in Figure 3.18.
Figure 3.18 The ellipsoids (50% probability level) of the independent ions (two cations and four anions) in the asymmetric unit of the Co compound structure at 90 K. H atoms are omitted for clarity.
The refinement of the RT structure was unstable without constraints on the displacement parameters. When the RT structure was refined freely, the ellipsoids of some carbon atoms were very eccentric, and some carbon atoms could not be refined anisotropically because they became NPD (non-positive-definite) (see Figure 3.19).
Figure 3.19 A plot of the ellipsoids (50% probability level) of the 294 K structure for the Co compound when the structure is refined freely. The H atoms and anions are omitted for clarity. C31 and C52 show very eccentric ellipsoids. C12 and C32 are NPD (non-positive-definite), hence could not be refined anisotropically.
The eccentric ellipsoids and NPD problems are because the two independent cations are related by significant pseudosymmetry. The displacement parameters between the two pseudosymmetrically related atoms are highly correlated. That is why these parameters could not be refined freely. The relationships of the displacement parameters are described in Appendix D. After the displacement parameters were constrained, the refinement became stable and the ellipsoids looked normal (see Figure 3.20).

The H atoms of the methylene groups were put in calculated positions ($AFIX$ 23) with isotropic displacement parameters of 1.2 times $U_{eq}$ of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map, and the coordinates were fixed. The displacement parameters of the water H atoms were set to 1.5 times $U_{eq}$ of the bonded O atoms.
Figure 3.20 The ellipsoids (50% probability level) of the independent ions (two cations and four anions) in the asymmetric unit of the Co compound structure at 294 K. H atoms are omitted for clarity.
The Structures of the Triclinic Polymorph of the Mn Compound at 90 K and 294 K

These structures are isosstructures of the Cu compound at 320 K. The twin law is the same. One of the twin fractions ($BASF$) refined to 0.0395(4) for the LT structure and 0.279(1) for the RT structure. Two different crystals were used for LT and RT data collection, which is why the twin fractions (i.e., $BASF$ values) are different for the two structures. The twinning for the LT crystal is very slight; only about 4% of the crystal belongs to the second twin domain. Actually the refinement of the LT structure is acceptable (just slightly worse) if the twinning is not included. In case of the RT structure the twinning is significant, the twin model must be used in order to obtain a stable and acceptable refinement.

The H atoms of the methylene groups were put in calculated positions ($AFIX$ 23) with isotropic displacement parameters of 1.2 times $U_{eq}$ of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.805(9) Å for the LT structure and 0.77(1) Å for the RT structure. The H-O-H angles were constrained to be 104.5°. The displacement parameters were set to 1.5 times $U_{eq}$ of the bonded O atoms. The ellipsoids of the independent ions in the asymmetric unit are shown in Figure 3.21.
Figure 3.21 The ellipsoids (50% probability level) of the independent ions (two cations and four anions) in the asymmetric unit of the 90 K and 294 K structures of the triclinic polymorph of the Mn compound. H atoms are omitted for clarity.
The Structures of the Tetragonal Polymorph of the Mn Compound at 90 K and 294 K

These structures are isostructures of the Co structure. The twin law is the same; BASF refined to 0.088(1) for the LT structure and 0.067(2) for the RT structure. Different crystals were used for LT and RT data collection, which is why the twin fractional ratios (i.e., BASF) are different for the two structures. The refinement difficulties encountered in the RT Co structure were not encountered in the RT Mn structure, probably because the twinning is less significant. Part of the crown ether is slightly disordered. The disorder has been absorbed into the displacement parameters. That is why some ellipsoids look eccentric (see Figure 3.22).

The H atoms of the methylene groups were put in calculated positions (AFIX 23) with isotropic displacement parameters of 1.2 times $U_{eq}$ of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.82(1) Å for the LT structure and 0.73(2) Å for the RT structure. The H-O-H angles were constrained to be 104.5°. The displacement parameters were set to 1.5 times $U_{eq}$ of the bonded O atoms.
Figure 3.22 The ellipsoids (50% probability level) of the independent ions (two cations and four anions) in the asymmetric unit of the 90 K and 294 K structures of the tetragonal polymorph of the Mn compound. H atoms are omitted for clarity.
The Structure of the Monoclinic Polymorph of the Mn Compound at 90 K

The structure is an isostructure of the Zn and Mg structures. The H atoms of the methylene groups were put in calculated positions (AFIX 23) with isotropic displacement parameters of 1.2 times \( U_{eq} \) of the preceding parent C atoms. The H atoms of the water molecules were located from a difference map. The O-H distances were all made equal to a free variable, which refined to 0.80(1) Å. The H-O-H angles were constrained to be 104.5°. The displacement parameters were set to 1.5 times \( U_{eq} \) of the bonded O atoms. The ellipsoids of the independent ions in the asymmetric unit are shown in Figure 3.23.
Figure 3.23 The ellipsoids (50% probability level) of the independent ions (three cations and six anions) in the asymmetric unit of the 90 K structure of the monoclinic polymorph of the Mn compound. H atoms are omitted for clarity.
Summary of Crystal Structures

In summary, five compounds \([M(15\text{-crown-5})(H_2O)_2](NO_3)_2\) \((M = \text{Cu, Zn, Mg, Co, Mn})\) have been characterized crystallographically at different temperatures. In the following discussions, LTP, RTP, and HTP will be used as abbreviations for low-temperature, room-temperature, and high-temperature phases. The Mn compound has two RTPs: the triclinic phase which was discovered first will be called RTP(I); while the tetragonal phase which was discovered afterwards will be called RTP(II). Symbols, such as Cu RTP, will be used to represent different phases of different compounds. For example, in the case of Mn RTP(I), the symbol represents the first (triclinic) room-temperature phase of the Mn compound. In this work, a total of nine phases have been characterized crystallographically. These nine phases are Cu RTP, Cu HTP, Zn RTP, Zn HTP, Mg RTP, Co RTP, Mn RTP(I), Mn RTP(II), and Mn LTP. All the RTPs were studied at both LT and RT. If the LT structure is the same as the RT structure, then the LT structure is not a new phase. This is why there is no Cu LTP, or Zn LTP, and so on. The only compound that has a new LTP is the Mn compound. The nine phases crystallize in only five structures because some of them are isostructures, e.g. Cu HTP and Mn RTP(I). Table 3.4 summarizes the five structures and nine phases.
Table 3.4 Summary of the five crystal structures and nine phases of compounds \([\text{M(15-crown-5)(H}_2\text{O)}_2]\)(\text{NO}_3)_2\) \((\text{M} = \text{Cu, Zn, Mg, Co, Mn})\). Different phases that have the same structure are isostructures.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_{2\text{I}}/n, Z = 5)</td>
<td>Cu RTP</td>
</tr>
<tr>
<td>(P_{\text{I}}, Z = 2)</td>
<td>Cu HTP, Mn RTP(I)</td>
</tr>
<tr>
<td>(P_{2\text{I}}/c, Z = 3)</td>
<td>Zn RTP, Mg RTP, Mn LTP</td>
</tr>
<tr>
<td>(P_{2\text{I}}, Z = 8)</td>
<td>Zn HTP</td>
</tr>
<tr>
<td>(P_{4\text{I}}) or (P_{4\text{3}}, Z = 2)</td>
<td>Co RTP, Mn RTP(II)</td>
</tr>
</tbody>
</table>
The Geometry of the Cations

