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PERSPECTIVE

Synchrotron chemical crystallography

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Recent years have seen a considerable development in the availability of single-crystal diffraction facilities with synchrotron radiation for use in non-biological crystallography, with access to several suitable beam-lines around the world. These can markedly extend the range of materials for which a full crystal structure can be determined, particularly in terms of micro-crystalline samples. Special features of synchrotron radiation such as X-ray wavelength tunability can be exploited. This article explains some of the important relevant properties of synchrotron radiation, demonstrates the importance of these facilities for chemists interested in structural characterisation, and provides examples of results from areas of topical concern, including microporous materials, pharmaceuticals, and supramolecular chemistry.

1 Introduction

There can be no disputing the immense importance of crystal structure determination in modern chemistry and the impact this powerful technique has had in the subject over the last few decades. Open the pages of *Dalton Transactions* at random, or any other major inorganic chemistry research journal, and the probability is high that one or more molecular structures obtained by X-ray diffraction will appear. Similar results are less prominent in organic publications, but this is partly due to different journal policies, whereby crystal structures are more often squeezed into footnotes or relegated to deposited supplementary material; it is still true that many of these structures would remain a mystery if investigated only by "sporting" spectroscopic methods, and the pharmaceutical industry, among others, relies heavily on crystallographic characterisation in order to be fully assured of the nature of its products.

X-Ray crystallography, more specifically the diffraction of X-rays by single-crystal samples, for which the more convenient if old-fashioned sounding and not entirely synonymous term "chemical crystallography" will be used in this Perspective, has made enormous strides forward since its introduction in the early part of the twentieth century, and its present speed and effectiveness would be unrecognisable to its first pioneers. Its development and success, and the fundamental part it continues to play in the detailed structural characterisation of a wide range of solid-state materials, both molecular and non-molecular, are reflected in the high proportion of Nobel Prizes which have been awarded for work which includes, in many cases predominantly, crystallographic research. It is regarded by many now as a routine, almost automatic, "black box" or "push button" technique, a view with some justification but also a dangerous one.[1] It is true that a complete structure determination, from the production of a freshly prepared sample to the generation of a detailed full-colour molecular graphics representation and extensive tables of geometry, can often be achieved easily within a single working day under favourable circumstances. This is by no means always the case, however, and the rapid and dramatic improvements in the experimental and computational aspects of crystallography in recent years have also opened up opportunities to tackle problems that were unthinkable previously, providing new and exciting challenges even for the expert practitioner.

Probably the most important developments in chemical crystallography in the last few years have been the enormous increase in low-cost computing power, speed and data storage capacity; the exploitation of these by increasingly sophisticated and automatic software for machine control, structure determination, graphics, and databases; the availability of reliable low-temperature equipment for data collection, making this essentially a routine procedure; the widespread introduction of area detectors in fully configured turnkey commercial diffractometer systems; and the use of high-intensity X-ray sources. In the last of these areas, developments in laboratory sources have


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William (usually called Bill) Clegg was born in 1949 in Lancashire and obtained degrees at the University of Cambridge. Apart from six years working with George Sheldrick in Göttingen, Germany, where he completed his Habilitation in the standard German pattern, he has spent his career at the University of Newcastle, where he currently holds a personal Professorship. In the last few years he has been closely associated with Daresbury Laboratory in Cheshire, the home of the UK Synchrotron Radiation Source, and has held a Joint Appointment there, leading a highly successful EPSRC-funded project to construct and commission a high-flux single-crystal diffraction facility for chemical and materials crystallography. He has particular interests in the development of crystallographic methods, especially in diffraction data collection, and carries out structural studies of a wide variety of organic, inorganic and organometallic materials in collaboration with research groups in Newcastle, elsewhere in the UK, and in other countries, as well as conducting some synthetic research in coordination chemistry. He is an author of nearly 700 research publications and of an undergraduate textbook on Crystal Structure Determination, and is jointly leading the editorial team of the new Acta Crystallographica Section E, a purely electronic journal being launched for 2001. He is married (Silver Wedding in 2000), with four children, who are all pursuing studies in science, engineering and medical subjects.

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included greater efficiency and reliability of rotating-anode generators, the introduction of new types of X-ray optics for concentrating and focusing beams, and new microfocus X-ray tubes.[2] These lead to increases of 1–2 orders of magnitude in intensity compared with conventional X-ray generators and tubes in use for several decades. In this Perspective we are concerned with the much greater intensities, together with other desirable and interesting properties, that can be achieved by the use of synchrotron radiation (SR).

