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The use of Fourier reverse transforms in crystallographic phase refinement

by

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A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

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1997

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This work is dedicated to my grandfather, Dr. R. F. Ringrose. Although he is not here to see the completion of this journey, his belief in my abilities and strength has brought me to this point.

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ACKNOWLEDGEMENTS

There are a number of people whom I would like to thank for their roles in this endeavor. My husband, Leonard Thomas, has provided a great deal of support and encouragement as well as putting up with me when I was thoroughly frustrated by graduate school (or medical school, for a time).

My research advisor, Dr. Robert Jacobson, has graciously served in many roles during my time at Iowa State: advisor and coach to name a few. Without his guidance and patience this dissertation might not have come to pass.

Brenda Smith provided valuable advice on the intricacies of Word Perfect as well as general support, and I owe Jim Anderegg a great deal for his assistance when it seemed that my recalcitrant computer might win the day. I also would like to acknowledge the multitude of graduate students who have offered various and sundry advice, assistance and encouragement over the course of my graduate career, particularly Michelle McPhillen, Neal Simmons, Dr. Mike Ferguson and Dr. Cathy Day Klein.

My parents deserve a note of thanks, at least, for standing by me as I have charted my own unique path through my life so far. My sister, Carol Kilpatrick, has listened patiently to many tales of research that just wouldn't go right. My brother, David Ringrose, my in-laws, Charlotte and

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John McDermott, and my sister-in-law, Susan Thomas, have also provided support and encouragement when needed.

And finally, Butch and Fourier have been the source of much of the joy in my life for many days as I have worked on this research and dissertation. They seem to understand and empathize

with the experience of graduate research and dissertation preparation far more than one would expect from a Border Collie and an Australian Shepard mix. They provided priceless assistance as they frequently cheered me up when things just wouldn't go right.

This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1780 to this thesis.

ABSTRACT

Often a crystallographer obtains an electron density map which shows only part of the structure. In such cases, the phasing of the trial model is poor enough that the electron density map may show peaks in some of the atomic positions, but other atomic positions are not visible. There may also be extraneous peaks present which are not due to atomic positions. A method for determination of crystal structures that have resisted solution through normal crystallographic methods has been developed. PHASER is a series of FORTRAN programs which aids in the structure solution of poorly phased electron density maps by refining the crystallographic phases. It facilitates the refinement of such poorly phased electron density maps for difficult structures which might otherwise not be solvable.

The trial model, which serves as the starting point for the phase refinement, may be acquired by several routes such as direct methods or Patterson methods. Modifications are made to the reverse transform process based on several assumptions. First, the starting electron density map is modified based on the fact that physically the electron density map must be nonnegative at all points. In practice a small positive cutoff is used. A reverse Fourier transform is computed based on the modified electron density map. Secondly, we assume that a

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better electron density map will result by using the observed magnitudes of the structure factors combined with the phases calculated in the reverse transform. After convergence has been reached, more atomic positions and less extraneous peaks are observed in the refined electron density map.

The starting model need not be very large to achieve success with PHASER; successful phase refinement has been achieved with a starting model that consists of only 5 percent of the total scattering power of the full molecule.

The second part of the thesis discusses three crystal structure determinations: a porphyrin compound containing two metal atoms, $PtCuCl_2N_8O_2C_{56}H_{52}$; a cage structure in which two titanium atoms are interconnected via oxygen atoms, $Ti_2S_2O_6N_2C_{18}H_{38}$; and a heterocycle, $C_{20}H_{27}OBr$, for which the optical isomer was determined. Several other structure solutions are discussed in the first section with respect to the application of PHASER.

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CHAPTER 1. INTRODUCTION

A new approach to solving difficult crystal structures has been developed. In this method, a Fourier reverse transform approach is used to refine the crystallographic phases. After the phase refinement process is completed, which usually requires between five and twenty-five minutes, an improved electron density map is produced. The final electron density map contains more of the atomic positions and less extraneous peaks than the starting electron density map.

Dissertation Organization

This thesis has two parts. The first section, composed of Chapters 2 through 4, discusses a new crystallographic phase determination method called PHASER. Chapter 2 gives an introduction to crystallographic structure determination along with background information. Chapter 3 describes the details of the new method that I have developed. The application of PHASER to the determination of several selected crystal structures is described in Chapter 4.

Chapter 5 discusses three representative crystal structures of the more than twelve structures determined by the author in the course of graduate study: a porphyrin compound containing two metal atoms, $PtCuCl_2N_8O_2C_{56}H_{52}$; a cage

structure in which two titanium atoms are interconnected via oxygen atoms, $Ti_2S_2O_6N_2C_{18}H_{38}$; and a heterocycle, $C_{20}H_{27}OBr$, in which the optical isomer was determined. Several other structures that were used in the testing of PHASER are included in Chapter 4. Since these compounds were prepared by other research groups at Iowa State University, discussion of their syntheses will be omitted and the determination of their crystal structures will be emphasized.

PART I. SOLUTION OF THE PHASE PROBLEM USING PHASER

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CHAPTER 2. FUNDAMENTALS OF A CRYSTAL STRUCTURE DETERMINATION

Single crystal x-ray diffraction techniques provide one of the most widely used methods for the characterization of materials and the determination of their molecular structures. Conventional structure solution techniques based on direct methods or Patterson methods work well in many cases, but still fail in others. Therefore, adding to our current repertoire of structure solution techniques remains an important task. Its importance will increase as area detectors make data collection more quickly obtainable and rapid solution of crystal structures becomes critical.

A new method of crystallographic structure determination has been developed which uses reverse Fourier transforms to refine crystallographic phases. A threshold removes low-lying features, improving the phases and the resulting electron density map. This new method has been applied to a number of test cases. Results thus far indicate that it will succeed in elucidation of the trial structures even in cases where direct methods failed and considerable work was needed to solve the structure.

The rest of this chapter is devoted to a review of some of the basics of x-ray diffraction and an introduction of terminology which will be useful in later discussion.

Steps in a Typical Single Crystal Data Collection^{1,2,3}

Selection of a crystal

Before data can be collected, an appropriate single crystal must be selected. A crystal with well-formed faces is preferred. Ideally the size of the crystal should be approximately $2/\mu$, where μ is the absorption coefficient, but less than 0.5-0.6 mm (The crystal must be completely bathed by the x-ray beam.).

The crystal is attached to the end of a glass fiber by an adhesive. Although many materials have been used to attach crystals to fibers, epoxy is generally used. Unstable crystals, those that are water- or air-sensitive or have solvent of crystallization, are mounted in a capillary and the capillary is then sealed to prevent decomposition of the crystal. To further guard against the reaction of the crystal with the air, the data can be collected at low temperature, where it is bathed in a cold nitrogen gas stream. Before mounting the crystal onto the glass fiber, the fiber is inserted into a metal pin which will in turn be inserted into a goniometer head.

Next, the goniometer head is mounted on the diffractometer and the crystal is optically centered on the diffractometer with the aid of the microscope. Photographs can be taken to determine if the crystal diffracts well and to

check on crystal quality.

Data collection

Modern crystallographic data collection has been highly automated. Diffractometers are often controlled by powerful software packages which are easy to use. Although some software packages allow the user to defer all decisions about the data collection to the computer, this is generally not advised. However, after a crystal is "indexed" (its lattice parameters determined along with the orientation information necessary to predict indices for all reflections) and the symmetry of the crystal has been confirmed by a Laue check, the remainder of the data collection can be controlled by the computer with little user intervention

Indexing of the crystal can be accomplished by several methods. Peak positions of diffraction maxima can be measured from a photograph and entered into the computer. After these peak positions are refined, the computer will attempt to index the crystal.

Alternatively, the user can instruct the computer to search for 15 to 25 reflections. The diffractometer will search through reciprocal space looking for peaks and then attempt to refine any peaks it locates to determine accurate angular settings.

The peaks obtained by either method should be examined

for indications of crystal quality. Poor peak shape characterized by split or broad peaks or the presence of a shoulder on a peak are indicative of poor crystal quality. In such cases, it is advised to screen other crystals before proceeding if other crystals are available. After a suitable number of reflections have been obtained and refined, the lattice parameters (the unit cell dimensions) are determined from the peak positions by indexing the reflections, i.e., assigning h,k, and l indices to each reflection. In some cases, the program will be unable to find a reasonable unit cell that is consistent with all of the reflections. This indicates that the crystal is probably twinned, a multiple crystal, or is "excessively imperfect".³ Since the data collected and the resulting structure solution depend on the accuracy of the unit cell determination, in these cases the best course of action is to select a better crystal if more crystals are available.

After the crystal has been accurately indexed, the reduced unit cell, the cell with minimum lengths, is calculated. Next the symmetry of the unit cell may be verified by measuring the intensities of symmetry equivalent reflections.

The intensities of the reflections or diffraction maxima are then collected for the crystal. A scintillation counter or an area detector is used to measure these intensities.

Finally, several psi-scans (azimuthal scans) are performed to obtain the necessary data in order to determine the absorption correction for the compound by a semi-empirical technique.

Once the data set has been collected, the investigator must select a method to extract a trial structure from this data. The two primary methods for structure solution are direct methods and "indirect" or Patterson methods.

The Phase Problem

Because the crystal structure is a periodic function, it can be expressed as a Fourier series. The electron density of a crystal structure at a general point (x,y,z) can be written in the form,

$$\rho(x, y, z) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} e^{-2\pi i (hx+ky+lz)} .$$
 (1)

Although a three-dimensional infinite sum is indicated, in practice one can determine a good representation of the electron density function with the data collected, assuming the missing reflections make inconsequential contributions. The measured data are not infinite and the indices for measured reflections extend in most cases from approximately -20 to +20.

However, to utilize this equation, one needs the structure factor, F_{hkl} . The amplitudes of the structure factors can be obtained from the measured diffraction intensities since the square of the structure factor must equal the intensity: $I_{hkl} = |F_{hkl}|^2$. Thus the intensities provide us with

the magnitude of the structure factors, but we still lack their phases angles:

$$F_{hkl} = |F_{hkl}| e^{i\alpha}$$
or $F_{hkl} = A_{hkl} + iB_{hkl}$
(2)

which are not determined experimentally. The phase angle, α , for each reflection \vec{h} is in the range from 0 to 2π radians (or

 $-\pi$ to π), where \vec{h} is some (hkl). For centrosymmetric

structures, because the phase angle, α , must be 0 or 180°, we speak of the sign s(hkl) (+ or -) of the reflection.

As was noted previously, to determine a three-dimensional image of the structure we must know both the amplitudes of the structure factors and their phase angles. (It might also be noted that the structure factor can be related to the atomic positions as follows:

$$F_{bkl} = \sum_{j}^{N} f_{j} e^{2\pi i (bx_{j} + ky_{j} + lz_{j})}$$
(3)

where f, is the thermally adjusted atomic scattering factor for the jth atom and (x_1, y_1, z_1) are the coordinates of the jth atom. The summation is performed over the N atoms in the unit cell. We will make use of this equation later.)

For centrosymmetric cases, Equation 1 simplifies to

$$\rho(x, y, z) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} \cos 2\pi (hx + ky + lz) .$$
 (4)

As noted above, the sum in practice extends over all observed reflections and the maxima in these functions are at or very near atomic positions. V is the volume of the unit cell. If the amplitudes and phases of the scattering F_{hkl} are known, the complete electron density map of the unit cell can be computed from Equation 4.

If a sufficient number of the phases of the larger amplitude reflections are determined and attached to their respective $|F_{hkl}|$, the Fourier series "refines"; the atomic peaks occur at positions somewhat shifted from their true positions and new peaks may appear corresponding to atoms not yet included. These new peaks, especially if they make chemical sense, can be included in the next cycle of leastsquares refinement. If most of the signs of the large $|F_{hkl}|$ have been included with the observed F_{hkl} and further additions to the trial structure are made wisely, the final complete structure may be reached through this process. However, an initial set of phases of the large $|F_{hkl}|$'s must somehow be chosen. This is the fundamental difficulty in the solution of crystal structures, and it is termed the phase problem. Random selection of the phases is impractical due to the size of the data set (in the centrosymmetric case, 2" combinations are possible for N reflections, where $2^{10} \approx 10^3$). Two common methods of determining an initial set of phases are direct methods and Patterson methods. These are both quite powerful in the cases for which they were intended, but can prove unsuccessful in other cases.

Direct Methods

The basic idea behind direct methods is that the phases are encoded in the |F| values. Even though the phases are not measured experimentally, direct methods assumes that knowledge of a few phases can lead to probable phases for other reflections through the use of appropriate statistical relations.

The practical objective of direct methods is to phase a sufficient number of reflections to produce an electron density map which allows the positions of the atoms in the molecule to begin to be located. By the use of direct methods, a starting set of phases can be obtained that allows more phases to be generated. The number of phases required to

generate a identifiable Fourier representation of the molecule depends on several factors, among them the nature of the molecular system and how much is already known of its structure.

Direct methods can be defined as "a set of mathematical equations that attempt to solve the phase problem from the observed amplitudes through purely mathematical or statistical techniques, without the use of structural chemical information."⁴

It is estimated that 80-90% of reported small-molecule structures are solved using direct methods.¹ These methods have been automated to the extent that they are commonly used as "black box" techniques where raw data are input into the program and the essentially solved crystal structure appears after minimal user input. This has made this technique widely popular.

Direct methods have the greatest likelihood of success with equal atom cases, or "similar atom" cases. These are the same problems to which heavy-atom or Patterson approaches do not apply.

Normalized structure factors^{1,5,6}

It is common in direct method calculations to replace |F(hkl)| by the corresponding normalized |E(hkl)|,

$$|E_{hkl}|^{2} = \frac{|F_{hkl}|^{2}}{\epsilon \sum_{j=1}^{N} f_{j}^{2}}.$$
 (5)

The atomic scattering factor for the j-th atom corrected for thermal vibrations, f_j , is given by

$$f_{j} = f_{0j} \exp^{-B(\sin^{2}\theta)/\lambda^{2}}.$$
 (6)

The factor ϵ in the denominator of Equation 5 takes account of the fact that reflections in certain reciprocal lattice zones may have an average intensity greater than that for the general reflections. The value of this ϵ -factor depends on the crystal class; for general classes of reflections, ϵ =1.