All the structures in this chapter have more than one independent formula unit in the asymmetric unit. Within each structure, the independent cations have nearly the same conformation. The cations from different structures have similar conformation as well (see Figure 3.24).
Figure 3.24 The overlay of the cations (including H atoms) of compounds \([M(15\text{-crown}-5)(\text{H}_2\text{O})_2]\)(\text{NO}_3)_2 (M = \text{Cu, Zn, Mg, Co, Mn}) using version 2.1 of the program *CrystMol* (Duchamp, 2004). Cations of different compounds are shown in different colors. In the top plot, blue = Cu, red = Zn, green = Mg, and magenta = Mn [darker = RTP(I), lighter = RTP(II)]. In the bottom plot, red = Zn, and purple = Co.
A cation of the Cu RTP structure at 90 K will be used as an example. The metal ion does not lie at the center of the crown ether ligand, i.e. the five M-O distances are not the same. Careful examination shows that the cation has approximate $C_2$ symmetry. In the case of the example discussed here, the approximate twofold axis is along the Cu-O5 bond (see Figure 3.25). A model fitting of the cation was made about this twofold axis by using the program \textit{XP-OFIT}, and the overall root-mean-square deviation is 0.08 Å, which means that this non-crystallographic twofold axis is nearly exact.
Figure 3.25 The structure of a cation of the Cu RTP structure. Cu, C and O atoms are colored in blue, gray, and red. H atoms are omitted for clarity. The cation has approximate $C_2$ symmetry, and the approximate twofold axis is along the Cu-O5 bond.
The crown ether ligand and the metal ion do not lie in one plane. A mean plane was calculated by using the program *XP-MPLN*. The atoms used to generate this plane are Cu, O1, O2, O3, O4, O5, C1, C2, C3, C4, C5, C6, C7, C8, C9, and C10. The overall root-mean-square deviation is 0.23 Å. The range of the individual atomic deviations from the mean plane is -0.42 ~ +0.41 Å. A positive value means that the atom is above the plane; a negative value means that the atom is below the plane; and a value of zero means that the atom is in the plane (see Figure 3.26).
Figure 3.26 The pattern of the individual atomic deviations from a mean plane generated by using the program \textit{XP-MLPN}. A ‘(+)' sign means that the atom is above the plane; a ‘(-)' sign means that the atom is below the plane; and a ‘(0)' sign means that the atom is in the plane. The up-down alternation pattern breaks down at O5. The cation is taken from the Cu RTP structure. Cu, C and O atoms are colored in blue, gray, and red. H atoms are omitted for clarity.
Since the crown ether ligand is a 15-member ring, and since 15 is an odd number, the up-down alternation pattern must break down at some point. The breaking point in this cation is O5, which lies in the plane (see Figure 3.26). Such an imperfect up-down alternation pattern is consistent with the $C_2$ symmetry of the cation. Thus it is not surprising that the twofold axis has to be along the Cu-O5 bond rather than one of the other four Cu-O bonds. The $C_2$ symmetric cation has two conformational enantiomers. The up-down alternation patterns of the two enantiomers are “out-of-phase”, i.e. the pattern from O1 to C10 in the cation of Figure 3.26 is $[(+)(-)]_6(0)(+)(-)$, while the pattern in the mirror-image cation of Figure 3.26 will be $[(-)(+)]_6(0)(-)(+)$. The two enantiomers can interconvert in solution, and co-crystallize in the same crystal.

**Crystal Packing**

The basic building block of the H-bonding is shown in Figure 3.27. Such H-bonding is found in all structures of the 15-crown-5 compounds discussed in this chapter. Each cation is H-bonded to four nitrate anions, and each nitrate anion is H-bonded to two cations. In terms of similarity in H-bonding, the five crystal structures found in nine phases (see Table 3.4) can be divided into two groups. One group includes four structures: $P2_1/n$ with $Z' = 5$, $P\overline{1}$ with $Z' = 2$, $P2_1/c$ with $Z' = 3$, and $P2_1$ with $Z' = 8$. The packing of these four structures is very similar. Each structure of this group consists of two-dimensional H-bonded layers. These structures are simply called the 2D structures in this chapter. The other group includes a single structure type: $P4_1$ or $P4_3$ with $Z' = 2$. The H-bonding in the latter group is three-dimensional, and the structure is simply called the 3D structure.
Figure 3.27 The basic building block of the H-bonding found in all crystal structures of compounds [M(15-crown-5)(H₂O)₂](NO₃)₂ (M = Cu, Zn, Mg, Co, Mn).
The 2D Structures

The H-bonded layers stack in a very similar way in the four 2D structures. Since the four structures have different space groups, and the unit-cell vectors are therefore defined differently, the directions in which the layers stack in the four structures are different. In the $P2_1/n$ and $P2_1/c$ structures the layers stack in the $a$ direction. In the $P2_1$ structure the layers stack in nearly the $a$ direction, but not quite, the actual direction is probably $[16 \ 0 \ -1]$. In the $P\bar{1}$ structure the layers stack in the $[1 \ 1 \ 0]$ direction. As an example, Figure 3.28 shows how the layers stack in the structure of Mn LTP (one of the three phases that crystallize in $P2_1/c$, see Table 3.4).
Figure 3.28 The packing of the Mn LTP structure looking down the c direction. Three H-bonded layers stack in the a direction. H atoms are omitted for clarity. H bonds are shown in black dotted lines.
As mentioned previously, the $C_2$ symmetric cation has two conformational enantiomers. In the crystals of all the four 2D structures, both enantiomers (50\%:50\%) are present, which means the crystals studied are racemic crystals. The different ways in which the enantiomers alternate in the crystals lead to the four different 2D structures. However, what is invariant in all the four 2D structures is the alternation pattern of the enantiomers in the directions in which the H-bonded layers stack in the crystals. As an example, the packing of Mn LTP in the $ac$ plane is shown in Figure 3.29, and the alternation pattern of the enantiomers in the $a$ direction is · · · D L D L D · · ·, in which D and L represent two enantiomers. This pattern has no alternation fault (i.e. D followed by D, or L followed by L), hence is a perfect alternation pattern. The $a$ direction is the direction in which the H-bonded layers stack in the Mn LTP structure. For all the four 2D structures, such a perfect alternation pattern is invariant in the directions in which the H-bonded layers stack in the crystals.
Figure 3.29 The packing of Mn LTP in the ac plane. The cations are colored in red and blue, which correspond to two conformational enantiomers. H atoms and nitrate anions are omitted for clarity.
In the H-bonded layer of each of the four 2D structures, the alternation patterns are more complicated. One example is given in Figure 3.30, which shows an H-bonded layer of the Mn LTP structure. In this layer the alternation pattern of the enantiomers in the first row is · · · D L D D L D D L D L D · · · in the \( c \) direction. Obviously there is an alternation fault after every third contact, or in other words there is 1 non-alternation in 3 contacts. The alternation pattern in the second row in Figure 3.30 can be worked out by applying a \( c \) glide plane (perpendicular to the \( b \) direction) to the first row. Table 3.5 summarizes the alternation patterns of the four 2D structures. The four 2D structures are different only in the way the enantiomers alternate in those directions listed in Table 3.5, or in other words the changes in space-group symmetry are the consequences of the different ways in which the enantiomers alternate.
Figure 3.30 One H-bonded layer of the Mn LTP structure looking down the a direction. H atoms are omitted for clarity. H bonds are shown in black dotted lines. The cations are colored in red and blue, which correspond to two conformational enantiomers.
Table 3.5 The alternation patterns of the four 2D structures in certain directions. The letters D and L represent the two conformational enantiomers of the cation.