Why is this of interest for chemists? Traditional chemical crystallography facilities have served us well for a long time. Demands on its capabilities, however, are constantly growing, not only in terms of the rate at which new materials are prepared, for which a definitive structure determination is wanted (a quantitative issue), but also in the feasibility of carrying out chemical crystallography with such samples (a qualitative issue). Examples of major growth areas in chemistry and materials science that are increasingly producing challenging samples are microporous solids and supramolecular assemblies of various kinds. In both of these broad areas it is often difficult to prepare single crystals of adequate size, say 0.1 mm upwards, for study with conventional equipment, and structures may include significant regions of disorder, such as in cavity template molecules and loosely held solvent of crystallisation or other guest species within a host framework. Molecules requiring structural characterisation can be very large, even outside biological macromolecule research areas beyond the scope of this review; this trend in synthetic interests is further encouraged by the growing use of area detectors in crystallography, which means that data collection times are no longer dictated by the sheer number of X-ray reflections which need to be measured one by one. The intensity of diffracted X-rays, however, decreases rapidly as the size of the structure increases (a more detailed consideration of this effect is given later), adding to the other factors producing relatively weak diffraction patterns.

With such demands, the limits of conventional laboratory facilities for chemical crystallography are reached and exceeded. They have been pushed outwards significantly by the recent charge-coupled device (CCD) area-detector revolution, and the available higher intensity laboratory X-ray sources certainly help, though at a considerable financial cost; these improvements have brought benefit to many groups worldwide.

When single crystals of reasonable size are unavailable for a particular material, it is sometimes possible to determine the crystal structure *ab initio* from powder diffraction data obtained from a microcrystalline sample. This is an important application in which huge advances are currently being made, but the compression into one dimension of data which would be three-dimensional with a single crystal sample introduces serious overlap problems and ambiguities of interpretation, and only relatively small structures can yet be confidently tackled in this way.[3] Even here, SR has considerable advantages over conventional X-ray sources, because of the marked improvement in resolution of the diffraction patterns, but that, as well as the use of neutron powder diffraction, is another story! It certainly does not detract much from the need for SR single-crystal diffraction.

2 Some synchrotron radiation fundamentals

Many chemists and other scientists who could benefit from appropriate SR facilities are probably discouraged by its perceived complication, incomprehensibility, and the exclusive culture of "SR-Speak" surrounding it. This does not have to be the case. After all, the analogous and probably even greater jargon permeating computers has not kept current generations from exploiting them very effectively. I have to admit to being quite baffled in my first experiences with SR applications and it has been necessary to learn many new concepts and important factors in order to promote a major project using it, but only a low-level understanding is really necessary for the purposes of this Perspective, including an explanation of some of the commonly used terms.

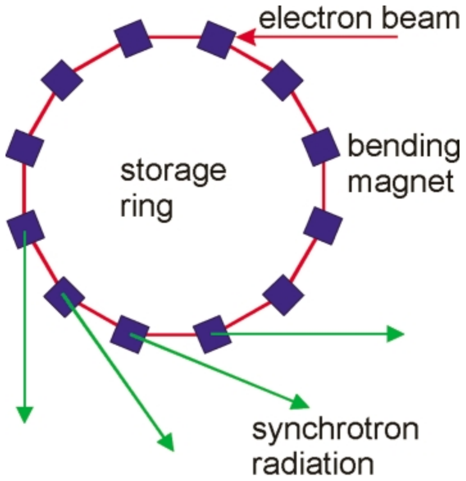

Fig. 1 Schematic diagram of a second-generation storage ring showing the tagential output of synchrotron radiation from bending magnets.

The phenomenon of synchrotron radiation was first observed around 50 years ago, as an unwelcome by-product of high energy physics research with particle accelerators, and its history over the intervening period has been summarised.[4] Acceleration of electrons (or positrons) in magnetic fields causes them to emit electromagnetic radiation over a wide range of the total spectrum, and this represented an undesirable loss of energy, quite apart from health and safety issues. Synchrotrons were (and still are) a particular kind of particle accelerator using complete circular orbits, in which the electron energy is varied and the electrons are used in collisions. The name "synchrotron radiation" has been retained, although SR is now produced deliberately from storage rings, in which a constant electron energy is maintained with maximum stability, and the electrons usually serve no other purpose than to generate the radiation. The first dedicated SR storage rings came into operation around 20 years ago, exploitation of SR before that being mainly parasitic on synchrotrons primarily built for high-energy physics. In this historical development, the terms "first generation" and "second generation" are used to refer to the original synchrotrons, used parasitically, and the succeeding dedicated storage rings, respectively.