The E values have properties similar to those obtained by scattering from a collection of point atoms, i.e., where all the real atoms have been replaced by point atoms. For the point atom, all of the electrons are situated at the nucleus. Due to this concentration of electrons, interference does not occur within the point atom and hence the scattering power of a point atom is not a function of $(\sin \theta)/\lambda$, in contrast to the case of the real atoms. The scattering power of a point atom is therefore a constant equal to the atomic number Z (Figure 2.1)⁷.



Figure 2.1. Scattering factor for a real atom and for a point atom

This has the effect of replacing the broad peaks that represent real atoms with peaks of very narrow breadth. Using E values confers an additional advantage in that maps with narrower peaks can be more readily interpreted. Such a "sharpened" electron density map from a crystal composed of point atoms should therefore show a much higher degree of resolution than a map from a normal crystal.

The radial decrease in $|F|^2$ is reduced by modifying $|F|^2$ by a function which decreases as $(\sin \theta)/\lambda$ increases:

$$\sum_{j=1}^{N} f_{j}^{2}.$$
 (7)

Due to this correction for the decrease in $|F|^2$ with increasing (sin θ)/ λ , high-angle reflections with small F values can have large E values. This correction for θ -

dependence can be quite important in direct methods calculations.⁵

The use of E's also allows all classes of reflections to be normalized to a common basis:

$$\langle E^2(\vec{h}) \rangle = 1. \tag{8}$$

Origin determination

The formulae used in direct methods phase determination require the use of a few reflections with known phases, either uniquely or symbolically. From the initial phase set, more phases can be generated.

In a centrosymmetric structure, the origin is taken at one of eight centers of symmetry in the unit cell. Shifting the origin arbitrarily does not affect the structure factor amplitudes, but it will usually change the phases drastically, depending on the values of h, k, and 1 for each reflection¹.

In any primitive, centrosymmetric space group in the triclinic, monoclinic, or orthorhombic systems, arbitrary signs can be allocated to three reflections in order to specify the origin at one of the centers of symmetry.¹ These signs form a basic set from which a progressively larger set of signed reflections can be built as the analysis proceeds.

However, certain combinations of phases, structure invariants, do exist that do not change regardless of the arbitrary assignment of the cell origin. Structure semiinvariants do not change sign with shifts among cell origins that have the same symmetry characteristics.

Sayre's relation^{6,3,1}

For a crystal structure composed of equal atoms, the electron density function, ρ , is composed of identical and well resolved peaks. Let us assume this is true in the xdirection so that, for mathematical simplicity, Buerger's onedimensional derivation can be used.⁹ For this type of structure, the electron density function is given by

$$\rho(x) = \frac{1}{V} \sum_{h=-\infty}^{\infty} F_h e^{-2\pi i h x}.$$
 (9)

Sayre made the assumption that ρ resembles its square, ρ^2 :

$$\rho(x)^{2} = \frac{1}{V} \sum_{h=-\infty}^{\infty} F_{h}^{*} e^{-2\pi i h x}, \qquad (10)$$

except that the peaks of ρ^2 are sharper than those of the original function. This operation changes the shape of each atom. The structure factors of the new Fourier series must be related to the original by some factor g which takes into account this change in shape.

$$F_h' = g_h F_h \tag{11}$$

For centrosymmetric crystals the square of the electron density can be rewritten as

$$\rho(x)^{2} = \rho(x) \rho(x) = \left[\frac{1}{V} \sum_{h_{1}=-\infty}^{\infty} F_{h_{2}} e^{-2\pi i h_{1}x}\right] \left[\frac{1}{V} \sum_{h_{2}=-\infty}^{\infty} F_{h_{2}} e^{-2\pi i h_{2}x}\right]$$

$$= \frac{1}{V^{2}} \sum_{h_{1}=-\infty}^{\infty} \sum_{h_{2}=-\infty}^{\infty} F_{h_{1}} F_{h_{2}} e^{-2\pi i (h_{1}+h_{2})x}$$

$$= \frac{1}{V} \sum_{h_{1}=-\infty}^{\infty} \left[\frac{1}{V} \sum_{h_{2}=-\infty}^{\infty} F_{h_{1}} F_{h_{2}}\right] e^{-2\pi i (h_{1}+h_{2})x}.$$
(12)

If you set $h_1 + h_2 = h$ and $h_1 = k$, then $h_2 = h-k$. The previous equation can be rewritten,

$$\rho(x)^{2} = \frac{1}{V} \sum_{k=-\infty}^{\infty} \left[\frac{1}{V} \sum_{h-k=-\infty}^{\infty} F_{k} F_{h-k} \right] e^{-2\pi i h x}].$$
 (13)

If you compare Equations 10, 11 and 13, it can be seen that

- ----

$$F_{h}' = g_{h}F_{h} = \frac{1}{V} \sum_{h-k=-\infty}^{\infty} F_{h-k}F_{k}$$
(14)

and

$$F_{h} = \frac{1}{g_{h}} F_{h}' = \frac{1}{g_{h}} V \sum_{k=-\infty}^{\infty} F_{h-k} F_{k}.$$
 (15)

The phases of crystals composed of equal, well-resolved atoms must obey this relation. Equation 15 implies that any structure factor F_h is determined by the products of all of the pairs of structure factors whose indices add to give h. Thus F_{10} depends on the products of F_8 and F_2 , F_7 and F_3 , and so on. Although Equation 15 states that to determine one F_h it is necessary to know the magnitudes and phases of all of the others, Sayre showed that for the case where F_h is large, the series must tend strongly in one direction (+ or -). If one term is large enough to dominate the sum, the sign of the sum must be controlled by that product. The other terms may be ignored. Equation 15 can then be expressed as

$$S_h = S_{h-k} S_k \tag{16}$$

where S_h indicates the sign of F_h . In other words, the sign of F_h tends to be the same as the product of the signs of two other F's, related as in Equation 15. This relation holds when F_h , F_{h-k} and F_k are all large.

It should be noted that the expression:

$$S_{h} = \sum_{k=-\infty}^{\infty} S_{h-k} S_{k}$$
(17)

known as the Σ 2 relation, does have a higher probability of being correct than any of the individual terms of the summation.

Although the equal atom restriction may seem impractical, this approach can be extended to "like atom problems," containing C, H, O, and N such as seen in typical organic compounds. It has been found that these relationships can also be applied successfully in many cases to structures involving heavier atoms.

Symbolic addition

The symbolic addition method was commonly used for the application of direct methods in their early years. This method, like most direct methods techniques, is a boot-strapping operation. One starts with a very limited number of phases and uses them in conjunction with Sayre's equation, Equation 16, and the Σ 2 relation, Equation 17, to build a phase set large enough to give a recognizable electron density map. It should be noted that the correctness of the initial phase set is critical, as all generated phases depend upon the initial phase selections.

Before the symbolic addition method can be used, E's must

be calculated for the entire data set. Using only the E's greater than some minimum, a list is compiled of all of the triples, $|E_k|$ and $|E_{n-k}|$, of reflections belonging to this set for which the indices sum to zero.

First the phases of three or fewer origin-determining reflections are chosen. The list of strongest relationships is used to select those relationships that are most often interconnected, and appropriate reflections are chosen for origin determination. The number of phases that may be chosen depends on the crystal system and symmetry. In addition the signs of several reflections are represented by algebraic symbols. Generally, less than five algebraic symbols are sufficient. Relations are usually obtained between some or all of these symbols and their reflections and phases, allowing these symbols to be reduced in number or the determination of the signs of some of the symbols definitively.

After all relations have been generated and analyzed for reduction of the symbols, if p unknown symbols are left, then each symbol could take the signs + or -. Therefore, 2^p electron density maps can be computed and investigated for structural features consistent with the expected structure. In this manner, the signs of the unknown symbols can be determined.

Patterson Methods

In his 1935 paper, A.L. Patterson pointed out the crystallographic utility of a Fourier calculation using the phaseless $|F|^2$ as the coefficients. This function, named after Patterson, is calculated by evaluating the Fourier series:

$$P(\vec{r}) = \frac{1}{V} \sum_{\vec{h}=-\infty}^{\infty} |F(\vec{h})|^2 \exp^{-2\pi i (\vec{h} \cdot \vec{r})}$$
(18)

A crystallographic Fourier transform with F's as coefficients shows the distribution of atoms in the unit cell; the Patterson function however, using F^2 values as coefficients, produces a map of all of the interatomic vectors in the unit cell.

To produce a "Patterson map" from a known structure, an atom is placed at the origin and the positions of all the other atoms in the unit cell are plotted. This is repeated for every atom in the unit cell.

Therefore, for a molecule with N atoms in the unit cell, the Patterson map consists of N images of the unit cell. The map has N^2 peaks that correspond to the N vectors that can be drawn from each of the N atoms to every other atom in the unit cell (Figure 2.2)¹⁰.



Figure 2.2. (a) A set of points. (b) Interatomic vectors. (c) Patterson peaks about the origin from one set. (d) Patterson peaks in four unit cells.

The N² peaks in a Patterson map are much more densely packed than the peaks in an electron density map. However, the magnitude of a single peak is proportional to the product of the atomic number of the atoms at the head and tail of the vector: $H(j,k) \propto Z_{head}Z_{tail}$. The fact that peak heights are not equal in a Patterson map can be used to unravel the information contained in the map. Because of this, Patterson methods are particularly useful in solving structures with one or more heavier atoms, where the other atoms are relatively light. The difference in the atomic numbers of the heavy atoms and the light atoms can be used to locate their atomic positions in the map.

One significant problem with Patterson methods comes in analyzing the Patterson map. The N^2 peaks occurring in the map make interpretation difficult. This may frustrate some, causing them to fall back on direct methods. If direct methods fail, the structure is often considered not to be solvable.

Patterson superposition method

The Patterson superposition method is one technique that can be used to clarify the many peaks in a Patterson map and produce a single image of the structure. If a single vector is chosen in the Patterson map, we can shift the Patterson map by this vector, \vec{s} , and compare this with the original map to

produce a new function which has fewer images of the unit cell. The minimum of the shifted function and the original Patterson map is calculated by using the equation:

$$M^{(\alpha+1)}(\vec{r}) = Min[M^{\alpha}(\vec{r}), wP(\vec{r}-\vec{s})]$$
(19)

where M^{α} is the map after α superpositions, $P(\vec{r})$ is the

Patterson function, $P(\vec{r}-\vec{s})$ is the shifted Patterson

function, w is a weighting factor, and \vec{s} is the shift

vector. For one superposition $\alpha=0$ and $M^{\alpha}=P(\vec{r})$, and the

function looks like:

$$M(\vec{r}) = Min[P(\vec{r}), wP(\vec{r} - \vec{s})].$$
 (20)

The shifted Patterson function can be calculated using:

$$P(\vec{r} - \vec{s}) = \frac{1}{V} \sum_{\vec{h} = -\infty}^{\infty} |F(\vec{h})|^2 \exp^{-2\pi i \vec{h} \cdot (\vec{r} - \vec{s})}.$$
 (21)

Performing a superposition with a single vector theoretically reduces the number of images in the map from N to two. Further superpositions can be performed to reduce the number of extra images.
In real world situations some early incorrect signs in direct methods procedures can propagate giving a resultant map which is uninterpretable. Many extraneous peaks can be present in a Patterson superposition map making this map uninterpretable. It would be desirable to have a procedure to "develop" the structural image from these (otherwise useless) maps. It is just such a method which is the subject of the research reported in this thesis.

CHAPTER 3. DETAILS OF PHASER

As noted in Chapter 2, a crystallographer often obtains an electron density map by one means or another which displays only part of the structure. The phasing of the model may be poor enough that the electron density map shows peaks in some of the atomic positions, but other atom peaks are not visible. There may also be extraneous peaks present which do not form part of the structure. In such a case, either it may not be possible to solve the crystal structure from this electron density map or a considerable amount of time may be needed to refine the structure.

A new approach to the problem of poorly phased electron density maps has been developed. PHASER is a series of Fortran programs which help to solve such crystal structures by refining the phases.

These poorly phased crystal structures may be obtained in several ways. An electron density map could be obtained though use of direct methods that does not contain a large enough portion of the structure to enable the remainder of the structure to be discovered. The location of one or more heavy atoms might have been determined by analyzing the Patterson map, but the heavy atom(s) might not be sufficiently heavy to phase the remainder of the structure. A Patterson superposition could be performed, but result in a map which

contains a large number of auxiliary peaks which make interpretation difficult. Any of these cases are candidates for this method.

Procedure

A flowchart summarizing the steps used in PHASER is shown in Figure 3.1. After a trial structure is obtained, PHASER proceeds as follows: A Fourier transform is computed based on the trial structure. This transform yields an electron density map with its coefficients $G_{\vec{h}}$. If a reverse Fourier transform

were to be performed on these $G_{\vec{h}}/s$ then the original structure

factors and phases would be obtained. Therefore, we modify the transform process in two ways. First, the original electron density map is modified before the reverse transform is performed. Several assumptions can be made which lead to these modifications of the map. Physically, the electron density map must be non-negative everywhere:

 $\rho(x, y, z) \ge 0.$ (22)

If we assume that only values above a certain height are significant, we can set all points below this threshold to zero. This truncated electron density map should yield a





better representation of the structure, as all of the negative regions and low-lying features have been removed.

When a reverse transform is performed on the truncated electron density map, calculated structure factors and their phases are obtained. We make a second assumption that a better electron density map will be produced by using the observed magnitudes of the structure factors combined with the phases calculated in the reverse transform in order to obtain the new electron density map.

Another cycle of phase refinement is begun by applying a threshold to this new electron density map, then performing a reverse transform calculation on the truncated map. This process is repeated until convergence is reached. In test cases which are discussed below, the use of PHASER generated electron density maps where more of the atoms in the structure could be located and less extraneous peaks were observed.

