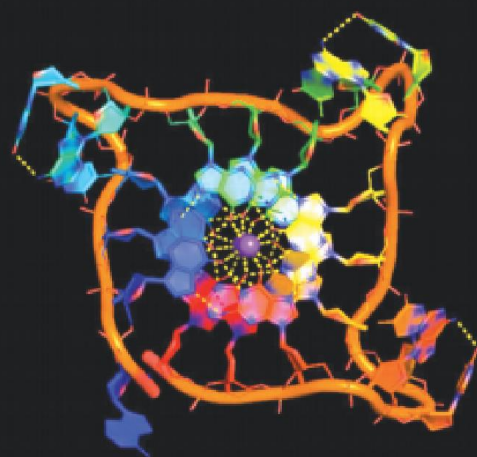


Dr. Naresh Kumar

A NEW APPROACH TO
X-Ray Structure of
Organometallic Compound



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Preface

There are several text books of XRD for OMC that treat the subject in considerably to less space than our book A New Approach to XRD of OMC. Moreover Most of them include a great deal of Introductory theory and net result is that these books contain very little of real content of uses of XRD for OMC. A New Approach of XRD of OMC is not only confined within the Chemistry students, students of many other branches like Physics, Material Science and Geology also need the subject. My purpose in this book is to meet the need of students, researchers & teachers who have no time to pursue it in depth but who may also require explicit coverage of basic knowledge of XRD of OMC. I therefore introduce material of this type, with new concept.

The present book "A New Approach of X-ray diffraction of OMC" has been written for M.Sc. students and researchers of various Indian Universities specially for organometallic chemistry.

I have consulted different sources (enlisted under the section bibliography reference at the end of this book) to borrow the views and concepts of various authors.



Much care has been taken to minimize the printing mistake in the book. I am sure that in spite of my best effort, the book is not free from error valuable suggestions will be welcome from the curious students, researchers and learned teachers for the improvement of this book.

I express my gratitude to Dr. Vinay Kumar Choudhary, Head, Univ. Deptt. Of Hindi, who inspired to write a book for Post Graduate & Research students and also Akshat Jha of Novelty & Company, Patna for providing all assistance and bringing out the book in present shape.

I am grateful to my wife Prof. Punam Kumari and son Kumar Nishant and daughter Ruchi to keep me away from all sorts of family responsibility during writing the book.

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 19 Nobel Prizes Based on X-ray Work	
CHEMISTRY:	PHYSICS:
1901 - Peter Debye	1901 - Wilhelm Röntgen
1902 - Max Perutz & Sir John Kendrew	1902 - Max Von Laue
1903 - Dorothy Hodgkin	1903 - Sir William Henry Bragg & Sir William Lawrence Bragg
1915 - William Lipscomb	1914 - Charles Barkla
1946 - Herbert Hauptman & Jerome Karle	1915 - Karl Manne Siegbahn
1962 - Johann Deisenhofer, Robert Huber & Hartmut Michel*	1917 - Arthur Compton
1980 - Paul D. Boyer & John E. Walker*	1918 - Niels Bohr
1988 - Peter Agre & Roderick MacKinnon*	
1995 - Roger Kornberg*	MEDICINE:
	1901 - Rosendo Joseph Muller
	1902 - Francis Crick, James Watson & Maurice Wilkins
	1915 - Alan H. Corneil & Sir Geoffrey H. Hounsfield

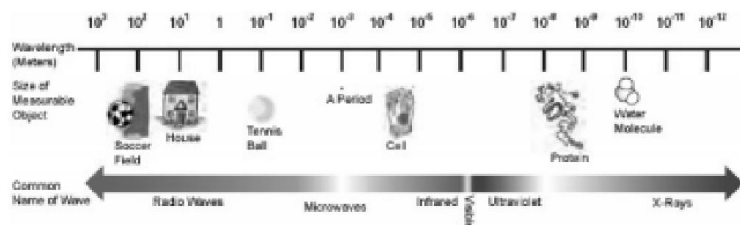
Chapter I

Introduction

In order to measure something accurately, we need the appropriate ruler. To measure the distance between cities, we would use miles or kilometers. To measure the length of your hand, we would use inches or centimeters.

