Chapter 1: Fundamentals of X-ray crystallography

Exercise 1.1

Why are X-rays used, rather than any other part of the electromagnetic spectrum, for crystal structure determination? Why is it not possible to build and use an X-ray microscope to observe molecules directly? Why is a single crystal used for the experiment?

X-rays have a wavelength comparable to the sizes of atoms and molecules and the distances between these components in a crystal structure, so they give significant and useful diffraction effects.

X-rays, unlike visible light, cannot be refracted by any known optical lens system except in very special circumstances, so there is no practical way to focus the diffracted X-rays to form an image in the same way that occurs for visible light in a normal microscope.

A single crystal consists of very large numbers of identical molecules (or molecules and their mirror images) arranged in a regular way on a three-dimensional lattice. The molecules are thus held in place so that their positions in the crystal structure can be determined by X-ray diffraction, and their combined cooperative scattering of X-rays gives sufficient intensity to be measured reliably. This would not be the case for a single molecule.

Exercise 1.2

For the cubic crystal system, many calculations are easier than in lower-symmetry systems. For example, the spacing of lattice planes d_{hkl} is simply $a/\sqrt{(h^2 + k^2 + l^2)}$. For a cubic unit cell with $a = 10$ Å, calculate the d spacings for the lattice planes (1 0 0), (2 0 0), (0 2 0) and (1 1 1). Using the Bragg equation (1.3), calculate the Bragg angle θ for the reflections from these lattice planes, with an X-ray wavelength $\lambda = 0.7$ Å.

(1 0 0): $d_{100} = 10/\sqrt{(1 + 0 + 0)} = 10/1 = 10$ Å

(2 0 0): $d_{200} = 10/\sqrt{(4 + 0 + 0)} = 10/2 = 5$ Å

(0 2 0): $d_{200} = 10/\sqrt{(0 + 4 + 0)} = 10/2 = 5$ Å [The same would be true for (0 0 2)]

(1 1 1): $d_{111} = 10/\sqrt{(1 + 1 + 1)} = 10/\sqrt{3} = 5.774$ Å

Bragg equation: $\lambda = 2d\sin\theta$ so $\sin\theta = \lambda/2d$

(1 0 0): $\sin\theta = 0.7/(2\times10) = 0.035$ $\theta = 2.01°$

(2 0 0) and (0 2 0): $\sin\theta = 0.7/(2\times5) = 0.07$ $\theta = 4.01°$

(1 1 1): $\sin\theta = 0.7/(2\times5.774) = 0.0606$ $\theta = 3.48°$

Exercise 1.3

What is the smallest observable d spacing in a diffraction pattern measured with X-rays from a copper target ($\lambda = 1.54184$ Å)? What implication does this have for the feasibility of resolving individual atoms in an electron density map?

$\lambda = 2d\sin\theta$ so $d_{\min} = \lambda/(2\sin\theta_{\max}) = \lambda/2 = 0.77092$ Å [$\sin\theta$ is a maximum of 1 when $\theta = 90°$]

Since no bond length is as short as 0.77 Å, atoms can be resolved as individual electron density maxima if data are measured to Bragg angles approaching 90°. In practice a maximum Bragg angle of around 70° is usually adequate for ordered structures with copper radiation.

Exercise 1.4

The complex [($C_{18}H_{18}N_4S$)$HgBr_2$] (relative molecular mass 682.8) crystallizes from solution in acetonitrile (CH_3CN) to give triclinic crystals with a unit cell volume of 1113.5 Å^3 and with a density of 2.16 g cm^{-3}. Calculate the number of molecules of complex per unit cell and the number of molecules of solvent per unit cell.

Density = unit cell mass / unit cell volume = ($M \times Z$) / (V × Avogadro's number)

$2.16 = (682.8 \times Z) / (1113.5 \times 10^{-24} \times 6.022 \times 10^{23})$ g cm^{-3}

So $Z = 2.16 \times 1113.5 \times 10^{-24} \times 6.022 \times 10^{23} / 682.8 = 2.12$

This is not a whole number, so there is presumably solvent present.

Assume $Z = 2$, so the true molecular mass of the asymmetric unit = $DVN_0/Z = 724.2$

This is 724.2−682.8 = 41.4 more than the molecular mass of the complex.

Molecular mass of acetonitrile is 41.1, so there is one molecule of solvent per molecule of complex.

Answer: the unit cell contains 2 molecules of complex and 2 molecules of acetonitrile solvent.

Exercise 1.5

A compound of supposed formula $K^+[In(NCS)_4(bipy)]^-$, where bipy is the chelating ligand 2,2′-bipyridyl, is obtained from solution in THF (C_4H_8O) as monoclinic crystals with a = 14.985 Å, b = 17.375 Å, c = 16.437 Å, β = 92.23 Å. The density of the crystals is 1.40 g cm^{-3}, and the relative molecular mass for the above formula is 542.4. Calculate the unit cell volume and deduce the number of cations and anions per unit cell (expected values are 2, 4 or 8) and the number of molecules of THF per cation (which are likely to be coordinated to it).

Unit cell volume $V = abc \sin\beta = 14.985 \times 17.375 \times 16.437 \times \sin 92.23 = 4276.4$ Å^3

Using the same method as for Exercise 1.4,

$Z = 1.40 \times 4276.4 \times 10^{-24} \times 6.022 \times 10^{23} / 542.4 = 6.65$

The correct value must be 4, so the true molecular mass of the asymmetric unit is

$1.40 \times 4276.4 \times 10^{-24} \times 6.022 \times 10^{23} / 4 = 901.3$

901.3 – 542.4 = 358.9 which is the mass of 5 molecules of THF (72.1 each)

Thus, there are 4 cation-anion pairs in the unit cell, and each cation is coordinated by 5 THF molecules as ligands.