Details

For some structures, direct methods and Patterson methods work quickly and refine very well to the final structure. However, there are other structures where such procedures do not readily give a solution. It is these "difficult" crystal structures to which this program is directed. If PHASER is to be successful, it should start with an initial model of the

structure or a superposition map and then refine the phases to create a new model of the structure that is much more complete than the starting one. In my test cases, it did just that.

In these trials the starting model of the molecule only contained a small number of the atoms contained in the complete structure. The starting model generally contained less than a quarter of the scattering power of the full structure which indicates the potential of this approach.

Calculation of the electron density map"

The observed structure factor magnitudes and the phases determined in the starting model of the structure are used to calculate an electron density map using the equation:

$$\rho(x_1, x_2, x_3) = \frac{k}{V} \sum_{h_1 = -\infty}^{\infty} \sum_{h_2 = -\infty}^{\infty} \sum_{h_3 = -\infty}^{\infty} F(h_1, h_2, h_3) e^{-2\pi i (h_1 x_1 + h_2 x_2 + h_3 x_3)}$$
(23)

where k is a scale factor and V is the volume of the unit cell. ALFTS, the Ames Lab Fourier Transform Superposition program, is used for computation of the electron density maps. ALFTS is a Fortran program for computation of threedimensional Patterson and electron density maps, as well as for computation of Patterson superposition maps. ALFTS efficiently calculates these maps from an averaged data set. ALFTS was based in part on earlier FFT programs written by this group.12,13

If the x_1 direction is across the page, the x_2 direction is down the page, and x_3 is the section direction, one can write

$$\rho(x_1, x_2, x_3) = \frac{k}{V} \sum_{h_1 = -\infty}^{\infty} \sum_{h_2 = -\infty}^{\infty} \left[\sum_{h_3 = -\infty}^{\infty} F(h_1, h_2, h_3) e^{-2\pi i h_3 x_3} \right] e^{-2\pi i (h_1 x_1 + h_2 x_2)} .$$
(24)

If the summation is performed over h_3 , the equation will yield

$$\rho(x_1, x_2, x_3) = \frac{k}{V} \sum_{h_1 = -\infty}^{\infty} \sum_{h_2 = -\infty}^{\infty} (R_{h_1 h_2 x_3} + i S_{h_1 h_2 x_3}) e^{-2\pi i (h_1 x_1 + h_2 x_2)}.$$
 (25)

The trigonometric factoring described in Equations 24 and 25 is advantageous because one only has to involve those terms representing non-zero values. If a three-dimensional fast Fourier transform (FFT) were used a large number of array elements would have to be padded with zeros. A two-dimensional array composed of the $R_{h_1h_2x_3}$ and $S_{h_1h_2x_3}$ is next passed to a twodimensional FFT subroutine. This subroutine uses a combination of base 4 and base 2 transform for fast execution.

The electron density function to be calculated is real; use is made of this fact to reduce execution time even further. In other words, the imaginary part of the FFT result would be expected to be zero as long as Friedel-related coefficients have been used in constructing the arrays. A new function can then be constructed:

$$\rho' = \rho(x_3^{(1)}) + i\rho(x_3^{(2)})$$
(26)

where $x_3^{(1)}$ and $x_3^{(2)}$ refer to the two different values of the x_3 section variable. Use of this function further reduces the number of transforms that need to be calculated (by approximately one-half) by calculating two sections at once. $X_3^{(1)}$ and $x_3^{(2)}$ are selected in the program to be adjacent sections; thus the transforms for sections 0 and 1 are done simultaneously, as are sections 2 and 3, etc.

To calculate ρ' , the coefficients of the array must be formed by

$$R_{h_1h_2} = R_{h_1h_2x_3}^{(1)} + S_{h_1h_2x_3}^{(2)}$$

$$S_{h_1h_2} = S_{h_1h_2x_3}^{(1)} + R_{h_1h_2x_3}^{(2)}$$
(27)

In addition, forming the coefficients in this way halves the number of passes that need to be made through the data file. Now for every hkl its contribution to $R_{h_1h_2x_3}^{(1)}$, $R_{h_1h_2x_3}^{(2)}$, $S_{h_1h_2x_3}^{(1)}$, and $S_{h_1h_2x_3}^{(2)}$ can all be calculated and added to the array.

With this algorithm no sorting of the data is necessary. The grid sizes are restricted to be 16, 32, 64, or 128. Therefore a sin-cos table-lookup is used in the formation of the R and S values.

Computation of the reverse transform¹¹

The electron density map is reverse transformed using a threshold to produce calculated structure factors and phases. The reverse transforms are also computed using ALFTS. A cutoff or threshold is used, so that all values in the electron density map below the cutoff are set at zero in the calculation of the reverse transform.

In the calculation of the reverse transform, as in the case of the regular transform, a combination of trigonometric factoring and use of a two-dimensional fast Fourier algorithm is employed,

$$F(h_1, h_2, h_3) = \sum_{u_1} \sum_{u_2} \left[\sum_{u_3} M(u_1, u_2, u_3) e^{2\pi i h_3 u_3} \right] e^{2\pi i (h_1 u_1 + h_2 u_2)}$$

=
$$\sum_{u_1} \sum_{u_2} M'(u_1, u_2, h_3) e^{2\pi i (h_1 u_1 + h_2 u_2)}$$
 (28)

where $M(u_1, u_2, u_3)$ is real and $M'(u_1, u_2, h_3)$ is complex. Values of $F(h_1, h_2, h_3)$ are calculated for data equivalent to the $\pm h_1$, $\pm h_2$, $\pm h_3$ hemisphere. If $M(u_1, u_2, u_3)$ has a center of symmetry at the origin, then only the first half of the map is used for the calculation of F.

Use of a threshold in the reverse transform

Use of a threshold in the computation of the reverse transform is based primarily on the fact that physically the electron density must be non-negative at every point: $\rho(x, y, z) \ge 0.$ (29)

Removing the negative points in the electron density map and setting them to zero ensures that this condition is satisfied, producing a more realistic map. In addition the phase of a strong reflection is more reliable than the phase of a weak reflection. Weak reflections are more likely to give rise to ripples in the map. The use of a cutoff tends to remove some of these effects, further strengthening the reverse transform process.

The data are also sharpened. Strong, sharpened high angle reflections are often much smaller in |F| than many reflections at low sin θ/λ . When the effect of the decrease in |F| with sin θ/λ is removed, the relative intensities of the reflections can be judged more accurately.

Determination of the cutoff

The cutoff used in the reverse transform is determined by multiplying a fraction by the largest negative value found in the electron density map. For light atom structures, a starting fraction of 1.00 is used, whereas for heavy atom structures, a starting fraction of 0.50 is preferred. Since

the electron density map improves with each cycle of phase refinement, the cutoff is lowered (decreased) in each successive cycle. This allows more of the electron density map to be used in the reverse transform calculation. The starting fraction is decremented by 0.05 in every cycle.

The starting fractions indicated above were determined from the results of many test calculations. Although the starting fractions used by the author for both light and heavy atom structures have been optimized for these cases, use of other reasonable starting fractions does not appear to prevent phase refinement. However, use of a different starting fraction other than those recommended does seem to slow the convergence of the phase refinement process.

Evaluation of the calculated structure factors and phases

The reverse transform generates new structure factors and phases. The reliability of the calculated phases is judged by the agreement of the magnitude of the calculated structure factors with those of the observed structure factors.

(Although the reflection data need not be sorted for the calculation of the electron density map or the reverse transform, at this point during the first cycle the data are sorted to allow efficient comparison of the structure factors and their phases obtained from the reverse transform with the original structure factors. A flag is set after the data are

sorted during the first cycle; in later cycles the sorting is not repeated.)

Determination of convergence of the process

This procedure is repeated, slightly lowering the threshold at each step, until convergence is reached. Convergence can be determined by the minimum in the largest positive value (LPV) in the electron density map or by the minimum in the residual. The residual is calculated by using:

$$R = \frac{\sum ||F_{o}| - |F_{c}||}{\sum |F_{o}|},$$
 (30)

where $|F_o|$ is the observed structure factor magnitude and $|F_c|$ is the magnitude of the structure factor calculated in the reverse transform. In most cases, the minimum of the LPV was separated no more than several cycles from the minimum in the residual. The electron density maps at the two minima show very slight differences.

CHAPTER 4. PRACTICAL APPLICATIONS OF PHASER

A variety of structures were chosen for phase refinement by PHASER. Some of the structures contain heavy atoms, while others contain no atoms heavier than sulfur or phosphorus. Several of these structures required considerable effort to solve initially by other methods. The strength of this approach is illustrated by the fact that in all of the trials only one or two atoms were included in the starting model. These initial models contained only a small fraction of the scattering power of the full molecule.

PHASER Solution of C29H26OPRuSeBF414

The first test compound was a heavy atom structure. The ruthenium atom in $C_{29}H_{26}OPRuSeBF_4$ contains more than one-third of the scattering power of the full molecule and is therefore likely to phase the structure well enough to allow the remainder of the atoms to be located by successive structure factor and electron density map calculations. Since this starting model should lead to a successful structure solution, this compound provided a simple first test to determine whether the program could refine the phases of a reasonably well-phased initial model.

Experimental data

A colorless crystal of $C_{29}H_{26}OPRuSeBF_4$ provided by Robert Angelici's group (Department of Chemistry, Iowa State University) having approximate dimensions of 0.120 x 0.180 x 0.080 mm was mounted on a glass fiber. Data collection measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo K α radiation and a 12KW rotating anode generator.

By using the setting angles of 25 carefully centered reflections in the range 25.56 < 2θ < 30.05° , the crystal was found to have formed in the triclinic system with cell constants of a = 10.594(2) Å, b = 14.276(2) Å, c = 9.402(2) Å, α = $97.97(2)^{\circ}$, β = $91.63(2)^{\circ}$, γ = $87.47(1)^{\circ}$, and a volume of 1406.5(8) Å. Complete experimental details are listed in Table 4.1.

Conventional structure solution

Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\overline{1}$.

The structure was originally solved by Patterson methods. The positions of the Ru, P, and Se atoms were determined by interpretation of the Patterson map. All remaining nonhydrogen atoms were found from a difference electron density

Table 4.1. Crystal and data collection parameters for $C_{29}H_{26}OPRuSeBF_{4}$

Experimental Details Empirical Formula C₂₉H₂₆OPRuSeBF₄ Formula Weight 688.23 Crystal Dimensions (mm) $0.120 \times 0.180 \times 0.080$ Crystal Color, Habit colorless, globular Crystal System triclinic Lattice Parameters: a = 10.594(2) Å 14.276(2) Å b = c = 9.402(2) Å 97.97(2)[°] 91.63(2)[°] 87.47(1)[°] $\alpha =$ B = γ = $V = 1406.5(8) Å^3$ Cell Determining Reflections: number, range (2θ) $25 (25.6 - 30.0^{\circ})$ Space Group **P1** Z 4 Density, calculated 1.457 g/cm^3 Absorption coefficient, $\mu_{(HoKa)}$ 36.89 cm⁻¹ Diffractometer Rigaku AFC6R Mo K α (λ = 0.71069 Å) 23°C Radiation Temperature Scan Type ω-2θ 50.1° $2\theta_{max}$ **Reflections Measured** Total: 5255 Unique: 4960 Reflections Observed $(I>4\sigma(I))$ 1702 Parameters Refined 343 Reflection/Parameter Ratio 4.96 Corrections Lorentz-polarization Absorption (trans. factors: 0.85 -1.00) Decay (0.41% decline) Structure Solution Patterson Method Refinement Full-matrix least-squares $4F_{\circ}^{2}/\sigma^{2}(F_{\circ}^{2})$ Least-squares Weights Residuals: R^{*}; R^{*} 0.051; 0.054 Goodness of Fit Indicator 1.46 0.66 $e^{-}/Å^{3}$ Maximum Peak in Final Diff. Map Minimum Peak in Final Diff. Map $-0.88 \text{ e}^{-}/\text{Å}^{3}$

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|.$ ${}^{b}R_{w} = [\Sigma W(|F_{o}| - |F_{c}|)^{2}/\Sigma W |F_{o}|^{2}]^{1/2}, W = 1/\sigma^{2}(|F_{o}|).$

map. Refinement of the complete structure led to a R-factor of 5.1%. An ORTEP drawing¹⁵ of $C_{29}H_{26}OPRuSeBF_4$ is given in Figure 4.1.

Phase refinement using PHASER

The position of the ruthenium atom, determined from a Patterson map, was input to a structure factor calculation to determine the phases for the starting electron density map. Since, as noted above, the ruthenium atom comprises thirtyeight percent of the scattering power of the full molecule, it was expected to phase the structure quite well. However the starting model contained significantly less of the scattering power of the full structure than the trial model which was used when the structure was solved by conventional methods. Following the initial electron density map calculation the positions of 24 of the 38 non-hydrogen atoms in the structure could be located in the 100 largest peaks of the electron density map. After 16 cycles of phase refinement six additional atoms could be located in the 100 largest peaks. In addition to being able to locate more atoms in the refined electron density map, the atom positions were more readily located in the final map as the peaks due to atom positions were enhanced compared to extraneous peaks.



Figure 4.1. ORTEP drawing of $C_{29}H_{26}OPRuSeBF_4$. The ellipsoids are drawn at the 50% probability level.

PHASER Solution of PH[MeNCH₂CH₂]₃N⁺Cl⁻•2CHCl₃

The second test case chosen for solution with PHASER was a light atom compound. As the phosphorus atom in PH[MeNCH₂CH₂]₃N⁺Cl⁻·2CHCl₃ contained less than ten percent of the scattering power of the full molecule, this case was a more challenging test than the first test case; a light atom will correctly phase many fewer reflections as compared to a heavy atom.