Crystallographers measure the distances between atoms in angstroms. One angstrom equals one ten-billionth of a meter, or 10^{-10}m . That's more than 10 million times smaller than the diameter of the period at the end of this sentence.

The perfect “rulers” to measure angstrom distances are X-rays. The X-rays used by crystallographers are approximately 0.5 to 1.5 angstroms long—just the right size to measure the distance between atoms in a molecule. There is no better place to generate such X-rays than in a synchrotron.



When using light to measure an object, the wavelength of the light needs to be similar to the size of the object. X-rays, with wavelengths of approximately 0.5 to 1.5 angstroms, can measure the distance between atoms. Visible light, with a wavelength of 4,000 to

Chapter II

2.2 What is Crystal

Crystals are solids that are exact repeats of a symmetric motif. What makes crystalline quartz different from non crystalline glass? Both have essentially the same chemical composition. The most telling difference is that the molecules in a crystal are arranged in an orderly fashion, while the molecules of an amorphous solid, like a glass, are disordered. By ordered, we mean regular, symmetric, and repeating. This is particularly evident when we compare broken pieces of glass with pieces of a crystal. A glass will shatter to form random shards, with no relationship between the shape of the intact and broken pieces. A crystal, however, can be cleaved very specifically to give fragments that are smaller versions of the original crystal. This can be done almost indefinitely, until we reach the basic unit that describes a crystal, called the unit cell. Thus a crystal can be generated from a molecule.

Since all unit cells within a crystal are identical, the morphology of a crystal is defined by the size and shape of a single unit cell (the lengths of a , b and c and the angles α , β , and γ) and the symmetry of the motif. Each level of the crystal, with the exception of the asymmetric unit, can be generated using mathematical operators; solving a crystal structure requires only that we determine the conformation of the atoms in the asymmetric unit. In the case of our hemoglobin example, the structure of the entire hemoglobin tetramer in a crystal can be solved by determining only the structure of a single $\alpha\beta$ -dimer in the asymmetric unit.

Chapter III

3.1 Diffraction and the Bragg Equation

Sir W.H. Bragg and his son Sir W.L. Bragg developed a in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ). The variable d is the distance between atomic layers in a crystal, and the variable λ is the wavelength of the incident X-ray beam; n is an integer. This observation is an example of X-ray wave interference diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

Deriving Bragg's Law: $n\lambda = 2d\sin\theta$

Constructive interference

occurs only when

$$n\lambda = AB + BC$$

$$AB = BC$$

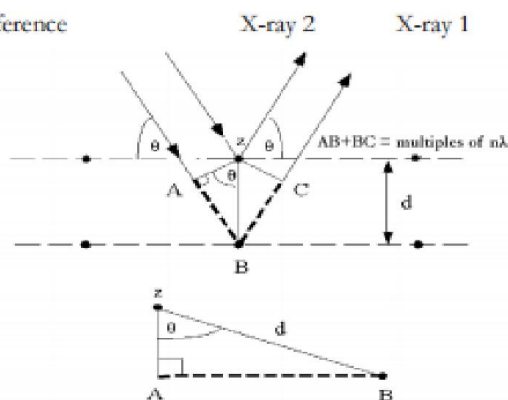
$$n\lambda = 2AB$$

$$\sin\theta = AB/d$$

$$AB = d\sin\theta$$

$$n\lambda = 2d\sin\theta$$

$$\lambda = 2d\sin\theta/n$$



Chapter IV

Determination of Crystal Structure by X-ray Diffraction

Introduction

X-radiation ("X-rays") is electromagnetic radiation with wavelengths between roughly 0.1 Å and 100 Å, typically similar to the interatomic distances in a crystal. This is convenient as it allows crystal structures to diffract X-rays.