<table>
<thead>
<tr>
<th>The 2D structure</th>
<th>Alternation pattern in [direction]</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P\bar{1}$, $Z' = 2$</td>
<td>$\cdots$ D L D L D L D L D L $\cdots$ in [1 –1 0]</td>
<td>Perfect alternation</td>
</tr>
<tr>
<td>$P2_1/c$, $Z' = 3$</td>
<td>$\cdots$ D L D L D L D L D D $\cdots$ in [0 0 1]</td>
<td>1 non-alternation in 3 contacts</td>
</tr>
<tr>
<td>$P2_1$, $Z' = 8$</td>
<td>$\cdots$ D L D L D L D L D D $\cdots$ in [1 0 2]</td>
<td>2 non-alternations in 8 contacts</td>
</tr>
<tr>
<td>$P2_1/n$, $Z' = 5$</td>
<td>$\cdots$ D L D L D L D L D L $\cdots$ in [0 0 1]</td>
<td>1 non-alternation in 5 contacts</td>
</tr>
</tbody>
</table>
Besides the four 2D structures, there could be an extreme structure in which the enantiomers alternate in a random way. In this structure the cations would have to be disordered because of the averaging of the two enantiomers. This structure, if it exists, is probably the one that was reported by Rogers and Song (Rogers & Song, 1995). The diffraction patterns of this structure were discussed previously. Unfortunately, no such diffraction pattern was ever observed in this work. Furthermore, a reasonable explanation has been found for why Rogers and Song might have made a mistake. It appears that the disordered structure is not preferred, or in other words the enantiomers do not prefer to alternate randomly. The reason is unclear.

Why do these compounds pack in a complicated way that is not often seen in most small-molecule structures? The question cannot be answered yet.

The 3D Structure
Only two out of nine phases crystallize in this structural type (see Table 3.4). The H-bonding is different from that of the 2D structures because the nitrate anions are H-bonded to the cations in different orientations (see Figure 3.31). The packing in two directions is shown in Figures 3.32 and 3.33. The example used is Mn RTP(II), of which the space group is $P4_3$, and $Z' = 2$. 
Figure 3.31 The basic building blocks of the H-bonding of the 3D (left) and 2D (right) structures. In the case of the 3D structure, Mn RTP(II) is used; in the case of the 2D structure, Mn LTP is used. H atoms are omitted for clarity. H bonds are shown in black dotted lines.
Figure 3.32 The packing of a 3D structure looking down the \( c \) direction. H atoms are omitted for clarity. H bonds are shown in black dotted lines.
Figure 3.33 The packing of a 3D structure looking down the a-b direction. H atoms are omitted for clarity. H bonds are shown in black dotted lines.
As in the 2D structures, each cation in the 3D structures has four nearest neighbors. A layer similar to those in the 2D structures is also found in the 3D structures (see Figures 3.29 and 3.34). If the handedness of the enantiomers is ignored, there will be two approximate repeat vectors in the layers in both the 2D and 3D structures. In the case of the 2D structure, the two vectors are not perpendicular to each other, and they do not have the same length, one vector is about 1 Å shorter than the other. The direction of the shorter vector is the same direction in which the H-bonded layers stack in the crystal, and the enantiomeric alternation pattern in this direction is always perfect and always unchanged in all the four 2D structures. The direction of the longer vector is the same direction in which the enantiomeric alternation pattern is more complicated and changed in different 2D structures (these directions are given in Table 3.5). In the case of the 3D structure, the two vectors are almost perpendicular to each other, and they have approximately the same length. In both directions the alternation patterns seem perfect. In the sense of simplicity and perfectness, the 3D structure ($P_{4_1}$ or $P_{4_3}$ with $Z = 2$) can be viewed as the most plausible structure for all the five compounds in this chapter.
Figure 3.34 One layer of the Mn RTP(II) structure looking down the c direction. All the Mn$^{2+}$ ions in this layer have approximately same z coordinates. The cations are colored in red and blue, which correspond to two conformational enantiomers. H atoms and nitrate anions are omitted for clarity.
Phase Transformation

The solid-solid phase transformation in molecular crystals is still not understood well (Dunitz, 1995; Westrum & McCullough, 1963). It might not be difficult to identify the occurrence of a phase transformation by using X-ray diffraction since changes in unit-cell dimensions, diffraction patterns, and space groups are all good indications of the occurrence of a possible phase transformation. Furthermore, the comparison of the structural changes before and after the transformation can give useful clues on how the transformation occurs. As a result, X-ray diffraction has become an important tool to study the solid-solid phase transformation in molecular crystals. On the other hand, what is actually happening during the phase transformation, i.e. the mechanism, is far more difficult to be studied by using X-ray diffraction. Indeed, the actual mechanism can be very complicated (Herbstein, 2002). The order of the phase transformation in molecular crystals can be uncertain. Discontinuous changes in unit-cell dimensions are typical indications of a first-order phase transformation. In reality, however, things can be more complicated. It has been reported that the phase transformation might show both first- and second-order behavior (Xia et al., 2001; Xia et al., 2002).