Experimental data

A colorless rectangular crystal of $PH[MeNCH_2CH_2]_3N^*Cl^-$ •2CHCl₃ provided by John Verkade's group (Iowa State University, Department of Chemistry) having approximate dimensions of 0.280 x 0.240 x 0.340 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo K α radiation and a 12KW rotating anode generator.

By using the setting angles of 25 carefully centered reflections in the range 34.01 < 20 < 34.99°, the crystal was found to have formed in the triclinic system with dimensions: a = 10.847(3) Å, b = 10.890(5) Å, c = 10.684(5) Å, $\alpha =$ 116.74(3)°, $\beta = 98.65(3)$ °, $\gamma = 85.06(3)$ °, and a volume of 1114.0(8) Å³. Complete experimental details are listed in Table 4.2.

Table 4.2. Crystal and data collection parameters for $PH[NCH_3CH_2CH_2]_3N^+Cl^- \cdot 2CHCl_3$

Experimental Details PC17N4C8H24 Empirical Formula Formula Weight 491.48 colorless, rectangular 0.280 x 0.240 x 0.340 Crystal Color, Habit Crystal Dimensions (mm) Crystal System triclinic Lattice Parameters: a = 10.847(3) Å b = 10.890(5) Å c = 10.684(5) Å $\alpha = 116.74(3)$ $\beta = 98.65(3)$ $\gamma = 85.06(3)^{\circ}$ $V = 1114.0(8) Å^3$ Cell-Determining Reflections: $25 (34.0 - 35.0^{\circ})$ number, range (2θ) Space Group **P1** Z 2 Density, calculated 1.465 g/cm^3 Absorption Coefficient, $\mu_{(MOKe)}$ 9.71 Cm_1 Rigaku AFC6R Diffractometer Radiation MoK α (λ = 0.71069 Å) 23°C Temperature Scan Type ω-20 50.1° $2\Theta_{max}$ Reflections Measured **Total: 4168** Unique: 3938 Corrections Lorentz-polarization Absorption (trans. factors: 0.95 -1.00) Decay (-15.00% decline) Direct Methods Structure Solution Refinement Full-matrix least-squares Least-squares Weights $4F_{o}^{2}/v^{2}(F_{o}^{2})$ Reflections Observed $(I > 3\sigma(I))$ 1771 Parameters Refined 304 Reflection/Parameter Ratio 5.83 Residuals: R^a; R^b 0.050; 0.052 Goodness of Fit Indicator 1.69 0.39 $e^{-}/Å^{3}$ Maximum Peak in Final Diff. Map Minimum Peak in Final Diff. Map $-0.38 \text{ e}^{-}/\text{Å}^{3}$

 ${}^{\mathbf{a}}\mathbf{R} = \Sigma ||\mathbf{F}_{o}| - |\mathbf{F}_{c}||/\Sigma |\mathbf{F}_{o}|.$ ${}^{\mathbf{b}}\mathbf{R}_{w} = [\Sigma w(|\mathbf{F}_{o}| - |\mathbf{F}_{c}|)^{2}/\Sigma w |\mathbf{F}_{o}|^{2}]^{1/2}, w = 1/\sigma^{2}(|\mathbf{F}_{o}|).$

Conventional structure solution

Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be P1. The structure was solved by direct methods.^{16,27} Refinement of the complete structure led to a residual of 5.0%. An ORTEP drawing¹⁵ of PH[MeNCH₂CH₂]₃N⁺Cl⁻·2CHCl₃ is shown in Figure 4.2.

Phase refinement using PHASER

The phosphorus atom, which contains only eight percent of the scattering power of the full molecule, was located by Patterson methods and input into a structure factor calculation to determine the phases for the starting electron density map. Following the initial electron density map calculation, the positions of 15 of the 23 non-hydrogen atoms in the structure could be located in the 50 largest peaks of the electron density map. After 21 cycles of phase refinement all of the non-hydrogen atoms and their symmetry partners (46 total) could be located in the 46 largest peaks without any intervening peaks due to noise.



CLI

Figure 4.2. ORTEP of $PH[NCH_3CH_2CH_2]_3N^+Cl^- \cdot 2CHCl_3$. The ellipsoids are drawn at the 50% probability level.

PHASER Solution of [NiO₂N₈C₅₆H₅₂]₂Pd(ClO₄)₂•8HCCl₃¹⁷

The $[NiO_2N_8C_{56}H_{52}]_2Pd(ClO_4)_2 \cdot 8HCCl_3$ crystal provided the most difficult test of PHASER yet. Eighty-nine non-hydrogen atoms are present in the asymmetric unit and therefore many more atom positions must be located in the electron density map.

Experimental data

A purple platelet crystal of $[NiO_2N_8C_{56}H_{52}]_2Pd(ClO_4)_2 \cdot 8HCCl_3$ provided by Keith Woo's group (Iowa State University, Department of Chemistry) having approximate dimensions of 0.360 x 0.360 x 0.100 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo K α radiation and a 12KW rotating anode generator.

By using the setting angles of 17 carefully centered reflections in the range $12.49 < 2\theta < 15.23^{\circ}$, the crystal was found to have formed in the monoclinic system with dimensions: a = 14.378(7) Å, b = 23.413(6) Å, c = 21.140(6) Å, B = $105.30(3)^{\circ}$, and a volume of 6865(4) Å³. Complete experimental details are listed in Table 4.3.

Table 4.3. Crystal and data collection parameters for $[NiO_2N_8C_{56}H_{52}]_2Pd(ClO_4)_2 \cdot 8HCCl_3$

Experimental Details Empirical Formula Ni₂O₁₂N₁₆C₁₂₀H₁₁₂PdCl₂₆ Formula Weight 2887.21 Crystal Dimensions (mm) $0.360 \times 0.360 \times 0.100$ Crystal Color, Habit purple, platelet monoclinic Crystal System Lattice Parameters: a = 14.378(7) Å b =23.413(6) Å c = 21.140(6) Å B = 105.30(3) $V = 6865(4) Å^{3}$ Cell Determining Reflections: $17 (12.5 - 15.2^{\circ})$ number, range (2θ) Space Group $P2_1/n$ Z 2 Density, calculated 1.397 g/cm^3 Absorption coefficient, $\mu_{(MoKg)}$ 8.51 Cm⁻¹ Diffractometer Rigaku AFC6R Radiation MoK α (λ = 0.71069 Å) -50°C Temperature Scan Type ω 50.1° 20max Reflections Measured Total: 21343 Unique: 10377 Reflections Observed $(I>3\sigma(I))$ 3273 Parameters Refined 429 Reflection/Parameter Ratio 7.63 Corrections Lorentz-polarization Absorption (trans. factors: 0.91 -1.00) Decay (-10.00% decline) Structure Solution Patterson Method Full-matrix least-squares Refinement Least-squares Weights $4F_{o}^{2}/\sigma^{2}(F_{o}^{2})$ Residuals: R*; R,^b 0.083; 0.090 Goodness of Fit Indicator 2.58 Maximum Peak in Final Diff. Map 0.82 $e^{-}/Å^{3}$ Minimum Peak in Final Diff. Map $-0.62 e^{-}/Å^{3}$

 ${}^{*}R = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|.$ ${}^{b}R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma w |F_{o}|^{2}]^{1/2}, w = 1/\sigma^{2}(|F_{o}|).$

Conventional structure solution

Based on the systematic absences of:

h01: h+l \neq 2n

 $0k0: k \neq 2n$

and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$.

Solving such a large crystal structure can be complicated by the difficulty of determining whether a peak truly forms a part of the structure. In many structure determinations it is a routine task to determine whether a peak has the proper bond distance and bond angles to the adjacent atoms in the structure which have already been determined, and whether its position makes chemical sense. However in such a large structure, the adjacent atoms may not have been found and the peak in question may not even have second-nearest-neighbors whose positions are known.

Conventional methods of structure determination were not successful on this structure due to its large size and the difficulty of building a trial structure with such a large planar molecule. The structure was solved by Patterson methods, but the structure determination could not be completed without modifications being made to the usual procedures.

First, the palladium and nickel positions were determined from a Patterson map. A superposition was performed using a

Pd-Ni vector and the resulting peaks were analyzed to determine which peaks had all of the necessary symmetry partners, so that extraneous peaks could be removed from further consideration. Next, least-squares refinement was performed using the positions of the palladium and nickel atoms and the highest 32 symmetry-unique peaks from a superposition map. Finally, remaining non-hydrogen atom positions were determined from successive structure factor and electron density map calculations.

Solvent molecule positions and thermal parameters were not well determined. Poor data quality and a fairly high degree of libration/disorder exhibited by the solvent molecules contributed to this problem. Reasonable solvent atom positions were located in difference maps, but on refinement the atoms had shifted from their original positions and possessed fairly large temperature factors. However, when the solvent atoms were removed from the refinement, peaks did reappear in Fourier difference maps in these general positions. Fortunately, the atoms in the porphyrin molecule are quite well-behaved and do not appear to be significantly affected by the positions used for the solvent.

The palladium, nickel, and chlorine atoms along with most of the lighter atoms were refined anisotropically. Refinement of the complete structure led to a R-factor of 8.3%. The relatively high residual can be attributed to the size of the

molecule, lack of sufficient data, and solvent disorder. An ORTEP drawing¹⁵ of $[NiO_2N_8C_{56}H_{52}]_2Pd(ClO_4)_2 \cdot 8HCCl_3$ is shown in Figure 4.3.

Phase refinement using PHASER

The position of the nickel atom, determined from a Patterson map, was input to a structure factor calculation to determine the phases for the starting electron density map. The nickel atom comprised only five percent of the scattering power of the full molecule. However this starting point produced very good phase refinement results.

Forty-two of the 89 non-hydrogen atoms in the structure could be located in the starting electron density map. Figure 4.4 displays the asymmetric unit, half of the molecule, with the atoms found in the initial electron density map drawn as solid. It should be noted that a number of extraneous (noise) peaks were also present which are not shown in the figure. After 24 cycles of phase refinement 60 of the 89 non-hydrogen atoms could be located in the electron density map (Figure 4.5).

As analysis of the Patterson map readily yielded the positions of both the nickel and palladium atoms, a second trial was performed using the positions of both heavy atoms. In this trial 61 non-hydrogen atoms could be located in the original electron density map. After 14 cycles of phase



Figure 4.3. ORTEP of $[NiO_2N_8C_{56}H_{52}]_2Pd(ClO_4)_2 \cdot 8HCCl_3$. The ellipsoids are drawn at the 30% probability level.



Figure 4.4. A view of the asymmetric unit of the $[NiO_2N_sC_{56}H_{52}]_2Pd(ClO_4)_2\cdot 8HCCl_3$ structure. Solid atoms indicate those atoms found in the initial electron density map. The ellipsoids are drawn at the 50% probability level.



Figure 4.5. A view of the asymmetric unit of the $[NiO_2N_8C_{56}H_{52}]_2Pd(ClO_4)_2 \cdot 8HCCl_3$ structure. Solid atoms indicate those atoms found in the refined electron density map. The ellipsoids are drawn at the 50% probability level.

refinement 68 of the 89 atoms were present in the electron density map.

The NiPdNi test case demonstrates one situation where this method is not appropriate. When both nickel and palladium were included in the starting model, less improvement was seen than when the nickel position was used alone. When the starting model yields an electron density map where almost all of the atoms can be located, use of PHASER may not yield significant improvement without some modifications to the method.

Conclusions

From these test cases, it can be seen that PHASER is a valuable tool in refining poorly phased electron density maps. It has been used to refine the phases of compounds with starting models that comprise between five and thirty-eight percent of the scattering power. It is most useful in the beginning stages of a structure determination when a significant portion of the structure is undetermined. In the final stages of a structure determination, the improvement yielded by PHASER may be minimal.

Either the largest positive value (LPV) in the electron density map or the residual can be used to determine convergence. In most cases, the minimum of the LPV was

separated at most by several cycles from the minimum in the residual. The differences in the electron density maps at the two minimums are usually minor. The value of the starting cutoff impacts the speed of refinement but does not prevent convergence.

The time required to perform phase refinement using PHASER is markedly reduced from the time needed to solve a crystal structure using other methods - only 25 minutes were needed for the $[NiO_2N_8C_{56}H_{52}]_2Pd(ClO_4)_2 \cdot 8HCCl_3$ phase refinement as compared to a month for the original structure determination. For the smaller crystal structures, phase refinement took only five to ten minutes.

PART II. CRYSTAL STRUCTURE DETERMINATIONS

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CHAPTER 5. SELECTED CRYSTAL STRUCTURE DETERMINATIONS

In addition to the development of PHASER described in the first part of this thesis, the author has completed a number of crystallographic structure determinations. Several of these will be discussed in this section.

Crystal Structure Determination of PtCuCl₂N₈O₂C₅₆H₅₂¹⁸

Interest in multinuclear transition-metal complexes such as PtCuCl₂N₆O₂C₅₆H₅₂, can be attributed to several reasons. They have been studied as active-site models of enzymes such as Factor 430¹⁹ whose functions are believed to require the presence of more than one metal.²⁰ The mutual interaction of two or more metal centers creates possibilities of special chemical and physical properties.²¹ Development of potential new catalysts provides another rationale for research in this area.¹⁸

A critical component of the synthesis of multinuclear transition-metal complexes is the design of the ligand. The ligand involved in a binuclear metal system must have two binding sites which place the metals in close proximity. This consideration along with the ability to vary the structure of the complex by binding different metals and changing the metal-metal separations from one system to the next led to the

use of porphyrins as the foundation of the binucleating ligand systems developed by Dr. Keith Woo's research group at Iowa State.¹⁸

A crystal structure determination provides an accurate characterization of the solid state configuration, and likely solution configuration, of the compound to the synthetic research group. Particularly in cases with molecules as large and complex as this, it is difficult to find other molecular structure techniques that can yield much detailed information. Solid evidence for the binding of the second metal atom to the porphyrin's ligating arms is also available from a single crystal x-ray structure determination.