A "basic" storage ring of this kind is shown in its simplest representation in Fig. 1. It consists of an array of several magnets, which constrain an electron or positron beam to move in a circular (more correctly, polygonal) path. The electron beam moves in a high vacuum pipe. At each bending magnet, which has its field perpendicular to the plane of the ring, the electrons change direction, being subjected to an inward radial acceleration. This produces electromagnetic radiation, which is emitted in a direction perpendicular to both the direction of acceleration and the magnetic field, hence at a tangent to the orbit. The loss of energy in this way has to be replenished, or the electron orbit would contract and collapse, and this is achieved by supplying an appropriate electromagnetic radiation input in one or more of the straight sections between bending magnets. "Appropriate" here means matched to the orbital period of the circulating electrons. These are moving at essentially the speed of light, there are usually many discrete bunches of electrons in the ring rather than a continuous stream, and storage rings are many metres in diameter, so the frequency with which bunches pass through a straight section corresponds to radio frequencies (tens or hundreds of MHz), and the energy compensator is a radio-frequency cavity. The emitted SR, however, is not in the radio-frequency spectral region. The

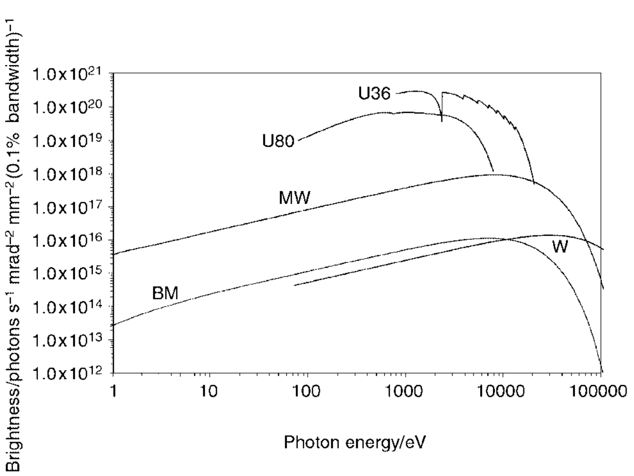

Fig. 2 Typical spectra (brightness against photon energy) of synchrotron radiation emitted by various types of magnetic device: BM = bending magnet, W = wavelength-shifting wiggler, MW = multipole wiggler, U = undulators with two different geometries.

relativistic properties of the electrons convert this into high harmonics, ranging from infrared through visible and ultraviolet, into the X-ray region, and their associated Heisenberg uncertainties mean that the observed output is a continuous spectrum across this wide range. The spectral distribution and its high-energy (low-wavelength) cut-off limit are determined by the operating parameters of the storage ring, particularly the electron energy, which is typically a few GeV (Fig. 2).

The straight sections of a storage ring contain other important devices for monitoring, steering and focusing the electron beam in order to maintain a stable and predictable orbit. It is also necessary for electrons to be injected into the ring at some point from a linear accelerator to start the process and to compensate for losses, for example through collisions with residual gas molecules in the imperfect vacuum, which lead to a steady decay in the SR intensity.

There are numerous uses, such as in spectroscopy and lithography, for the intense radiation emitted in the IR, visible, UV and soft X-ray regions (up to a few keV in photon energy, or down to a few Ångstrom units in wavelength), but for crystallography we need “hard” X-rays of energy 8 keV upwards (λ below about 1.5 Å). A simple storage ring using bending magnets with an operating electron energy of about 2 GeV gives a spectrum in which the intensity rapidly drops off at these higher energies. Additional magnetic components are required to extend the energy range and increase the intensity of SR at the upper end of the spectrum. The simplest such device is a set of three magnets that deflect the electron beam passing through one of the straight sections, send it round a small curve, and return it to its original path. This is called a wiggler, for obvious reasons, or a wavelength shifter. It causes extra SR emission from the electron path wiggle, and this is shifted to higher photon energy (shorter wavelength) than the bending magnet SR output, the extent of the shift being determined by the radius of curvature of the small wiggle (Fig. 2). A higher magnetic field is needed than for the bending magnets; for example at the Daresbury Laboratory SRS (Synchrotron Radiation Source), the 16 bending magnets have 1.2 T fields, and there are two wavelength shifting wigglers with fields of 5 and 6 T.