Besides X-ray diffraction, differential scanning calorimetry (DSC) is another powerful tool to study solid-solid phase transformations. The enthalpy of the solid-solid transformation ($\Delta H$) and the onset temperature ($T_{onset}$) can be determined from DSC, as can the enthalpy of fusion ($\Delta H_f$) and the melting point ($T_m$). However, the temperature and enthalpy values can be variable because the $\Delta H$ measured by DSC depends on the way in which the integration is done and $T_{onset}$ depends on the heating rate. Other factors, such as sample quality and the way in which the sample is loaded into the sample container can affect these values as well. If the DSC instrument is equipped with a reliable cooling accessory, $T_{onset}$ can be determined from both heating and cooling processes. The two values of $T_{onset}$ are not necessarily the same because of the hysteresis of the phase transformation. The average of the two can be a good estimate of the actual $T_{onset}$. The DSC device used in this work does not have any reliable cooling accessory; therefore $T_{onset}$ could only be determined from the heating process. Appendix C gives all the plots from the DSC measurements, and Table 3.6 summarizes the $T_{onset}$, $\Delta H$, $T_m$, and $\Delta H_f$ values.
Table 3.6 The $T_{\text{onset}}$, $\Delta H$, $T_m$, and $\Delta H_f$ values determined from DSC measurements for the five compounds [M(15-crown-5)(H$_2$O)$_2$](NO$_3$)$_2$ (M = Cu, Zn, Mg, Co, Mn). The Mn compound has two room-temperature phases: the triclinic and tetragonal phases. The heating rate is 1 °C/min when $T < 60$ °C, and 5 °C/min when $T > 60$ °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Cu compound</td>
<td>39</td>
<td>$\sim 10^{-1}$</td>
<td>132</td>
<td>$\sim 0.5 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>$\sim 10^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>109</td>
<td>$\sim 10^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Zn compound</td>
<td>31</td>
<td>$\sim 10^{-1}$</td>
<td>148</td>
<td>$\sim 0.5 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>$\sim 1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Mg compound</td>
<td>28</td>
<td>$\sim 10^{-1}$</td>
<td>201</td>
<td>$\sim 0.5 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>$\sim 1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Co compound</td>
<td>33</td>
<td>$\sim 10^{-1}$</td>
<td>147</td>
<td>$\sim 0.5 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>$\sim 10$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Mn compound (the triclinic phase)</td>
<td>41</td>
<td>$\sim 10^{-1}$</td>
<td>145</td>
<td>$\sim 0.5 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>$\sim 1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>$\sim 10^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Mn compound (the tetragonal phase)</td>
<td>56</td>
<td>$\sim 10^{-1}$</td>
<td>144</td>
<td>$\sim 0.5 \times 10^2$</td>
</tr>
<tr>
<td></td>
<td>106</td>
<td>$\sim 10$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For each compound, there always exists more than one endothermic peak in the DSC plot before the melting peak is observed (see Table 3.6). For example, the DSC plot of the Cu compound shows three peaks before the melting peak. The first process indicated by the first peak (i.e. the one with the lowest $T_{\text{onset}}$) is always reversible in the DSC measurements of the six phases. Multi-temperature diffraction studies of the Cu and Zn compounds showed that the crystallinity was also preserved through the first process. The high-temperature phases, Cu HTP ($T_{\text{onset}} = 39 \, ^{\circ}\text{C}$) and Zn HTP ($T_{\text{onset}} = 31 \, ^{\circ}\text{C}$) were structurally characterized. This means that the first process is indeed a reversible solid-solid phase transformation for the Cu and Zn compounds. Based on the similarity in the DSC measurements of the six phases, it is reasonable to assume that the statement that the first process is a reversible solid-solid phase transformation is also true for the rest of the four phases. In other words, the existence of the other four HT phases, Mg HTP ($T_{\text{onset}} = 28 \, ^{\circ}\text{C}$), Co HTP ($T_{\text{onset}} = 33 \, ^{\circ}\text{C}$), Mn HTP(I) ($T_{\text{onset}} = 41 \, ^{\circ}\text{C}$), and Mn HTP(II) ($T_{\text{onset}} = 56 \, ^{\circ}\text{C}$) is supported by the DSC measurements, but the structures of these four HT phases are not determined. HT data collection depends primarily on the temperature-controlling device, with which the diffractometer is equipped. Temperatures above room temperature controlled by the device in this work are difficult to stabilize. Furthermore, the device has the HT limit of about 50 $^{\circ}\text{C}$. Therefore, it was decided that the four undetermined HT phases should preferably be studied by using the newly installed diffractometer because the new temperature-controlling device controls temperatures at HT more stably and the HT limit is higher (about 140 $^{\circ}\text{C}$).

The six RT phases were also studied at low temperatures. The crystals were cooled to 90 K through both flash cooling and slow cooling. The only RT phase that transforms to a new LT phase under slow cooling is Mn RTP(I). The phase transformation between Mn RTP(I) and Mn LTP is reversible, and the $T_{\text{onset}}$ is about 278 ~ 283 K. An important feature of the phase transformation from Mn RTP(I) to Mn LTP is that the crystal of Mn RTP(I) must be cooled in a slow manner. In the actual experiment the cooling rate was 0.2 K/min. The phase transformation will be missed if the crystal is cooled too fast (from RT to 90 K within several seconds). This is why the data collection of Mn RTP(I) can be done at 90 K. The structure of Mn RTP(I) is frozen in at 90 K if the crystal is cooled too fast. Once the temperature is 90 K, there will not be enough
energy for the structure to cross the activation-energy barrier, hence the transformation will not happen.

All the phase transformations observed in this work are reversible solid-solid phase transformations driven by changes in temperature except for the transformation from Mn RTP(I) to Mn RTP(II). The transformation from Mn RTP(I) to Mn RTP(II) happens at room temperature spontaneously, and the process seems to be irreversible. No Mn RTP(II) crystals have been observed to convert to Mn RTP(I). Furthermore, the transformation is not a solid-solid process. The solvent must be present in order for the transformation to happen. The actual observation is that the Mn compound crystallized out of the aqueous solution first as Mn RTP(I). When these crystals were kept contact with the solution in which they were grown, the crystal habit changed significantly within one month (see Figure 3.35). This is the phase transformation from Mn RTP(I) to Mn RTP(II). On the other hand, when the Mn RTP(I) crystals were removed from the solution, e.g. dried or kept in paratone (an inert oil), the transformation did not happen (at least not for a period of 1.5 yrs). These observations indicate that the transformation from Mn RTP(I) to Mn RTP(II) requires the dissolution of the Mn RTP(I) crystals, followed by the recrystallization of the Mn RTP(II) phase. Table 3.7 shows that Mn RTP(II) has the closest packing among the three Mn phases because Mn RTP(II) has the smallest value of the average volume per formula unit and the largest density. Mn LTP and Mn RTP(I) have very similar values of the average volume per formula unit and the density, therefore the packing efficiency in Mn LTP and Mn RTP(I) should be very similar. The conclusion drawn from Table 3.7 is consistent with the observations that the Mn RTP(I) crystals convert to Mn RTP(II) spontaneously, and that the phase transformation between Mn LTP and Mn RTP(I) is reversible.
Figure 3.35 A photograph of single crystals of the Mn compound. The two crystals of Mn RTP(I) are viewed from different directions.
Table 3.7 The volume of the unit cell (V), the number of the formula unit in the unit cell (Z), the average volume per formula unit (V/Z), and the density (ρ) for the three phases of the Mn compound at low and room temperatures*.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Mn LTP</th>
<th>Mn RTP(I)</th>
<th>Mn RTP(II)</th>
<th>Mn RTP(I)</th>
<th>Mn RTP(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>90.0(2)</td>
<td>90.0(2)</td>
<td>90.0(2)</td>
<td>294(2)</td>
<td>294(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>5311.8(18)</td>
<td>1773.5(6)</td>
<td>3504.9(10)</td>
<td>1819.5(6)</td>
<td>3615.2(10)</td>
</tr>
<tr>
<td>Z</td>
<td>12</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>V/Z (Å³)</td>
<td>442.6(2)</td>
<td>443.4(2)</td>
<td>438.1(2)</td>
<td>454.9(2)</td>
<td>451.9(2)</td>
</tr>
<tr>
<td>ρ (g/cm³)</td>
<td>1.633</td>
<td>1.630</td>
<td>1.650</td>
<td>1.589</td>
<td>1.599</td>
</tr>
</tbody>
</table>