Data collection

A purple platelet crystal of $PtCuCl_2N_8O_2C_{56}H_{52}$ provided by Keith Woo's group (Iowa State University) having approximate dimensions of 0.240 x 0.030 x 0.440 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated MoK α radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 15 carefully centered reflections in the range $12.80 < 20 < 15.09^{\circ}$ corresponded to a triclinic cell with dimensions:

$$a = 19.3333(8)$$
Å $\alpha = 103.28(4)^{\circ}$ $b = 23.74(1)$ Å $\beta = 108.29(3)^{\circ}$ $c = 12.984(5)$ Å $\gamma = 76.47(3)^{\circ}$ $V = 5422(4)$ Å

For Z = 4 and F.W. = 1198.62, the calculated density is 1.468 g/cm³. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P1 (#2)

The data were collected at a temperature of $23 \pm 1^{\circ}$ C using the ω -20 scan technique to a maximum 20 value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.67° with a take-off angle of 6.0°. Scans of (1.63 + 0.30 tan 0)° were made at a speed of 16.0°/min (in omega). The weak reflections (I < 10.0 σ (I)) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Data reduction

Of the 19697 reflections which were collected, 19072 were unique ($R_{int} = .136$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for MoK α is 31.4 cm⁻¹. Azimuthal scans of several reflections indicated no need for an absorption correction.

Structure solution and refinement

Structure determination was made more difficult by the presence of two molecules in the asymmetric unit. Positions of non-hydrogen atoms were determined in the following manner. First, platinum, copper, and chlorine positions were determined from a Patterson superposition using a platinumplatinum vector. Next, least-squares refinement was performed using the positions of platinum, copper, and chlorine atoms and the highest 129 symmetry-unique peaks from the superposition. Finally, remaining non-hydrogen atom positions were determined from successive structure factor and electron density map calculations.

Hydrogen atom positions were calculated. Non-hydrogen atoms were refined either anisotropically or isotropically.
The final cycle of full-matrix least-squares refinement was based on 4114 observed reflections (I > $3.00\sigma(I)$) and 719 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \sum ||Fo| - |Fc|| / \sum |Fo| = 0.073$$

$$R_{w} = \left[\left(\sum w(|Fo| - |Fc|)^{2} / \sum wFo^{2} \right) \right]^{1/2} = 0.085$$

Twenty-eight reflections under 5° 20 were deleted due to beam stop shadow effects; their background counts were highly asymmetric. Plots of $\Sigma \approx (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ , and various classes of indices showed no unusual trends.

All calculations were performed using the CHES²² crystallographic software package. Complete experimental details are listed in Table 5.1.

Structural Details of the PtCuCl_N.O.C., H., Compound

As mentioned above, the asymmetric unit of this compound contains two molecules. An ORTEP¹⁵ drawing for molecule A is given in Figure 5.1. Molecule B is numbered similarly, except Cl1 and Cl2 have been interchanged. The relationship between molecules A and B is shown in Figure 5.2. Final positional parameters for the non-hydrogen atoms are given in Table 5.2 and Tables 5.3 and 5.4 give bond distances and angles.

The porphyrinato core of the molecule is distorted from planarity and approximates S. symmetry. A slight S. distortion

Table 5.1. Crystal and data collection parameters for $PtCuCl_2N_8O_2C_{s6}H_{s2}$

Experimental	Details
Empirical Formula	PtCuCl ₂ N ₈ O ₂ C ₅₆ H ₅₂
Formula Weight	1198.62
Crystal Dimensions (mm)	$0.240 \times 0.030 \times 0.440$
Crystal Color, Habit	purple, platelet
Crystal System	triclinic
Lattice Parameters:	
	a = 19.333(8) Å
	b = 23.74(1) Å
	c = 12.984(5) Å
	$\alpha = 103.28(4)^{\circ}$
	$B = 108.29(3)^{\circ}$
	$\gamma = 76.47(3)^{\circ}$
	$V = 5422(4) Å^3$
Cell Determining Reflections:	
number, range (20)	$15 (12.8 - 15.1^{\circ})$
Space Group	P1 (#2)
z	4
Density, calculated	1.468 q/cm^3
Absorption coefficient, $\mu_{(MoKg)}$	31.42 cm^{-1}
Diffractometer	Rigaku AFC6R
Radiation	MoKa ($\lambda = 0.71069$ Å)
Temperature	23°C
Scan Type	ω - 2 0
20 _{max}	50.1°
Reflections Measured	Total: 19697
	Unique: $19072 (R_{int} = .136)$
Reflections Observed $(I>3.00\sigma(I))$	4114
Parameters Refined	719
Reflection/Parameter Ratio	5.72
Corrections	None
Structure Solution	Patterson Method
Refinement	Full-matrix least-squares
Least-squares Weights	$4F_{o}^{2}/\sigma^{2}(F_{o}^{2})$
Residuals: R^* ; R_{μ}^5	0.073; 0.085

 ${}^{a}R= \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|.$ ${}^{b}R_{w}= [\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma w |F_{o}|^{2}]^{1/2}, w=1/\sigma^{2}(|F_{o}|).$

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Figure 5.1. ORTEP drawing of $PtCuCl_2N_8O_2C_{56}H_{52}$. The ellipsoids are drawn at the 50% probability level.



Figure 5.2. Asymmetric unit of PtCuCl₂N₈O₂C₅₆H₅₂

Atom	x	У	2
PT1A	0.8077(1)	0.78326(7)	0.5974(1)
PT1B	0.3344(1)	0.20635(7)	0.2531(1)
CU1A	0.0178(2)	0.1155(2)	0.0381(3)
CU1B	0.4174(3)	0.3934(2)	0.5697(3)
CL1A	0.7394(7)	0.7445(5)	0.4334(8)
CL1B	0.3789(7)	0.2844(4)	0.3759(9)
CL2A	0.8867(6)	0.8216(4)	0.7564(9)
CL2B	0.2987(7)	0.1290(4)	0.1217(8)
N1A	0.036(2)	-0.188(1)	0.020(2)
N1B	0.342(1)	0.458(1)	0.505(2)
N2A	0.086(1)	0.094(1)	-0.059(2)
N2B	0.356(1)	0.392(1)	-0.331(2)
N3A	0.935(1)	0.961(1)	0.906(2)
N3B	0.494(2)	0.334(1)	-0.358(2)
N4A	0.046(1)	0.140(1)	0.141(2)
N4B	0.478(2)	0.390(1)	0.471(2)
N5A	0.708(1)	0.001(1)	-0.176(2)
N5B	0.425(2)	0.192(1)	-0.303(2)
N6A	0.082(2)	0.660(1)	-0.212(2)
N6B	0.300(2)	0.424(1)	0.154(2)
N7A	0.239(1)	0.133(1)	0.423(2)
N7B	0.593(2)	-0.155(1)	-0.350(3)
N8A	0.148(2)	0.298(1)	0.380(2)
N8B	0.256(2)	0.259(1)	0.158(2)
OIA	0.347(1)	-0.060(1)	0.305(2)
OIB	0.531(2)	-0.092(1)	0.298(2)
02A	1.076(2)	0.566(1)	0.705(3)
028	0.193(2)	0.442(1)	0.029(2)
	0.095(2)	0.700(2)	-0.005(3)
CIB	0.337(2)	0.460(1) 0.272(1)	
C2A	0.123(2)	0.2/3(1)	
	0.2/9(2)	0.055(2)	-0.142(3)
CIA	0.070(2)	0.250(1) 0.541(1)	
	0.244(2) 0.022(2)	-0.202(2)	0.401(3)
CAR	0.022(2)	-0.202(2) 0.491(1)	0.538(3)
C4B C53	0.203(2)	0.491(1) 0.828(1)	1 159(3)
C5R	0.261(2)	0.475(1)	-0.379(3)
C63	0.906(2)	0.871(1)	1,125(3)
C6B	0.294(2)	0.427(2)	0.674(3)
C7A	0.849(2)	0.894(2)	1,175(3)
C7B	0.254(2)	0.408(1)	-0.260(3)
C8A	0.809(2)	0.937(2)	1.125(3)
C8B	0.309(2)	0.363(2)	0.777(3)

.

Table 5.2. Positional parameters for $PtCuCl_2N_8O_2C_{56}H_{52}$

Atom	x	У	2
C9A	0.145(2)	0.053(1)	-0.058(3)
C9B	0.630(2)	0.647(1)	0.260(2)
C10A	0.163(2)	0.002(1)	-0.001(2)
C10B	0.437(2)	0.314(2)	0.771(3)
C11A	0.885(2)	1.003(1)	0.932(2)
CllB	0.494(2)	0.303(2)	-0.271(3)
C12A	0.868(2)	1.055(1)	0.876(3)
C12B	0.565(2)	0.263(2)	0.754(3)
C13A	-0.089(2)	0.038(1)	-0.188(3)
C13B	0.388(2)	0.735(2)	0.305(3)
C14A	0.047(2)	0.020(1)	0.177(2)
C14B	0.560(2)	0.310(2)	0.627(3)
C15A	0.001(2)	-0.054(1)	-0.231(3)
C15B	0.418(2)	0.678(2)	0.461(3)
C16A	0.039(2)	-0.111(2)	-0.224(3)
C16B	0.541(2)	0.359(2)	0.466(3)
C17A	1.078(2)	0.852(1)	0.703(3)
C17B	0.569(2)	0.361(2)	0.374(3)
C18A	0.111(2)	-0.200(2)	-0.266(3)
C18B	0.482(2)	0.595(2)	-0.325(3)
C19A	0.092(1)	-0.192(1)	-0.162(2)
C19B	0.456(2)	0.424(1)	0.383(3)
C20A	-0.121(2)	0.237(1)	0.097(3)
C20B	0.607(2)	0.532(1)	-0.363(3)
C21A	-0.183(2)	0.325(2)	-0.086(3)
C21B	0.254(2)	0.575(2)	0.327(3)
C22A	0.081(2)	0.723(2)	0.252(3)
C22B	-0.183(2)	0.417(2)	0.494(3)
C23A	-0.052(7)	0.314(5)	-0.24(1)
C23B	0.118(3)	0.566(2)	0.440(4)
C24A	0.168(2)	0.140(1)	-0.253(3)
C24B	0.182(2)	0.435(2)	-0.255(3)
C25A C25A	0.216(3)	0.1/9(2)	-0.184(4)
	0.119(3)	0.405(2)	
CZ6A CD6B	0.739(3)	0.900(2)	$1 \cdot 141(4)$
C20B	0.719(2)	0.075(2)	0.108(3)
C27A	0.105(2)	-0.113(1)	0.100(3)
C27D	0.596(2)	-0.066(2)	0.047(3)
C20A 029P	0.00/(2)	-0.000(2)	0.629(3)
C20D	0.003(3)	-0.052(2) -0.052(2)	0.382(3)
C23A	0.130(2)	-0.052(2) 0 183(2)	0.302(3)
C290	-0.075(2)	0.130(2)	0 408(3)
CIUR	0.640(2)	0.333(2)	0.354(3)
	0.010(2)	0.00(2)	0.334(3)

Table 5.2. (continued)

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Table 5.2. (continued)

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Atom	x	У	Z
C31A	-0.007(3)	0.134(2)	0.497(4)
C31B	0.633(3)	0.275(2)	0.294(4)
C32A	1.147(2)	0.750(2)	0.672(3)
C32B	0.522(2)	0.422(2)	0.216(3)
C33A	0.228(2)	-0.040(1)	-0.007(2)
C33B	0.437(2)	0.275(1)	0.850(3)
C34A	0.296(2)	-0.042(1)	0.082(2)
C34B	0.431(2)	0.217(1)	-0.191(3)
C35A	0.641(2)	0.083(2)	-0.075(3)
C35B	0.574(2)	0.821(2)	0.115(3)
C36A	0.643(2)	1.125(1)	1.021(3)
C36B	0.437(2)	0.207(2)	0.993(3)
C37A	0.294(2)	-0.127(1)	-0.107(3)
C37B	0.444(2)	0.260(2)	0.035(3)
C38A	0.231(2)	-0.085(1)	-0.100(3)
C38B	0.444(2)	0.301(2)	0.962(3)
C39A	1.174(2)	0.714(2)	0.881(3)
C39B	0.376(2)	0.495(1)	0.255(3)
C40A	-0.156(2)	0.338(2)	0.173(3)
C40B	0.330(2)	0.475(2)	0.159(3)
C41A	0.792(2)	0.386(1)	0.192(3)
C41B	0.319(2)	0.499(2)	0.062(3)
C42A	1.282(2)	0.623(2)	0.844(3)
C42B	0.361(3)	0.545(2)	0.079(4)
C43A	0.300(2)	0.675(2)	-0.102(3)
C43B	0.405(3)	0.567(2)	0.174(4)
C44A	0.755(2)	0.282(2)	0.085(3)
C44B	0.421(2)	0.541(2)	0.267(3)
C45A	0.316(2)	-0.013(1)	0.284(3)
C45B	0.551(2)	-0.137(2)	0.348(3)
C46A	0.708(2)	-0.036(1)	-0.366(2)
C46B	0.547(2)	-0.127(2)	0.465(3)
C47A	0.744(2)	-0.091(1)	-0.350(2)
C47B	0.408(2)	0.164(1)	0.456(3)
C48A	0.256(2)	0.120(1)	0.529(3)
C48B	0.444(2)	0.104(2)	0.318(3)
C49A	0.709(2)	0.937(2)	0.449(3)
C49B	0.492(2)	0.063(2)	0.383(4)
C50A	0.691(2)	-0.023(1)	0.530(3)
C50B	0.495(2)	0.077(2)	0.492(4)
C51A	1.042(2)	0.617(2)	0.727(3)
C51B	0.237(2)	0.413(2)	0.090(3)
C52A	-0.045(2)	0.633(2)	-0.312(3)
C52B	0.782(2)	0.648(1)	-0.094(3)

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Atom	x	У	Z
C53A	-0.079(3)	0.693(2)	-0.338(3)
C53B	0.274(2)	0.315(2)	0.155(3)
C54A	-0.187(2)	0.659(2)	-0.380(3)
C54B	0.193(3)	0.256(2)	0.115(3)
C55A	0.161(2)	0.395(2)	0.357(3)
C55B	0.133(2)	0.289(2)	0.062(3)
C56A	0.913(2)	0.587(2)	0.681(3)
C56B	-0.151(2)	0.657(2)	-0.054(3)