X-ray diffraction is an important tool used to identify phases by comparison with data from known structures, quantify changes in the cell parameters, orientation, crystallite size and other structural parameters. It is also used to determine the (crystallographic) structure (i.e. cell parameters, space group and atomic coordinates) of novel or unknown crystalline materials.

In crystallography, measurements are expressed in Ångströms (Å). An Ångström corresponds to 1×10^{-10} m; so one Ångström is equal to 0.1 nm.

The crystal structure of a compound was determined from an X-ray powder diffraction pattern. The powder method is limited to the use of cubic systems, but allowed for the determination of the crystal lattice and the dimensions of the unit cell.

Theory

Perfect crystals are comprised of a repetition of smaller structures called unit cells. The repeating unit cells form lattice structures. It is the planes of these lattice structures that diffract the X-rays. Crystals are most often described in terms of three crystal axes, a, b, and c. These axes which

may be any length and do not have to be at right angles, form the basis for the coordinate system. Within cubic systems $a = b = c$ and all angles of the unit cell are 90° . All crystals can be described using equation one:

$$ha + kb + lc = \text{positive constant} \quad \dots(1)$$

h , k and l are called Miller indices and are the reciprocals of intersection distances of the lattice planes. Each type of cubic system is defined by a Miller indices series and more specifically by the gaps that are present. The Miller indices are used to determine the interplanar distance by the following equation:

$$d = a/(h^2 + k^2 + l^2)^{1/2} = a/M \quad \dots(2)$$

where a is the unit cell length

$$\text{and } M^2 = h^2 + k^2 + l^2$$

There are three types of cubic cells, primitive, face-centered and body-centered.

In a primitive cubic system the lattice points are located only at the corners. Face-centered cubic cells contain lattice points at the corners and at the centers of its six faces.

Body-centered cubic cells have lattice points at the corners and also the center.

These lattice points determine the lattice planes that are produced. Therefore, each cubic system has M^2 values that correspond to each diffraction powder line. The X-ray powder method consists of a strip of film which was enclosed in a cylinder. The resulting X-ray contains two bulls-eyes and specific diffraction powder lines. The X-ray beam enters at one bulls-eye, reflects off the powder sample, producing the diffraction lines, and exits at the other bulls-eye.

The concept of X-ray diffraction by crystal lattice structures is similar to the principle of light diffraction by a ruled grating. The angles of incidence and reflection are equal. Bragg defined the following relationship between this angle and the wavelength of the X-ray beam:

$$\lambda = 2 d \sin \theta \quad \dots(3)$$

The interplanar distance from equation two can be substituted in Bragg's equation to derive the following linear equation:

$$(4 \sin^2 \theta)/\lambda^2 = (h^2 + k^2 + l^2)/a^2 \quad \dots(4)$$

Using θ from the diffraction pattern and a graph of $(4 \sin^2 \theta)/\lambda^2$ vs $h^2 + k^2 + l^2$, the correct Miller indices series resulting in a straight line verifies the type of cubic system present. The unit cell length can be calculated from the slope, which is $1/a^2$.

6. Simple inorganic molecules. By X-ray study, it becomes possible to elucidate the structure of a crystal of a given type of compound by the radius ratio is calculated if the ionic radii are known. This radius ratio is known as the limiting radius r^+/r^- where r^+ = radius of the cation and r^- = radius of the anion.

For each co-ordination number and geometry of the ionic crystal the value of radius ratio is calculated if the ionic radii are known. This radius ratio is known as the limiting radius ratio. If the radius ratio of an ionic crystal falls below the limiting radius ratio, then the structure is unstable.

Co-ordination numbers of 1, 4, 6, and 8 are common, the appropriate limiting radius ratio can be worked out and their corresponding shapes may be predicted. The information is shown in table I.