* RT data collection for Mn LTP is impossible because the LT phase is not stable at RT.
In summary, three reversible solid-solid phase transformations have been observed. They are between Cu RTP and Cu HTP, between Zn RTP and Zn HTP, and between Mn LTP and Mn RTP(I). The respective onset temperatures are 39, 31, and 5 ~ 10 °C. The enthalpies of the first two transformations are very small (both ~ 0.1 kJ/mol). The enthalpy of the third transformation is not determined, but is expected to be as small as the first two. Structures of these six phases were determined. All of them belong to the 2D structural type. As mentioned previously, all the 2D structures pack very similarly, and they are different only in the way the enantiomers of the cation alternate in certain directions. In terms of the alternation patterns (see Table 3.5), Cu RTP shows 1 non-alternation in 5 contacts; Cu HTP and Mn RTP(I) show perfect alternation; Zn RTP and Mn LTP show 1 non-alternation in 3 contacts; Zn HTP shows 2 non-alternations in 8 contacts. The trend in alternation patterns is that the patterns become simpler (i.e. fewer alternation faults) as the temperature increases, but become more complicated (i.e. more alternation faults) as the temperature decreases. As a result, the three phase transformations can be viewed as the interconversion of the enantiomers in a cooperative way in the crystals. The change in handedness does not require much energy since the two enantiomers are conformational isomers; therefore it is not surprising that the phase transformations are reversible and can take place in the solid state. On the other hand, the spontaneous transformation at RT from Mn RTP(I) to Mn RTP(II) seems irreversible, and requires the dissolution of the Mn RTP(I) crystals, followed by the recrystallization of the Mn RTP(II) phase. Mn RTP(I) shows 2D H-bonding, while Mn RTP(II) shows 3D H-bonding. It is not surprising that such a relatively major change in the H-bonding pattern cannot happen in the solid state. Furthermore, the cation layer in the 3D structure (see Figure 3.34) is simpler and more even than the similar layer in any of the 2D structures (see Figure 3.29).

**Conclusion**

Five compounds, [M(15-crown-5)(H2O)2](NO3)2 (M = Cu, Zn, Mg, Co, Mn) were studied in this work. The system turned out to be rich in polymorphs, which is invaluable for people who study polymorphism of molecular crystals. Nine definite solid-state phases were identified using X-ray single-crystal diffraction and differential scanning calorimetry. More phases probably exist in the solid state at temperatures slightly above the room temperature. All phase transformations in this
system take place in single crystals without the loss of crystallinity except for the transformation from Mn RTP(I) to Mn RTP(II). The nine phases crystallize in five crystal structures. In terms of H-bonding, the five structures can be divided into two groups: the 2D H-bonding structure and the 3D H-bonding structure. The four 2D structures have very similar packing, and are different only in the ways in which the two enantiomeric cations alternate in certain directions. The one remaining 3D structure, although it seems very different, has cation layers that are similar to the layers found in all the 2D structures. The 15-crown-5 ligands have a very similar conformation in all the structures. The two enantiomers of the cation cannot be resolved in solution, and can interconvert in the solid state. All the structures have \( Z' > 1 \). The asymmetric units in all the structures are complicated and pseudosymmetric.

The obvious question is, why do similar-shaped cations and nitrate anions produce a series of structures that show varieties of complex packing? The answer seems to be that each cation and its four nearest neighbors have problems in achieving complementary contacts. To partially circumvent such packing problems the cations change the conformation and become the ones of the opposite handedness. The origin of the packing problems is the odd number of \(-\text{CH}_2\text{-O-CH}_2\)-units in the crown ether ligand.

**Unanswered Questions**

The Cu, Zn, and Mg compounds crystallize in structures with 2D H-bonding only. The Co compound crystallizes in the structure with 3D H-bonding only. The Mn compound is the only compound that crystallizes in structures with both 2D and 3D H-bonding. These compounds differ in the metal ions only, and the metal ions differ in the \( d \)-orbital electronic configurations. Therefore, an obvious question is, how do the \( d \)-orbital electrons affect packing? The existence of high-temperature phases of the Mg, Co, and Mn compounds is supported by the differential scanning calorimetry measurements only. The crystal structures of these high-temperature phases need to be determined if possible. Other metal ions, such as Fe\(^{2+}\), Ni\(^{2+}\) and Cd\(^{2+}\) may also produce similar compounds, but the structures are unknown.
Appendix A

In Appendix A each file is a linking file, which is named Exp##.pdf. The file can be opened with Adobe Acrobat Reader. The file summarizes the experimental details of the X-ray diffraction experiment for each compound. The file was originally generated in html format by using the Nonius software, SUPERGUI. The file is known as the “nreport” file in the Nonius software. On a Redhat Linux computer each html file was first converted to a postscript file. Afterwards the postscript file was converted to a pdf file.

Exp01.pdf
A1. Experimental details of X-ray diffraction for anhydrous pinacol at 90 K (k03278).

Exp02.pdf
A2. Experimental details of X-ray diffraction for anhydrous pinacol at 173 K (k01154).

Exp03.pdf

Exp04.pdf
A4. Experimental details of X-ray diffraction for pinacol monohydrate at 90 K (k03227).

Exp05.pdf
A5. Experimental details of X-ray diffraction for pinacol hexahydrate at 90 K (k03226).

Exp06.pdf

Exp07.pdf


A12. Experimental details of X-ray diffraction for the Mg 15-crown-5 compound at 90 K (k02119).


A16. Experimental details of X-ray diffraction for the Mn 15-crown-5 compound at 90 K (k03012, the triclinic).

A17. Experimental details of X-ray diffraction for the Mn 15-crown-5 compound at 294 K (k03125, the triclinic).

A18. Experimental details of X-ray diffraction for the Mn 15-crown-5 compound at 90 K (k03098, the tetragonal).

A19. Experimental details of X-ray diffraction for the Mn 15-crown-5 compound at 294 K (k03100, the tetragonal).

A20. Experimental details of X-ray diffraction for the Mn 15-crown-5 compound at 90 K (k03126, the monoclinic).