Atom	Atom	Distance	Atom	Atom	Distance
PT1A	CL1A	2.24(1)	N3B	C11B	1.49(4)
PT1A	CL2A	2.29(1)	N3B	C14B	1.33(4)
PT1A	N7A	2.02(2)	N4A	C16A	1.36(3)
PT1A	N8A	1.96(3)	N4A	C19A	1.37(3)
PT1B	CL1B	2.29(1)	N4B	C16B	1.28(4)
PT1B	CL2B	2.27(1)	N4B	C19B	1.45(4)
PT1B	N7B	1.96(3)	N5A	C34A	1.38(3)
PT1B	N8B	2.00(3)	N5A	C45A	1.41(4)
CU1A	N1A	1.96(3)	N5B	C34B	1.42(4)
CU1A	N2A	2.01(2)	N5B	C45B	1.33(4)
CU1A	N3A	2.02(2)	N6A	C40A	1.38(4)
CU1A	N4A	2.00(2)	N6A	C51A	1.37(4)
CU1B	N1B	2.00(2)	N6B	C40B	1.45(4)
CU1B	N2B	2.02(2)	N6B	C51B	1.28(4)
CU1B	N3B	1.95(3)	N7A	C47A	1.28(3)
CU1B	N4B	1.97(3)	N7A	C48A	1.39(4)
NIA	C1A	1.43(4)	N7B	C47B	1.35(4)
NIA	C4A	1.45(4)	N7B	C48B	1.30(4)
N1B	C1B	1.42(3)	N8A	C53A	1.26(4)
N1B	C4B	1.34(4)	N8A	C54A	1.42(4)
N2A	C6A	1.38(4)	N8B	C53B	1.46(4)
N2A	C9A	1.32(4)	N8B	C54B	1.18(4)
N2B	C6B	1.30(4)	01A	C45A	1.18(3)
N2B	C9B	1.39(3)	01B	C45B	1.30(4)
N3A	C11A	1.28(3)	02A	C51A	1.25(4)
N3A	C14A	1.42(3)	02B	C51B	1.19(4)
CIA	C2A	1.53(4)	C9A	C10A	1.48(4)
CIA	C20A	1.41(4)	C9B	C10B	1.41(4)
C1B	C2B	1.41(4)	C10A	C11A	1.51(4)
C1B	C20B	1.40(4)	C10A	C33A	1.43(4)
C2A	C3A	1.31(4)	C10B	C11B	1.32(4)
C2A	C21A	1.49(5)	C10B	C33B	1.53(4)
C2B	C3B	1.27(4)	C11A	C12A	1.50(4)
C2B	C21B	1.48(5)	C11B	C12B	1.47(5)
C3A	C4A	1.55(5)	C12A	C13A	1.28(4)
C3A	C22A	1.56(5)	C12A	C27A	1.53(4)
C3B	C4B	1.48(4)	C12B	C13B	1.37(5)
C3B	C22B	1.41(4)	C12B	C27B	1.53(5)
C4A	C5A	1.47(5)	C13A	C14A	1.44(4)
C4B	C5B	1.44(4)	C13A	C28A	1.43(4)
C5A	C6A	1.32(4)	C13B	C14B	1.50(5)
C5B	C6B	1.37(4)	C13B	C28B	1.42(5)
C6A	C7A	1.40(4)	C14A	C15A	1.33(4)

Table 5.3. Intramolecular distances (Å) involving the nonhydrogen atoms for $PtCuCl_2N_8O_2C_{56}H_{52}^{a}$

Atom	Atom	Distance	Atom	Atom	Distance	
C6B	C7B	1.51(4)	C14B	C15B	1.44(5)	
C7A	C8A	1.29(4)	C15A	C16A	1.39(4)	
C7A	C24A	1.58(5)	C15B	C16B	1.36(5)	
C7B	C8B	1.37(5)	C16A	C17A	1.41(4)	
C7B	C24B	1.41(5)	C16B	C17B	1.48(5)	
C8A	C9A	1.51(4)	C17A	C18A	1.33(4)	
C8A	C26A	1.42(5)	C17A	C30A	1.57(5)	
C8B	C9B	1.37(4)	C17B	C18B	1.39(5)	
C8B	C26B	1.66(5)	C17B	C30B	1.45(5)	
C18A	C19A	1.46(4)	C37A	C38A	1.41(4)	
C18A	C32A	1.45(5)	C37B	C38B	1.52(4)	
C18B	C19B	1.53(4)	C39A	C40A	1.34(4)	
C18B	C32B	1.59(5)	C39A	C44A	1.33(4)	
C19A	C20A	1.41(4)	C39B	C40B	1.34(4)	
C19B	C20B	1.40(4)	C39B	C44B	1.49(4)	
C20A	C39A	1.40(4)	C40A	C41A	1.36(4)	
C20B	C39B	1.59(4)	C40B	C41B	1.45(5)	
C22A	C23A	1.1(1)	C41A	C42A	1.42(5)	
C22B	C23B	1.36(5)	C41B	C42B	1.43(5)	
C24A	C25A	1.44(5)	C42A	C43A	1.35(4)	
C24B	C25B	1.58(5)	C42B	C43B	1.33(5)	
C28A	C29A	1.44(5)	C43A	C44A	1.32(4)	
C28B	C29B	1.37(6)	C43B	C44B	1.40(5)	
C30A	C31A	1.46(5)	C45A	C46A	1.48(4)	
C30B	C31B	1.44(6)	C45B	C46B	1.50(4)	
C33A	C34A	1.45(4)	C46A	C47A	1.34(4)	
C33A	C38A	1.41(4)	C46A	C50A	1.38(4)	
C33B	C34B	1.38(4)	C46B	C47B	1.44(4)	
C33B	C38B	1.41(4)	C46B	C50B	1.38(5)	
C34A	C35A	1.38(4)	C48A	C49A	1.42(4)	
C34B	C35B	1.52(4)	C48B	C49B	1.40(5)	
C35A	C36A	1.40(4)	C49A	C50A	1.33(4)	
C35B	C36B	1.39(5)	C49B	C50B	1.37(5)	
C36A	C37A	1.37(4)	C51A	C52A	1.57(5)	
C36B	C37B	1.25(5)	C51B	C52B	1.59(4)	
C52A	C53A	1.50(5)	C52A	C56A	1.46(5)	
C52B	C53B	1.38(4)	C52B	C56B	1.29(5)	
C54A	C55A	1.32(5)	C54B	C55B	1.31(5)	
C55A	C56A	1.36(5)	C55B	C56B	1.46(5)	

Table 5.3. (continued)

*Estimated standard deviations in the least significant figure are given in parentheses.

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
CL1A	PT1A	CL2A	174.2(4)	CIA	NIA	C4A	106(3)
CL1A	PT1A	N7A	93.5(8)	CU1B	N1B	C1B	131(2)
CL1A	PT1A	N8A	86.8(8)	CU1B	N1B	C4B	129(2)
CL2A	PT1A	N7A	87.3(8)	C1B	N1B	C4B	100(3)
CL2A	PT1A	N8A	92.4(8)	CU1A	N2A	C6A	127(2)
N7A	PT1A	N8A	179.0(1)	CU1A	N2A	C9A	130(2)
CL1B	PT1B	CL2B	174.1(4)	C6A	N2A	Ċ9A	101(3)
CL1B	PT1B	N7B	87.0(1)	CU1B	N2B	C6B	126(2)
CL1B	PT1B	N8B	92.5(9)	CU1B	N2B	C9B	126(2)
CL2B	PT1B	N7B	93.0(1)	C6B	N2B	C9B	107(3)
CL2B	PT1B	N8B	87.5(9)	CU1A	N3A	CIIA	132(2)
N7B	PT1B	N8B	177.0(1)	CU1A	N3A	C14A	124(2)
NIA	CULA	N2A	95.(1)	C11A	N3A	C14A	104(2)
NIA	CU1A	N3A	175(1)	CU1B	N3B	C11B	130(2)
NIA	CULA	N4A	85(1)	CU1B	N3B	C14B	130(3)
N2A	CU1A	N3A	88(1)	C11B	N3B	C14B	100(3)
N2A	CU1A	N4A	176(1)	CU1A	N4A	C16A	124(2)
N3A	CULA	N4A	93(1)	CU1A	N4A	C19A	130(2)
N1B	CU1B	N2B	90(1)	C16A	N4A	C19A	105(2)
N1B	CU1B	N3B	176(1)	CU1B	N4B	C16B	130(3)
N1B	CU1B	N4B	92(1)	CU1B	N4B	C19B	124(2)
N2B	CU1B	N3B	89(1)	C16B	N4B	C19B	106(3)
N2B	CU1B	N4B	177(1)	C34A	N5A	C45A	125(3)
N3B	CU1B	N4B	89(1)	C34B	N5B	C45B	130(3)
CU1A	NIA	CIA	134(2)	C40B	N6A	C51A	134(4)
CU1A	NIA	C4A	120(2)	C40B	N6B	C51B	125(3)
PT1A	N7A	C47A	127(2)	C4A	C3A	C22A	116(3)
PTIA	N7A	C48A	117(2)	C2B	C3B	C4B	101(3)
C47A	N7A	C48A	116(3)	C2B	C3B	C22B	134(4)
PT1B	N7B	C47B	119(3)	C4B	C3B	C22B	125(3)
PT1B	N7B	C48B	126(3)	N1A	C4A	C3A	107(3)
C47B	N7B	C48B	112(3)	N1A	C4A	C5A	125(4)
PT1A	N8A	C53A	116(3)	C3A	C4A	C5A	128(4)
PT1A	N8A	C54A	125(2)	N1B	C4B	СЗВ	116(3)
C53A	N8A	C54A	117(3)	N1B	C4B	C5B	120(3)
PT1B	N8B	C53B	117(3)	C3B	C4B	C5B	124(3)
PT1B	N8B	C54B	130(3)	C4A	C5A	C6A	128(3)
C53B	N8B	C54B	112(4)	C4B	C5B	C6B	127(3)
NIA	CIA	C2A	110(3)	N2A	C6A	C5A	121(3)
NIA	CIA	C20A	123(3)	N2A	C6A	C7A	114(3)
C2A	CIA	C20A	127(3)	C5A	C6A	C7A	122(3)
N1B	C1B	C2B	110(3)	N2B	C6B	C5B	127(4)
N1B	CIB	C20B	118(3)	N2B	C6B	C7B	113(3)

Table 5.4. Intramolecular Bond Angles Involving the Nonhydrogen Atoms for $PtCuCl_2N_8O_2C_{56}H_{52}^{a}$

Table	5.4.	(continued)	

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C2B	C1B	C20B	131(3)	C5B	C6B	C7B	120(3)
CIA	C2A	C3A	108(3)	C6A	C7A	C8A	106(4)
CIA	C2A	C21A	128(3)	C6A	C7A	C24A	121(3)
C3A	C2A	C21A	124(3)	C8A	C7A	C24A	130(4)
C1B	C2B	C3B	113(4)	C6B	C7B	C8B	97(3)
C1B	C2B	C21B	127(4)	C6B	C7B	C24B	123(3)
C3B	C2B	C21B	119(4)	C8B	C7B	C24B	140(4)
C2A	C3A	C4A	110(3)	C7A	C8A	C9A	104(3)
C2A	C3A	C22A	133(4)	C7A	C8A	C26A	123(4)
C9A	C8A	C26A	132(4)	C11B	C12B	C27B	128(4)
C7B	C8B	C9B	116(3)	C13B	C12B	C27B	117(4)
C7B	C8B	C26B	111(3)	C12A	C13A	C14A	113(3)
C9B	C8B	C26B	132(3)	C12A	C13A	C28A	128(3)
N2A	C9A	C8A	112(3)	C14A	C13A	C28A	119(3)
N2A	C9A	C10A	124(3)	C12B	C13B	C14B	97(3)
C8A	C9A	C10A	124(3)	C12B	C13B	C28B	133(4)
N2B	C9B	C8B	106(3)	C14B	C13B	C28B	130(4)
N2B	C9B	C10B	125(3)	N3A	C14A	C13A	106(3)
C8B	C9B	C10B	129(3)	N3A	C14A	C15A	122(3)
C9A	C10A	C11A	120(3)	C13A	C14A	C15A	131(3)
C9A	C10A	C33A	118(3)	N3B	C14B	C13B	122(4)
C11A	C10A	C33A	121(3)	N3B	C14B	C15B	120(4)
C9B	C10B	C11B	127(4)	C13B	C14B	C15B	118(4)
C9B	C10B	C33B	114(3)	C14A	C15A	C16A	131(3)
C11B	C10B	C33B	119(4)	C14B	C15B	C16B	127(4)
N3A	C11A	C10A	123(3)	N4A	C16A	C15A	124(3)
NJA	C11A	C12A	115(3)	N4A	C16A	C17A	109(3)
C10A	CIIA	C12A	121(3)	C15A	C16A	C17A	127(3)
N3B	C11B	C10B	122(3)	N4B	C16B	C15B	124(4)
N3B	C11B	C12B	107(3)	N4B	C16B	C17B	117(4)
Clob	C11B	C12B	131(4)	C15B	C16B	C17B	119(4)
C11A	C12A	C13A	101(3)	C16A	C17A	C18A	112(3)
C11A	C12A	C27A	129(3)	C16A	C17A	C30A	122(3)
C13A	C12A	C27A	130(3)	C18A	C17A	C30A	125(3)
C11B	C12B	C13B	114(3)	C16B	C17B	C18B	102(4)
C16B	C17B	C30B	129(4)	C17A	C30A	C31A	117(4)
C18B	C17B	C30B	128(4)	C17B	C30B	C31B	108(4)
C17A	C18A	C19A	101(3)	C10A	C33A	C34A	123(3)
C17A	C18A	C32A	127(4)	C10A	C33A	C38A	122(3)
C19A	C18A	C32A	131(3)	C34A	C33A	C38A	115(3)
C17B	C18B	C19B	108(3)	C10B	C33B	C34B	118(3)
C17B	C18B	C32B	121(4)	C10B	C33B	C38B	119(3)
C19B	C18B	C32B	130(3)	C34B	C33B	C38B	124(3)