Table I

Co-ordination number	Shape	Limiting radius ratio
2	Linear	0 to 0.155
3	Plane triangle	0.155 to 0.225
4	Tetrahedral	0.225 to 0.414
4	Square planar	0.414 to 0.732
6	Octahedral	0.414 to 0.733
8	Body-centered cubic	0.732 to 1.000

Let us now apply the concept of radius ratio to the different examples.

- (i) The radius ratio of sodium chloride is 0.52. It appears from table I, that it should have octahedral arrangement. Experimentally, it has been found to be so.
- (ii) In zinc sulphide, the limiting radius ratio is 0.40. This suggests a tetrahedral arrangement in which each Zn^{+2} ion is tetrahedrally surrounded by four S^{2-} ions and each S^{2-} is tetrahedrally surrounded by four Zn^{2+} ions. Actually, this has been found to be so.

- (iii) In caesium chloride, the radius ratio is 0.98, indicating a body centered cubic arrangement where each Cs^+ is surrounded by eight Cl^- ions and vice versa. This has been confirmed experimentally.

From the above examples, it appears that radius ratios values are useful. But it is reported that they do not apply with great accuracy. This is only to be expected because the whole conception of ionic radius is based on the spherical nature of an ion which is only an approximation.

7. Isomerisation: Two compounds having analogous formulas (e.g. the pairs of compounds NiF_2 I CaO and CaF_2 I ThO_2) and related structures are said to be isomorphous. Isomorphous compounds give similar X-ray powder patterns. Thus, if a compound can be shown to have a powder pattern like that of another compound of known structure, the structure of the first compound is probably the same. For example, Donoghue and Drago (1982) reported that the powder pattern of $\text{Ni}[\text{OP}(\text{NMe}_2)_3] (\text{ClO}_4)_2$ is the same as that of the corresponding zinc compound. It was argued that because the $\text{OP}(\text{NMe}_2)_3$ groups are undoubtedly tetrahedrally grouped around the zinc atom in the zinc compound, the same sort of structure exists in the nickel compound. One must use this technique with caution. For instance, the zinc and copper (II) dithiocarbamates have the same unit cell and space groups but there are important differences in structure between these complexes.
8. Ions of Oxyacids. X-ray diffraction has been used to study the crystal structures of a number of oxysalts of non-metals like C, N, S, P, etc. This study shows that NO_3^- and CO_3^{2-} ions are planar, ClO_3^- , BrO_3^- and SO_3^{2-} ions are pyramidal while PO_4^{3-} , SO_4^{2-} , CrO_4^{2-} , ClO_4^- and MnO_4^{2-} are tetrahedral.
9. Hydrogen bonds. In the usual methods of X-ray diffraction, the position of the hydrogen atoms in a crystal are difficult to determine directly unless very accurate data are available and the other atoms in the crystal are not too heavy. However, their positions may be inferred indirectly in the following way:

When the distances between certain pairs of atoms are unusually short, and the numbers of these short distances correspond to the number of hydrogen bonds required by the formula, then the short distances may be considered to indicate the positions of hydrogen bonds. For example



Dr. Naresh Kumar, passed the both the B.Sc.(Hons.) in Chemistry examination in 1983 ,and M.Sc. (specialization in Inorganic Chemistry) examination in 1985, standing First Class from Lalit Narayan Mithila University, Darbhanga. He received his Ph.D degree from the same University on 'X-Ray Structure of Organometallic Complexes'. He has published more than 25 papers in the field of Organometallic Compound & Environmental Chemistry in reputed Journals and has supervised 11 Ph.D Students. Dr. Kumar is presently working as a Associate Professor of Chemistry in University Department Of Chemistry in B. N. Mandal University, Madhepura (Bihar)-852113. His research interest is in Coordination Chemistry and Environmental Chemistry.