**Appendix B**

In Appendix B each file is a linking file, which is named Tab##.pdf. The file can be opened with Adobe Acrobat Reader. The file was originally generated in a plain-text format by using the Bruker software, *SHELXTL/XCIF*. The file is known as the “*.tab” file in the Bruker software. On a Windows computer each file was first converted to a document file by using Microsoft Office/Word. Afterwards the document file was converted to a pdf file by using Adobe Acrobat.

In each file there are six tables. Table 1 shows the information about crystal data and structure refinement. Table 2 shows the atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms. Table 3 shows the bond lengths and angles. Table 4 shows
the anisotropic displacement parameters for the non-hydrogen atoms. Table 5 shows the coordinates and isotropic displacement parameters for the hydrogen atoms. Table 6 lists the torsion angles.

Tab01.pdf
B1. Crystallographic tables for anhydrous pinacol at 90 K (k03278).

Tab02.pdf
B2. Crystallographic tables for anhydrous pinacol at 173 K (k01154).

Tab03.pdf
B3. Crystallographic tables for hexagonal pinacol at 173 K (k01235).

Tab04.pdf
B4. Crystallographic tables for pinacol monohydrate at 90 K (k03227).

Tab05.pdf
B5. Crystallographic tables for pinacol hexahydrate at 90 K. The refinement is done in two models: \(P4_{2}/mnm\) (k03226) and \(Pnnm\) (k03226o).

Tab06.pdf

Tab07.pdf
B7. Crystallographic tables for the Cu 15-crown-5 compound at 294 K (k02122).

Tab08.pdf

Tab09.pdf
B9. Crystallographic tables for the Zn 15-crown-5 compound at 90 K (k04160).
B10. Crystallographic tables for the Zn 15-crown-5 compound at 294 K (k02168).

B11. Crystallographic tables for the Zn 15-crown-5 compound at 311 K (k04134).

B12. Crystallographic tables for the Mg 15-crown-5 compound at 90 K (k02119).

B13. Crystallographic tables for the Mg 15-crown-5 compound at 294 K (k02169).


B15. Crystallographic tables for the Co 15-crown-5 compound at 294 K (k02155).

B16. Crystallographic tables for the Mn 15-crown-5 compound at 90 K (k03012, the triclinic).

B17. Crystallographic tables for the Mn 15-crown-5 compound at 294 K (k03125, the triclinic).

B18. Crystallographic tables for the Mn 15-crown-5 compound at 90 K (k03098, the tetragonal).

B19. Crystallographic tables for the Mn 15-crown-5 compound at 294 K (k03100, the tetragonal).
Appendix C

Appendix C lists the files of the DSC measurements. Each file is in a pdf format, which can be opened with Adobe Acrobat Reader. Five compounds were investigated. The Mn compound has two polymorphs, and each polymorph was studied individually. That is why there are two files related to the Mn compound.

C1. The DSC measurement of the Cu 15-crown-5 compound.

C2. The DSC measurement of the Zn 15-crown-5 compound.

C3. The DSC measurement of the Mg 15-crown-5 compound.

C4. The DSC measurement of the Co 15-crown-5 compound.

C5. The DSC measurement of the Mn 15-crown-5 compound (the triclinic polymorph).

C6. The DSC measurement of the Mn 15-crown-5 compound (the tetragonal polymorph).

Appendix D

The Atomic Displacement Parameters
The Equiprobability Displacement Ellipsoid

In X-ray structure analysis the 3-D distribution of the atomic displacement $\Delta x$ from the mean position $x$ (vector of fractional coordinates, no unit) is described by a Gaussian probability distribution function (pdf). The surface of constant probability density is ellipsoidal (Nelmes, 1980). The formula of a Gaussian pdf is shown in Equation AD-1 (Johnson & Levy, 1974).

$$p(\Delta x) = (1/2\pi)^{3/2}[\det(\sigma^{-1})]^{1/2}\exp(-\Delta x^T \sigma^{-1} \Delta x/2) \quad \text{(AD-1)}$$

Where $\sigma^{-1}$ is the inverse of the dispersion (variance-covariance) matrix $\sigma$ (no unit). According to Sands (Sands, 1982), $\sigma$ is a tensor ($U$ is used instead of $\sigma$ in Sands’ book). In a Cartesian coordinate system Equation AD-1 can be rewritten in the form of Equation AD-2.

$$p(\Delta x_1, \Delta x_2, \Delta x_3) = (1/2\pi)^{3/2}[1/(u_1u_2u_3)]\exp[-(1/2)(\Delta x_1^2/u_1^2 + \Delta x_2^2/u_2^2 + \Delta x_3^2/u_3^2)] \quad \text{(AD-2)}$$

Where $u_1$, $u_2$ and $u_3$ are the root-mean-square displacements (RMSDs, no unit) along the three principal axes in direct space. The directions of the three principal axes are actually the same as those of the three eigenvectors of the $\sigma$ tensor in direct space (Sands, 1982).

$$\Delta x_1^2/u_1^2 + \Delta x_2^2/u_2^2 + \Delta x_3^2/u_3^2 = C^2 \quad \text{(AD-3)}$$

Equation AD-3 describes a surface of constant probability density or an equiprobability ellipsoid, which is known as the displacement ellipsoid in X-ray structure analysis. If $P(C)$ is the probability, of which a displacement falls within the ellipsoid, then it is equal to the integration of pdf over the volume of the ellipsoid, which is shown in Equation AD-4 (Owen, 1962).

$$P(C) = \int p(\Delta x_1, \Delta x_2, \Delta x_3) d\tau$$

$$= (1/2\pi)^{3/2} \int_0^{2\pi} \int_0^\pi \int_0^C r^2 \exp(-r^2/2) dr d\phi d\theta$$

$$= (2/\pi)^{1/2} \int_0^C r^2 \exp(-r^2/2) dr \quad \text{(AD-4)}$$
The values of $P(C)$ with respect to $C$ are tabulated (Owen, 1962), in which $B$ was used instead of $C$. Usually the displacement ellipsoids in X-ray structure analysis are drawn at 50% probability, which means $P(C) = 0.5$. The corresponding $C$ value is 1.5382. This means that in the picture of displacement ellipsoids the semi-axial lengths of the displacement ellipsoid are 1.5382 times as big as the RMSDs. However, this is true only along the three principal axes (Nelmes, 1980; Johnson & Levy, 1974). When $C$ is unity, the semi-axial lengths are exactly the same as the RMSDs, which again is true only along the principal axes. The corresponding displacement ellipsoids are then scaled down to include about 20% probability, i.e. $P(C) \approx 0.2$ when $C = 1$.

