# Chapter 4: Related topics

## Exercise 4.1

What advantages would there be in the use of neutron diffraction for crystal structure determination of each of the following with one exception, and why would X-ray diffraction be preferable for that one case?

a) The product of a reaction of an organic compound with $D_2O$ in a study of stereochemistry.

b) A polynuclear osmium carbonyl complex in which differences in the C–O bond lengths of terminal and bridging ligands is of importance.

c) A natural product containing C, H, N, and O for which the chemical identity needs to be confirmed.

d) An aluminosilicate mineral which may have the framework Al and Si atoms ordered or disordered.

e) A platinum complex of a boron hydride which may involve Pt–H–B bridging bonds.

a) If the point of the experiment is to identify the sites of deuteration, i.e. to distinguish between H and D atoms, then neutron diffraction is essential: these isotopes are indistinguishable by X-ray diffraction (as are isotopes of any element).

b) X-ray scattering by Os is much stronger than by C and O atoms, so the lighter atoms will be located with relatively low precision, as will the distances between them. These high s.u. values may mask genuine differences between terminal and bridging carbonyl bond

lengths and will certainly reduce their statistical significance. Use of neutron diffraction avoids this problem, as the scattering by the various elements present is much more nearly equal.

c) There is no advantage in using neutron diffraction here; X-ray diffraction is simpler and more economical, and will provide the required information.

d) Al has 13 electrons and Si has 14; the difference in their X-ray scattering factors is therefore quite small, and it is likely to be difficult on the basis of electron density alone to distinguish Al and Si atoms or to decide whether they are disordered over common sites (differences in Al–O and Si–O distances may help to some extent). The neutron scattering factors of Al and Si are in the approximate ratio 1:1.44, sufficiently different for a clear distinction between atoms of the two elements.

e) H atoms have so little electron density that they are located with only low precision by X-ray diffraction; in addition, the centroid of the electron density distribution is often displaced from the position of the nucleus by valence effects. The problem is even greater in a case like this, where heavy atoms (Pt, 78 electrons) are present and dominate X-ray scattering: H atoms close to Pt may be masked by electron density artefacts in the Fourier calculations, caused by imperfect absorption and other corrections, by other systematic errors, and by Fourier series termination (the fact that the reverse Fourier transform has a finite rather than infinite number of contributions, often leading to apparent electron density 'ripples' around heavy atoms). Neutron diffraction will give a more accurate and more precise result for the location of the H atoms.

## Exercise 4.2

Why might neutrons be preferable to X-rays as the radiation source in the structural study of samples contained in special apparatus for controlling the sample environment, such as some high-pressure cells or devices for maintaining a particular gaseous atmosphere? Why are air-sensitive crystals sometimes encased in a vanadium capsule for neutron diffraction study?

Absorption of neutrons by any material is considerably lower than absorption of X-rays. This is true not only of the sample under investigation, but also of any other material intercepting the incident and diffracted beams of radiation. Absorption by sample environment cells is often a significant problem in X-ray diffraction (both overall and in variation with direction), but not in neutron diffraction.

Vanadium has a neutron scattering factor close to zero. This is, of course, a problem if a vanadium-containing compound is to be investigated with neutrons, but can be exploited in using vanadium as a material for encasing air-sensitive samples.

## Exercise 4.3

Why does a powder diffractometer usually include provision to rotate the sample around one axis, but only one?

Rotation of a powder sample effectively increases the randomness of orientation of the individual microcrystal grains, especially when these grains are tiny needles or plates giving

preferred orientation, and thus improves the powder pattern by minimizing variation of intensity with direction at each Bragg angle.

It is mechanically simple to provide rotation of the sample about one axis (especially one coincident with the rotation axis for the detector, i.e. the $2\theta$ axis). Rotation about other axes would be more difficult and would probably interfere with any devices for control of temperature, sample environment, etc. as well as the detector.

## Exercise 4.4

What difference would twinning make to a powder diffraction pattern?

Twinning leads to overlap of reflections that are not symmetry-equivalent but have the same Bragg angle. Such reflections are overlapped anyway in powder diffraction, so twinning makes no difference.

## Exercise 4.5

Use equation 2.1 to calculate the approximate relative scattering power of crystals of the following materials, assuming all the crystals to have the same volume; this serves to illustrate some of the difficulty encountered in macromolecular crystallography and the reason why even tiny crystals of simple compounds can readily be studied with synchrotron radiation. For simplicity, consider all atoms present to be carbon.

- Diamond, with 8 atoms in each cubic unit cell, $a$ = 3.57 Å.

- A benzene solvate of buckminsterfullerene, $C_{60}{\cdot}4C_6H_6$ (ignore the H atoms), with $Z$ = 2 in a triclinic unit cell of volume 2294 Å$^3$.
- A protein with about 300 amino acids (2750 atoms), $Z$ = 4, in an orthorhombic unit cell, $a$ = 50.1, $b$ = 67.2, $c$ = 92.2 Å.

The relative scattering power (equation 2.1) is $(V_{crystal}/V_{cell}^2) \times \Sigma f^2$ with the sum taken over the contents of the complete unit cell. Here we assume the same crystal volume in each case, so the variables are the unit cell volume and the sum of $f^2$ for the unit cell contents. Considering only carbon atoms, this sum is simply proportional to the number of C atoms in the unit cell, $N$, and we need only to calculate $N/V^2$ where $V$ is the unit cell volume.

- Diamond: $8 / 3.57^6$ $= 3.86 \times 10^{-3}$ $\propto$ 34,000
- Fullerene solvate: $2 \times 84 / 2294^2$ $= 3.19 \times 10^{-5}$ $\propto$ 280
- Protein: $4 \times 2750 / (3.10 \times 10^5)^2$ $= 1.14 \times 10^{-7}$ $\propto$ 1

This simple calculation should provide a convincing demonstration that the unit cell volume, which reflects the size of the molecules present, is a dominant factor influencing the intensity of the diffraction pattern.