Table 5.4. (continued)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N4A	C19A	C18A	113(2)	N5A	C34A	C33A	115(3)
N4A	C19A	C20A	128(3)	N5A	C34A	C35A	123(3)
C18A	C19A	C20A	119(3)	C33A	C34A	C35A	122(3)
N4B	C19B	C18B	106(3)	N5B	C34B	C33B	123(3)
N4B	C19B	C20B	125(3)	N5B	C34B	C35B	118(3)
C18B	C19B	C20B	129(3)	C33B	C34B	C35B	119(3)
CIA	C20A	C19A	118(3)	C34A	C35A	C36A	119(4)
CIA	C20A	C39A	118(3)	C34B	C35B	C36B	112(3)
C19A	C20A	C39A	124(3)	C35A	C36A	C37A	122(4)
C1B	C20B	C19B	130(3)	C35B	C36B	C37B	132(4)
C1B	C20B	C39B	114(3)	C36A	C37A	C38A	118(3)
C19B	C20B	C39B	115(3)	C36B	C37B	C38B	118(3)
C3A	C22A	C23A	112(8)	C33A	C38A	C37A	123(3)
C3B	C22B	C23B	110(4)	C33B	C38B	C37B	115(3)
C7A	C24A	C25A	107(3)	C20A	C39A	C40A	123(4)
C7B	C24B	C25B	114(3)	C20A	C39A	C44A	120(3)
C13A	C28A	C29A	118(4)	C40A	C39A	C44A	118(4)
C13B	C28B	C29B	113(4)	C20B	C39B	C40B	122(3)
C20B	C39B	C44B	114(3)	C45B	C46B	C50B	122(4)
C40B	C39B	C44B	123(3)	C47B	C46B	C50B	114(3)
N6A	C40A	C39A	116(3)	N7A	C47A	C46A	127(3)
N6A	C40A	C41A	121(4)	N7B	C47B	C46B	126(3)
C39A	C40A	C41A	123(4)	N7A	C48A	C49A	120(3)
N6B	C40B	C39B	118(4)	N7B	C48B	C49B	129(4)
N6B	C40B	C41B	122(4)	C48A	C49A	C50A	119(3)
C39B	C40B	C41B	120(4)	C48B	C49B	C50B	115(4)
C40A	C41A	C42A	116(3)	C46A	C50A	C49A	120(3)
C40B	C41B	C42B	114(4)	C46B	C50B	C49B	123(4)
C41A	C42A	C43A	122(4)	N6A	C51A	02A	118(4)
C41B	C42B	C43B	127(4)	N6A	C51A	C52A	120(3)
C42A	C43A	C44A	117(4)	02A	C51A	C52A	122(4)
C42B	C43B	C44B	120(4)	N6B	C51B	02B	127(4)
C39A	C44A	C43A	125(4)	N6B	C51B	C52B	115(3)
C39B	C44B	C43B	115(3)	02B	C51B	C52B	118(3)
N5A	C45A	01A	122(3)	C51A	C52A	C53A	118(4)
N5A	C45A	C46A	114(3)	C51A	C52A	C56A	117(3)
01A	C45A	C46A	123(3)	C53A	C52A	C56A	125(4)
N5B	C45B	018	125(3)	C51B	C52B	C53B	116(3)
N5B	C45B	C46B	118(3)	C51B	C52B	C56B	119(3)
018	C45B	C46B	117(3)	C53B	C52B	C56B	124(4)
C45A	C46A	C47A	128(3)	NSA	C53A	C52A	117(4)
C45A	C46A	CSUA	L14(3)	NSB	C53B	C52B	TT9(3)
C47A	C46A	COUA	TTR(3)	NSA	C54A	CDDA	129(4)
C45B	C46B	C47B	123(3)	NSB	C54B	C228	139(5)

Table 5.4. (continued)

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Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C54A	C55A	C56A	120(4)	C54B	C55B	C56B	110(4)
C52A	C56A	C55A	112(4)	C52B	C56B	C55B	119(4)

*Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

is also exhibited by the CuN, coordination unit, with the nitrogens alternately displaced above and below the mean N, plane by an average of 0.06(2) Å. A similar but slightly smaller S, distortion is shown by the porphyrin fragment in molecule B.

The CuN, and PtCl₂N₂ planes are oriented nearly perpendicular to one another. The dihedral angles formed by these two planes are 75 and 83° in molecules A and B respectively. A chlorine atom is directed at the copper atom with a Cu-Cl distance of 3.21(1) Å in molecule B and 3.02(1) Å in molecule A. Other square-pyramidal copper(II) complexes where a chlorine ligand from an adjacent metal fragment serves as a ligand on Cu exhibit Cu-Cl distances ranging from 2.41 to 3.36 Å.¹⁸ Another unusual aspect of this structure is the short Pt_A-Pt_B distance, 3.766(3) Å.

Crystal Structure Determination of Ti₂S₂O₆N₂C₁₈H₃₈²³

Titanatranes allow single substitution reactions on Ti(IV) esters and amides to be investigated. Due to the stability of the polycyclic tetradentate ligand, titanatranes are more robust to displacements beyond that of the axial substituent.²³ A primary goal of this crystal structure determination was to establish the environment around the titanium atom.

Data collection

A yellow rectangular crystal of $\text{Ti}_2\text{S}_2\text{O}_6\text{N}_2\text{C}_{18}\text{H}_{38}$ provided by John Verkade's group (Iowa State University) having approximate dimensions of 0.400 x 0.600 x 0.800 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated MoK α radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 14 carefully centered reflections in the range 12.31 < 20 < 17.36° corresponded to a triclinic cell with dimensions:

For Z = 1 and F.W. = 538.43, the calculated density is 1.435 g/cm³. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P1 (#2)

The data were collected at a temperature of $-25 \pm 1^{\circ}$ C using the ω -20 scan technique to a maximum 20 value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.38° with

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a take-off angle of 6.0°. Scans of $(1.31 + 0.30 \tan \theta)$ ° were made at a speed of $8.0^{\circ}/\text{min}$ (in omega). The weak reflections $(I < 10.0\sigma(I))$ were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Data reduction

Of the 2393 reflections which were collected, 2207 were unique ($R_{int} = .062$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for MoK α is 8.3 cm⁻¹. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by a combination of Patterson and direct methods. The non-hydrogen atoms were refined

anisotropically. Hydrogen atom positions were calculated. The final cycle of full-matrix least-squares refinement was based on 2008 observed reflections (I > $3.00\sigma(I)$) and 136 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum ||Fo| - |Fc|| / \sum |Fo| = 0.043$$

$$R_{w} = \left[\left(\sum w(|Fo| - |Fc|)^{2} / \sum wFo^{2} \right) \right]^{1/2} = 0.061$$

The standard deviation of an observation of unit weight was 3.23. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. Plots of Σ w (|Fo| - |Fc|)² versus |Fo|, reflection order in data collection, sin θ/λ , and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.93 and -0.65 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.²⁴ Anomalous dispersion effects were included in Fcalc;²⁵ the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.²⁶

All calculations were performed using the TEXSAN²⁷ and the CHES²⁸ crystallographic software packages. Complete experimental details are listed in Table 5.5.

Structural Details of the Ti_S,O_N_C1,H. Compound

An ORTEP¹⁵ drawing is given in Figure 5.2. Final positional parameters for the non-hydrogen atoms are given in Table 5.6 and Tables 5.7 and 5.8 give bond distances and angles. The metal-metal distance of 3.273(1) Å is intermediate between other similar complexes. The average Ti-O bond length is 1.845(2) Å. The Ti-S bond length, 2.373(1) Å compares favorably with other similar structures.²³

Crystal Structure Determination of C20H270Br29

The chirality of molecules in biological reactions is often fundamental to the progress of the reaction. Therefore, effective methods of preferentially synthesizing one enantiomer are of interest to many organic chemists. One area currently being investigated is the use of palladium as a catalyst in enantioselective, hetero- and carboannulation reactions.²⁹ Single x-ray crystallography is a powerful method to determine the absolute configuration of such compounds.

Several related compounds were studied prior to $C_{20}H_{27}OBr$. The author was able to determine that these other compounds were racemic mixtures which will not be reported in this thesis.

Table 5.5. Crystal and data collection parameters for $Ti_2S_2O_6N_2C_{18}H_{38}$

Experimental	Details
Empirical Formula Formula Weight Crystal Dimensions (mm) Crystal Color, Habit Crystal System Lattice Parameters:	$Ti_{2}S_{2}O_{6}N_{2}C_{18}H_{38}$ 538.43 0.400 x 0.600 x 0.800 yellow, rectangular triclinic $a = 7.434(5) \text{ Å}$ $b = 12.540(3) \text{ Å}$ $c = 7.034(3) \text{ Å}$ $\alpha = 105.72(3)^{\circ}$ $\beta = 98.87(3)^{\circ}$
Cell Determining Reflections: number, range (20) Space Group Z Density, calculated Absorption coefficient, $\mu_{(HoK\alpha)}$ Diffractometer Radiation Temperature Scan Type $2\theta_{max}$ Reflections Measured	$\gamma = 85.30(4)^{\circ}$ $V = 623.1(5)^{\circ} Å^{3}$ 14 (12.3 - 17.4°) PI (#2) 1 1.435 g/cm ³ 8.28 cm ⁻¹ Rigaku AFC6R MoKa ($\lambda = 0.71069^{\circ} Å$) -25 °C ω -20 50.1° Total: 2393
Reflections Observed (I>3.00σ(I)) Parameters Refined Reflection/Parameter Ratio Corrections Structure Solution Refinement Least-squares Weights Residuals: R [*] ; R,b Goodness of Fit Indicator Maximum Peak in Final Diff. Map Minimum Peak in Final Diff. Map	Unique: 2207 ($R_{int} = .062$) 2008 136 14.76 Lorentz-polarization Patterson Method Full-matrix least-squares $4F_o^2/\sigma^2(F_o^2)$ 0.043; 0.061 3.23 0.93 e ⁻ /Å ³ -0.65 e ⁻ /Å ³

 $\label{eq:R_solution} \begin{array}{l} {}^{a}R= \ \Sigma \left| \left| \left| F_{o} \right| \right. - \left| \left| F_{c} \right| \right| / \Sigma \left| F_{o} \right| \right. \right. \\ {}^{b}R_{w}= \ \left[\Sigma W \left(\left| \left| F_{o} \right| \right. - \left| \left| F_{c} \right| \right. \right)^{2} / \Sigma W \left| \left| F_{o} \right|^{2} \right]^{1/2}, \ W=1/\sigma^{2} \left(\left| \left| F_{o} \right| \right. \right). \end{array}$



Figure 5.2. ORTEP drawing of $\text{Ti}_2\text{S}_2\text{O}_6\text{N}_2\text{C}_{16}\text{H}_{36}$. The ellipsoids are drawn at the 50% probability level.

Atom	x	У	2
Ti	0.00104(6)	0.12576(4)	-0.02574(7)
S	0.2071(1)	0.27177(6)	0.0662(1)
01	0.0705(3)	0.1024(2)	-0.2750(3)
02	-0.1445(3)	0.2082(2)	0.1562(3)
03	-0.1468(3)	-0.0204(2)	-0.0977(3)
N	-0.2596(3)	0.1652(2)	-0.2133(3)
C1	0.1753(4)	0.3667(3)	0.3094(5)
C2	0.3222(6)	0.3502(4)	0.4717(6)
C3	0.1680(8)	0.4855(3)	0.2929(7)
C4	-0.2824(4)	0.2857(3)	0.1163(5)
C5	-0.3133(5)	0.2778(3)	-0.1038(5)
C6	-0.2232(5)	0.1548(4)	-0.4171(5)
C7	-0.0185(5)	0.1611(3)	-0.4108(5)
C8	-0.3994(5)	0.0872(3)	-0.2074(5)
C9	-0.3154(4)	-0.0248(3)	-0.2254(5)

Table 5.6. Positional parameters for $Ti_2S_2O_6N_2C_{18}H_{38}$

Table 5.7. Intramolecular distances involving the nonhydrogen atoms for $Ti_2S_2O_6N_2C_{18}H_{38}^{4}$

Atom	Atom	Distance	Atom	Atom	Distance
TI	S	2.373(1)	N	C5	1.470(4)
TI	01	1.845(2)	N	C6	1.469(4)
TI	02	1.845(2)	N	C8	1.496(5)
TI	N	2.269(3)	C1	C2	1.498(5)
TI	03	2.117(2)	C1	C3	1.522(5)
TI	03	1.941(2)	C4	C5	1.507(5)
S	Cl	1.837(4)	C6	C7	1.524(6)
01	C7	1.413(4)	C8	C9	1.472(5)
02	C4	1.404(4)	03	C9	1.421(4)
TI	TI	3.273(1)			•

*Estimated standard deviations in the least significant figure are given in parentheses.