The Dispersion Matrix: $\sigma$ tensor

The Fourier Transform of $p(\Delta x)$ is given in Equation AD-5 (Dunitz et al., 1988).

$$T = \exp(-2\pi^2 \mathbf{h}^T \sigma \mathbf{h}) = \exp(-2\pi^2 \sum_i \sum_j \sigma_{ij} h_i h_j)$$

(AD-5)

Where $\mathbf{h}$ is the vector of reflection indices (no unit), and $T$ is called temperature factor, which might have nothing to do with temperature (Dunitz et al., 1988). The structure factor can then be expressed in a simple equation shown in Equation AD-6.

$$F(\mathbf{h}) = \Sigma / \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) T$$

(AD-6)

The mean-square displacement (MSD, unit: Å$^2$) of an atom in the direction of any vector $\mathbf{v}$ (fractional coordinates, no unit) in direct space is calculated based on $\sigma$ tensor (Johnson & Levy, 1974), which is shown in Equation AD-7.

$$\text{MSD}(\mathbf{v}) = \mathbf{v}^T g^T \sigma g v / \mathbf{v}^T g v$$

(AD-7)

Where $g$ is metric tensor whose components are the scalar products of the unit cell vectors, $\mathbf{a}_i \cdot \mathbf{a}_j$ (unit: Å$^2$). In the directions of three eigenvectors ($\mathbf{v}_i$, $i = 1, 2, 3$), i.e. principal axes, Equation AD-8 can be obtained. The three eigenvectors should be orthogonal (Sands, 1982).

$$\sigma g v_i = \lambda_i \mathbf{v}_i, \quad i = 1, 2, 3$$

(AD-8)
If Equations AD-7 and AD-8 are combined, the MSDs along the three principal axes can be calculated, which are shown in Equation AD-9.

\[ MSD(v_i) = \lambda_i, \ i = 1, 2, 3 \quad (AD-9) \]

\( \lambda_i (i = 1, 2, 3) \) are called eigenvalues. The physical meaning of them is that they are principal MSDs. The values are calculated and written to the .lst file when least-squares refinements are performed with program SHELXL (Sheldrick, 1997). The physical meaning of these three quantities requires them to be real and positive. As a result, \( \sigma \) tensor must be positive-definite. If one of eigenvalues is negative, \( \sigma \) tensor will be non-positive-definite (NPD). The corresponding atom is called an NPD atom. The electron density distribution of that atom will no longer be described by a Gaussian pdf, and the surface of constant probability density is not ellipsoidal any more. When such a situation rises, the refinement will be unstable. Large correlations can cause NPD problems, which may be a result of the wrong space group or disorder. If NPD is caused by pseudosymmetry, the refinement should be restrained.

An important property of the \( \sigma g \) matrix is that its trace is invariant under transformation. The trace is equal to the sum of \( \lambda_i \) (i = 1, 2, 3). When a structure is reported, an equivalent isotropic MSD \( (U_{eq} \) or \( U_{iso} \), unit: \( \text{Å}^2 \)) for each atom will be calculated by averaging the three principal MSDs (see Equation AD-10).

\[ U_{eq} = (1/3)(\lambda_1 + \lambda_2 + \lambda_3) = (1/3)\text{trace}(\sigma g) = (1/3)\sum_i \sum_j \sigma_{ij} a_i \cdot a_j \quad (AD-10) \]

It can be proved that the isotropic temperature factor, \( B \), can be expressed in terms of \( U_{eq} \) (see Equation AD-11; Sands, 1982).

\[ B = 8\pi^2 U_{eq} \quad (AD-11) \]

Then \( T \) can be written in terms of \( B \) (see Equation AD-12).
\[ T = \exp[-B(\sin \theta / \lambda)^2] \] (AD-12)

Where \( \lambda \) is the X-ray wavelength (unit: Å).

If all atoms are assumed to have the same isotropic temperature factor, then \( B \) can be estimated by making an overall Wilson plot. In this case the individual \( \sigma \) tensor for each atom is not necessary to be known.

**One Confusing Thing**

When the results of structure analysis are presented graphically, the distribution of the atomic displacements from the mean position is represented by an equiprobability ellipsoid. The square of the distance, \([d(v)]^2\) (unit: Å\(^2\)), from the mean position to an equiprobability surface in the direction of any vector \( v \) in direct space is defined in Equation AD-13 (Johnson & Levy, 1974).

\[ [d(v)]^2 = C^2 v^T g v / v^T \sigma^{-1} v \] (AD-13)

Note Equations AD-7 and AD-13 are not equivalent in a general direction even if \( C \) is unity. The two equations are equivalent only along the three principal axes (see Equation AD-14).

\[ [d(v_i)]^2 = C^2 \text{MSD}(v_i) = C^2 \lambda_i, \ i = 1, 2, 3 \] (AD-14)

This is the reason why it is only along the three principal axes that the semi-axial lengths of the displacement ellipsoid are equal to the RMSDs multiplied by a factor of \( C \). Since \([d(v)]^2\) of the displacement ellipsoid is proportional to MSD(\(v\)) in the principal directions, it is tempting to assume that this proportional relationship is true in other directions as well. However, it is not true. This may be confusing for a person who first comes across a plot of the displacement ellipsoids of a molecule. Graphically the RMSD surface is peanut-shell shaped rather than ellipsoidal (Nelmes, 1980; Johnson & Levy, 1974; Dunitz *et al.*, 1988). Buergi and co-workers wrote a program called *PEANUT* to display these surfaces (Hummel *et al.*, 1990).
**The U matrix in SHELXTL**

When the results of structure analysis are reported, the $\sigma$ tensor is usually not given. Instead the components of a 3x3 $U$ matrix are reported. Since $U$ is symmetric, only six $U_{ij}$ components (unit: Å$^2$) are independent. They are usually called ADPs when using SHELXL (Sheldrick, 1997) to refine the structures. A typical atom instruction line in a .res or .ins file is shown below.

Atomname   sfac   x   y   z   sof   $U_{iso}$ or $U_{11}$ $U_{22}$ $U_{33}$ $U_{13}$ $U_{12}$

These $U_{ij}$ components are defined in Equation AD-15.

\[
T = \exp(-2\pi^2\sum_i\sum_j U_{ij}a_i^*a_jh_ih_j) \tag{AD-15}
\]

Where $a_i^*$ and $a_j^*$ are lengths of reciprocal basis vectors (unit: Å$^{-1}$).

Comparing Equations AD-5 and AD-15, it can be inferred that:

\[
U_{ij} = \frac{\sigma_{ij}}{a_i^*a_j^*} \tag{AD-16}
\]

The $U$ matrix is actually defined in reciprocal space. The diagonal elements, $U_{ij}$ ($i = j$) have numerical values equal to the MSDs along the reciprocal axes (Johnson & Levy, 1974). However, the off-diagonal elements, $U_{ij}$ ($i \neq j$) do not have a direct physical interpretation because the reciprocal axes are defined in an oblique coordinate system (Johnson & Levy, 1974). This is why the diagonal elements are always positive, while the off-diagonal elements might be negative. The off-diagonal elements are not MSDs because a negative MSD has no physical meaning. If the off-diagonal elements are very negative, then the determinant may be negative, which means that the atom is NPD (non-positive-definite).

If Equation AD-16 is plugged into Equation AD-10, then the equivalent isotropic MSD, $U_{eq}$ can be described in terms of $U_{ij}$ components.

\[
U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*a_i^*a_j \tag{AD-17}
\]
Obviously $U_{eq}$ is not equal to one-third of the trace of the $U$ matrix, \emph{i.e.} $(1/3)(U_{11} + U_{22} + U_{33})$, but equal to one-third of the trace of the $\sigma_g$ matrix. Since the trace of a matrix is invariant under transformation, the $U$ matrix is certainly not the transformation of the $\sigma_g$ matrix. However, the traces of the $U$ and $\sigma_g$ matrices happen to be the same in orthorhombic, tetragonal and cubic crystal systems because $a_i \cdot a_j = 0 \ (i \neq j)$ and $a_i^t a_i = 1$. But this not true in the other four crystal systems, of which the unit-cell vectors are defined in the oblique coordinate system. In a strict mathematical sense the $U$ matrix is not a tensor (Sands, 1982).

For the $\sigma$ tensor, if the fractional coordinates are transformed as below:

\[ x' = Rx + t \]  \hspace{1cm} (AD-18)

Then the $\sigma$ tensor will be transformed as following since it is invariant to translation (Johnson & Levy, 1974; Sands, 1982).

\[ \sigma' = R\sigma R^T \]  \hspace{1cm} (AD-19)

However, the above transformation might not be generally true for the $U$ matrix since $U$ is not a tensor. It is possible that the transformation matrix of the $\sigma$ tensor happens to be the same for the $U$ matrix by chance.

For example, if the transformation matrix is:

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

Then $\sigma$ tensor will be transformed as following:
\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
\sigma^{11} & \sigma^{12} & \sigma^{13} \\
\sigma^{21} & \sigma^{22} & \sigma^{23} \\
\sigma^{31} & \sigma^{32} & \sigma^{33}
\end{pmatrix}
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
= 
\begin{pmatrix}
\sigma^{11} & -\sigma^{12} & \sigma^{13} \\
-\sigma^{21} & \sigma^{22} & -\sigma^{23} \\
\sigma^{31} & -\sigma^{32} & \sigma^{33}
\end{pmatrix}
\]  \hspace{1cm} (AD-20)

Since the lengths of reciprocal basis vectors do not change under this transformation, the following equation is also correct.

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
\sigma^{11} / a^1 a^1 & \sigma^{12} / a^1 a^2 & \sigma^{13} / a^1 a^3 \\
\sigma^{21} / a^2 a^1 & \sigma^{22} / a^2 a^2 & \sigma^{23} / a^2 a^3 \\
\sigma^{31} / a^3 a^1 & \sigma^{32} / a^3 a^2 & \sigma^{33} / a^3 a^3
\end{pmatrix}
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
= 
\begin{pmatrix}
\sigma^{11} / a^1 a^1 & -\sigma^{12} / a^1 a^2 & \sigma^{13} / a^1 a^3 \\
-\sigma^{21} / a^2 a^1 & \sigma^{22} / a^2 a^2 & -\sigma^{23} / a^2 a^3 \\
\sigma^{31} / a^3 a^1 & -\sigma^{32} / a^3 a^2 & \sigma^{33} / a^3 a^3
\end{pmatrix}
\]  \hspace{1cm} (AD-21)

If Equation AD-16 is plugged into Equation AD-21, Equation AD-22 will be obtained. This means that such a transformation also happens to be true for the \( U \) matrix.

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
U_{11} & U_{12} & U_{13} \\
U_{21} & U_{22} & U_{23} \\
U_{31} & U_{32} & U_{33}
\end{pmatrix}
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
= 
\begin{pmatrix}
U_{11} & -U_{12} & U_{13} \\
-U_{21} & U_{22} & -U_{23} \\
U_{31} & -U_{32} & U_{33}
\end{pmatrix}
\]  \hspace{1cm} (AD-22)

Equation AD-22 describes the relationships of the atomic displacement parameters of the two independent cations in the room-temperature structure of the Co 15-crown-5 compound in Chapter Three. For example, C11 and C12 are the two carbon atoms related by the pseudosymmetry. If the \( U_{ij} \) components of C11 are \( U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, \) and \( U_{12} \), then the \( U_{ij} \) components of C12 will be \( U_{11}, U_{22}, U_{33}, -U_{23}, U_{13}, \) and \( -U_{12} \).

**Appendix E**

A single polarizer will convert randomly polarized light into linearly polarized light. In crossed polarizers, a second polarizer, with its polarization vector perpendicular to that of the first will
effectively block out the transmission of light. If a single crystal is placed between crossed polarizers, the linearly polarized light from the first polarizer will travel through the crystal first before it passes through the second polarizer. When the light is leaving the crystal, the orientation of the polarization vector will be changed by the crystal. As a result, the second polarizer cannot block the light completely; therefore, there will be net transmission of light so that the crystal will appear bright. However, if the crystal is properly aligned so that the orientation of the polarization vector from the first polarizer is not changed when leaving the crystal, then the second polarizer will block out the transmission of light; therefore, the crystal will appear dark. As the crystal is rotated so that it is no longer aligned, then the crystal will again change the orientation of the polarized light from the first polarizer such that some light will be transmitted through the second polarizer again, and the crystal will appear bright again. Thus there will be a particular set of rotation angles, at which the crystal appears dark (or extinguished), but suddenly gets bright if the crystal is rotated further. Visually it is as if the crystal is blinking on and off. The sharper the blinking or the sharper the extinction of the light, the better the crystal. This is the most practical way to examine the quality of single crystals by using a polarized microscope. The physics behind this phenomenon is called double refraction or birefringence. Amorphous materials, on the other hand, do not affect the orientation of polarized light; therefore, they are easily differentiated from crystalline materials.

Triclinic, monoclinic, and orthorhombic crystals obey the extinction condition in any crystallographic direction. Tetragonal, trigonal, hexagonal, and cubic crystals, however, do not obey the extinction condition in at least one special crystallographic direction, i.e. when such crystals are viewed along the special direction, the extinction condition will cover the whole 360º of rotation. In the case of tetragonal crystals, this special direction is the fourfold axis, i.e. the c direction by crystallographic convention. If a tetragonal crystal is viewed along the c direction, it will always look dark during the whole 360º of rotation, but an orthorhombic crystal will look dark only if it is properly aligned with either of the polarizers.
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Vita

Name: Xiang Hao

Date of birth: September 25, 1973

Place of birth: Daqing, Heilongjiang, CHINA

Education:
- 1997, B.S. in Chemistry with Prof. Shiwei Zhang, Department of Chemistry, Peking University, Beijing, CHINA.
- 2000, M.S. in Physical Chemistry with Prof. Shiwei Zhang, Department of Chemistry, Peking University, Beijing, CHINA.

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