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Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
S	TI	01	84.16(8)	TI	N	C5	103.3(2)
S	TI	02	89.73(8)	TI	N	C6	109.4(2)
S	TI	N	112.64(8)	TI	N	C8	107.7(2)
S	TI	03	171.03(6)	C5	N	C6	114.8(3)
S	TI	03	98.89(7)	C5	N	C8	108.8(3)
01	TI	02	146.5(1)	C6	N	C8	112.3(3)
01	TI	N	76.9(1)	S	C1	C2	112.2(3)
01	TI	03	95.3(1)	S	C1	C3	109.0(3)
01	TI	03	106.1(1)	C2	C1	C3	110.6(3)
02	TI	N	75.2(1)	02	C4	C5	109.6(3)
02	TI	03	95.5(1)	N	C5	C4	108.9(3)
02	TI	03	107.4(1)	N	C6	C7	108.0(3)
N	TI	03	75.84(9)	01	C7	C6	107.9(3)
N	TI	03	148.44(9)	N	C8	C9	109.9(3)
03	TI	03	72.60(9)	TI	03	TI	107.40(9)
TI	S	C1	111.5(1)	TI	03	C9	118.2(2)
TI	01	C7	120.8(2)	TI	03	C9	134.3(2)
TI	02	C4	124.8(2)	C8	C9	03	110.5(3)

Table 5.8. Intramolecular Bond Angles Involving the Nonhydrogen Atoms for $Ti_2S_2O_6N_2C_{18}H_{38}^{-4}$

*Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Data collection

A colorless, rectangular crystal of $C_{20}H_{27}BrO$ provided by Richard Larock's group (Iowa State University) was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated MoK α radiation and a 12kW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 12.73 < 2θ < 15.28° corresponded to a primitive orthorhombic cell with dimensions:

a = 9.120 (3) Å b = 22.483 (3) Å c = 8.582 (2) Å V = 1759.7 (5) Å³

For Z = 4 and F.W. = 464.50, the calculated density is 1.75 g/cm³. The systematic absences of:

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h00: h \neq 2n
0k0: k \neq 2n
001: 1 \neq 2n
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uniquely determine the space group to be:

P2₁2₁2₁ (#19).

The data were collected at a temperature of $23 \pm 1 \circ C$ using the ω -20 scan technique to a maximum 20 value of 45.0°. Omega scans of several intense reflections, made prior to data

collection, had an average width at half-height of 0.38° with a take-off angle of 6.0° . Scans of $(1.05 + 0.34 \tan \theta)^{\circ}$ were made at a speed of 16.0° /min (in omega). The weak reflections $(I < 10.0\sigma(I))$ were rescanned (maximum of 4 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 400 mm, and the detector aperture was 9.0 x 13.0 mm (horizontal x vertical).

Data reduction

Of the 3902 reflections which were collected, 1165 were unique ($R_{int} = 0.121$). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ , for MoK α radiation is 23.7 cm⁻¹. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structure was solved by direct methods³⁰ and expanded using Fourier techniques.³¹ Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined.

The final cycle of full-matrix least-squares refinement was based on 1746 observed reflections (I > $3.00\sigma(I)$) and 144 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.046$$
$$R_w = \sqrt{(\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)} = 0.042$$

The standard deviation of an observation of unit weight was 1.64. The weighting scheme was based on counting statistics and included a factor (p = 0.013) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus |Fo|, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.38 and -0.33 e⁻Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.²⁴ Anomalous dispersion effects were included in F_{calc} ;²⁵ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.³² The values for the mass attenuation coefficients are those of Creagh and Hubbell.³³ All calculations were performed using the texsan³⁴ crystallographic software package of Molecular Structure Corporation, except for the Flack parameter which was calculated using SHELXL-93.³⁵ Complete experimental details are listed in Table 5.9.

The absolute configuration of the compound was verified by measurement of the Flack absolute structure parameter³⁶ x =-0.0051 with esd 0.0245. The Flack absolute structure parameter, x, describes the crystal as an inversion twin. 1-x and x are the fractions of the structure and its inverse in a macroscopic sample. The structure factor equation is then given as:³⁶

 $|F(h,k,l,x)|^2 = (1-x)|F(h,k,l)|^2 + x|F(-h,-k,-l)|^2.$

A correct structure has an expected value of zero within three esd's. The Hamilton significance test³⁷ was calculated to equal 1.134, which indicates that the absolute configuration is correct to a probability which exceeds 99 percent, further confirming the absolute configuration.

Structural Details of the C20H270Br Compound

An ORTEP¹⁵ drawing is given in Figure 5.3. Final positional parameters are given in Table 5.10 and Tables 5.11 and 5.12 gives bond distances and angles.

The absolute configuration was determined to be (S). The Br-C bond length is 1.86(1) Å. The mean deviation of atoms C1 through C6 from the plane is 0.0260 Å. The Br atom is

displaced 0.012 Å from the plane and C3 and C4 are displaced -0.01 and -0.03 Å from the plane respectively.

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Table 5.9. Crystal and data collection parameters for $C_{20}H_{27}OBr$

Experimental	Details
Empirical Formula Formula Weight Crystal Color, Habit Crystal Dimensions Crystal System Lattice Type Lattice Parameters:	$C_{20}H_{27}OBr$ 464.50 colorless, rod 0.4 X 0.1 X 0.1 mm orthorhombic Primitive a = 9.120(3) Å b = 22.483(3) Å c = 8.582(2) Å
Cell Determining Reflections:	$V = 1/59.7(7) \text{ A}^{-}$ 25 (12.7 - 15.3°)
number, range (20)	P2_12_12_1 (#19)
Space Group	4
Z	1.753 g/cm ³
Density, calculated	23.68 cm ⁻¹
Absorption coefficient, $\mu_{(HoKa)}$	Rigaku AFC6R
Diffractometer	MoKa ($\lambda = 0.71069 \text{ Å}$)
Radiation	23.0°C
Temperature	$\omega - 2\theta$
Scan Type	45.0°
$2\theta_{max}$	Total: 3902
Reflections Measured	Unique: 1165 (R _{int} = 0.121)
Reflections Observed $(I>3.00(\sigma(I))$	1746
Parameters Refined	144
Reflection/Parameter Ratio	12.13
Corrections	Lorentz-polarization
Structure Solution	Direct Methods (SHELXS86)
Refinement	Full-matrix least-squares
Least Squares Weights	$1/(\sigma^2(F_{\circ})) = 4F_{\circ}^2/(\sigma^2(F_{\circ}^2))$
Residuals: R [*] ; Rw ^b	0.046; 0.042
Goodness of Fit Indicator	1.64
Maximum peak in Final Diff. Map	0.38 e ⁻ Å ³
Minimum peak in Final Diff. Map	-0.33 e ⁻ Å ³

 $\label{eq:R_states} \begin{array}{l} {}^{*}R= \Sigma \left| \left| F_{o} \right| - \left| F_{c} \right| \left| / \Sigma \right| F_{o} \right| . \\ {}^{b}R_{w}= \left[\Sigma W \left(\left| F_{o} \right| - \left| F_{c} \right| \right)^{2} / \Sigma W \left| F_{o} \right|^{2} \right]^{1/2}, \hspace{0.1cm} w=1/\sigma^{2} \left(\left| F_{o} \right| \right) . \end{array} \right.$



Figure 5.3. ORTEP drawing of $C_{20}H_{27}OBr$. The ellipsoids are drawn at the 50% probability level.

Atom	x	У	2
Br1	-0.4115(1)	-0.96636(6)	-0.2107(2)
01	-0.3052(8)	-0.8166(3)	-0.8534(8)
C1	-0.355(1)	-0.9028(5)	-0.338(1)
C2	-0.361(1)	-0.9076(5)	-0.497(1)
C3	-0.321(1)	-0.8620(5)	-0.593(1)
C4	-0.267(1)	-0.8084(6)	-0.531(1)
C5	-0.253(1)	-0.8047(5)	-0.367(1)
C6	-0.302(1)	-0.8496(5)	-0.277(1)
C7	-0.324(1)	-0.8698(5)	-0.767(2)
C8	-0.179(1)	-0.7819(5)	-0.804(2)
C9	-0.214(1)	-0.7595(5)	-0.640(1)
C10	-0.153(1)	-0.7359(5)	-0.929(1)
C11	-0.282(1)	-0.6969(4)	-0.970(1)
C12	-0.236(1)	-0.6347(5)	-1.027(1)
C13	-0.362(1)	-0.5959(5)	-1.062(1)
C14	- 0.459(1)	-0.5798(4)	-0.928(1)
C15	-0.3850(10)	-0.5408(4)	-0.806(1)
C16	-0.460(1)	-0.5429(5)	-0.647(1)
C17	-0.431(1)	-0.5994(4)	-0.557(1)
C18	-0.279(1)	-0.6058(5)	-0.494(1)
C19	-0.234(1)	-0.6694(5)	-0.456(1)
C20	-0.198(1)	-0.7042(5)	-0.603(1)

Table 5.10. Positional parameters for $C_{20}H_{27}OBr$

Atom	Atom	Distance	Atom	Atom	Distance
BR1	C1	1.86(1)	01	C7	1.41(2)
01	C8	1.46(1)	C1	C2	1.34(2)
C1	C6	1.39(2)	C2	C3	1.34(2)
C2	Hl	1.11	C3	C4	1.41(2)
C3	C7	1.51(2)	C4	C5	1.40(2)
C4	C9	1.53(2)	C5	C6	1.35(2)
C5	H2	0.99	C6	H3	0.97
C7	H4	1.03	C7	H5	1.03
C8	C9	1.53(2)	C8	C10	1.48(2)
C8	H6	0.95	C9	C20	1.28(1)
C10	C11	1.53(2)	C10	H7	0.96
C10	H8	0.92	C11	C12	1.55(1)
C11	H9	0.94	C11	H10	0.95
C12	C13	1.46(2)	C12	H11	0.97
C12	H12	0.93	C13	C14	1.47(1)
C13	H13	0.96	C13	H14	0.95
C14	C15	1.50(1)	C14	H15	0.96
C14	H16	0.96	C15	C16	1.53(1)
C15	H17	0.93	C15	H18	0.96
C 16	C17	1.52(2)	C16	H19	0.94
C16	H20	0.98	C17	C18	1.50(2)
C17	H21	0.96	C17	H22	0.92
C18	C19	1.51(1)	C18	H23	0.93
C18	H24	0.96	C19	C20	1.54(2)
C19	H25	0.95	C19	H26	0.92
C20	H27	1.05			

Table 5.11. Intramolecular distances involving all of the atoms for $C_{20}H_{27}OBr^{a}$

*Estimated standard deviations in the least significant figure are given in parentheses.

-	Atom	Atom	atom	Angle	Atom	Atom	Atom	Angle
	01	НЗ	BR1	111.0	01	H4	BR1	170.0
	01	H8	01	134.7	C1	C2	H	118.3
	C3	C2	H	109.4	C4	C5	H2	94.0
	C6	C5	H2	125.0	C1	C6	H3	112.2
	C5	C6	H3	123.1	01	C7	H4	112.9
	01	C7	H5	114.5	C3	C7	H4	108.0
	C3	C7	H5	107.4	H4	C7	H5	97.7
	01	C8	H6	105.4	C9	C8	H6	107.1
	C10	C8	H6	113.1	C8	C10	H7	104.5
	C8	C10	H8	105.5	C11	C10	H7	108.4
	C11	C10	H8	111.3	H7	C10	H8	111.5
	C10	C11	H9	107.6	C10	C11	H10	106.4
	C12	C11	H9	111.5	C12	C11	H10	109.3
	H9	C11	H10	110.2	C11	C12	H11	106.1
	C11	C12	H12	108.5	C13	C12	H11	109.5
	C13	C12	H12	110.8	H11	C12	H12	109.4
	C12	C13	H13	107.2	C12	C13	H14	106.4
	C14	C13	H13	108.7	C14	C13	H14	108.4
	H13	C13	H14	109.2	C13	C14	H15	108.2
	C13	C14	H16	108.6	C15	C14	H15	108.5
	C15	C14	H16	109.6	H15	C14	H16	107.9
	C14	C15	H17	109.8	C14	C15	H18	108.2
	C16	C15	H17	107.7	C16	C15	H18	106.4
	H17	C15	H18	110.3	C15	C16	H19	111.7
	C15	C16	H20	109.2	C17	C16	H19	108.7
	C17	C16	H20	104.8	H19	C16	H20	107.9
	C16	C17	H21	107.7	C16	C17	H22	108.6
	C18	C17	H21	105.8	C18	C17	H22	108.7
	H21	C17	H22	111.7	C17	C18	H23	110.2
	C17	C18	H24	107.3	C19	C18	H23	107.7
	C19	C18	H24	107.7	H23	C18	H24	110.3
	C18	C19	H25	108.4	C18	C19	H26	110.2
	C20	C19	H25	105.8	C20	C19	H26	108.8
	H25	C19	H26	111.8	C9	C20	H27	142.3
	C19	C20	H27	82.				

Table 5.12. Intramolecular bond angles involving all the atoms of $C_{20}H_{27}OBr^4$

*Estimated standard deviations in the least significant figure are given in parentheses.

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CHAPTER 6. GENERAL CONCLUSIONS

PHASER has the ability to aid the crystallographer in her work by facilitating the solution of difficult crystal structures. It has been used to refine the phases of a variety of compounds whose starting models ranged from quite small to relatively large. Either of two criteria can be used to determine convergence of the process, although the use of a residual function may be a more general method.

The use of PHASER offers two primary advantages to the crystallographer. First, PHASER allows determination of crystal structures that might not have otherwise been solved. Secondly, even for structures that can be readily solved, PHASER offers significant time savings over conventional methods. In difficult cases, PHASER can reduce the time needed to solve a crystal structure dramatically; in the [NiO₂N₈C_{5s}H₅₂]₂Pd(ClO₄)₂.8HCCl₃ case, although a month was required for the original structure solution, less than a week would have been needed using PHASER. In addition, PHASER has been automated and requires little user input, allowing its use by chemists with varying levels of crystallographic knowledge.

Of the more than a dozen crystal structures I have solved, three were discussed in Chapter 5. The determination of the absolute configuration of $SO_2NC_{26}H_{40}$ was a particularly

interesting challenge. Several related compounds were studied previously, but determination of the enantiomer was not possible for the earlier compounds as the crystals contained racemic mixtures of both enantiomers.

Several areas of future research include the use of the 52 relation with the phase refinement process described in this thesis. The combination of the two methods should increase the power of the method and hasten refinement. Another promising extension to this method involves varying the amount of sharpening applied to the data over the course of the phase refinement. As refinement proceeds, less sharpening would be applied to the data. This should extend the utility of the method further toward the final stages of a structure solution.

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