A storage ring can thus be thought of, in very simple terms, as a device that exploits relativity to convert what is, for crystallography, useless radio-frequency energy into useful X-rays, by means of what is effectively a massive doppler shift.

A wavelength-shifting wiggler is an example of an insertion device, a special magnetic component inserted into a straight section of a storage ring to produce enhanced SR with particular desirable properties, in this case shorter wavelengths. Other kinds of insertion devices have been developed, which are more complicated, consisting of many magnets, all having the property that they return the electron beam to its original direction after some kind of excursion. The most commonly used devices are multipole wigglers and undulators, both of which induce a periodic wave movement for the electrons. The total combined SR generated from the many wiggles has a much boosted intensity compared with the bending magnet SR as well as changes in the spectral distribution. The main difference between multipole wigglers and undulators is the extent to which constructive interference is generated by the radiation from successive wiggles, and this affects the spectral distribution; undulator SR has a marked wavelength-dependent structure, some particular wavelengths being of very high intensity. Both devices can be used for generation of X-rays for crystallography (Fig. 2). Third generation storage rings are those in which insertion devices provide the most important SR output, and they produce X-rays of shorter wavelength and considerably higher intensity than second generation machines. The next, fourth, generation being developed currently is based on the principle of the Free Electron Laser, but for practical crystallography, this is a future prospect rather than a current reality.

So much for the origin and basic nature of SR. What are its properties, compared with those of a conventional laboratory X-ray source? There are a number of differences; some of them are important for chemical crystallography, while others are less relevant or even disadvantageous, though not greatly so.

The feature of SR that is of particular interest for chemical crystallography is its very high intensity compared with conventional sources. There are various formal measures of intensity, depending on the factors that matter for an experiment: flux is the number of photons per second in a beam of radiation, but taking into account also the cross-sectional size of the beam, its angular divergence or convergence, and the distribution of the intensity across the wavelength spectrum, terms such as brightness and brilliance are also used. What matters for our purposes is the selection of a very narrow range of wavelengths (treated as a single known wavelength, *i.e.* a monochromatic beam of X-rays) and the concentration of its total flux into a cross-sectional area similar to that of a typical sample crystal. This is achieved with optical components (monochromators and mirrors), the detailed workings of which are not important here. A monochromator is itself a single crystal (often of silicon or germanium), which selects one wavelength of X-rays from the SR spectrum by diffraction; a similar method applies in conventional laboratory equipment, but a SR monochromator has to withstand a much greater incident flux and hence heat loading, and often also serves a beam focusing purpose by being slightly bent. Long mirrors exploit glancing angle reflection (refractive index for X-rays slightly smaller than unity) to provide further focusing effects and rejection of harmonics of the desired wavelength produced in the monochromator ($\lambda/2$, $\lambda/3$, *etc.*). These components make a SR diffraction station look very large compared with a standard laboratory system, and this contrast is further enhanced by the need for the whole set of equipment to be reliably enclosed for radiation protection of its users, involving lead-lined rooms with safety interlocks. The essential net result of all this is an X-ray beam several orders of magnitude more intense than the most powerful conventional laboratory source (high flux).

This raw intensity gain is by no means the only advantage. The relativistic origin of SR means that the beam of radiation is naturally highly collimated, and modern high-stability storage rings provide beams that are very narrow (high brightness and high brilliance, not just high flux). Adjustment of the optics components on a beam-line can further tailor the beam dimensions to suit the sample size. The high degree of collimation, considerably surpassing what is obtained from a standard laboratory X-ray generator (though these can also be improved by focusing optics), means that diffraction peaks are usually substantially narrower in their angular spread, the width being almost entirely dictated by the sample crystal quality. This makes them stand out more clearly from the general background, just as narrower peaks are clearer in a spectrum obtained with a high-resolution spectrometer.

A standard laboratory X-ray tube produces just a few characteristic wavelengths depending on its target material, the most intense of which is generally selected and used for crystallography (Cu-Kα with $\lambda = 1.54184$ Å and Mo-Kα with $\lambda = 0.71073$ Å are the most commonly used). With SR X-rays, any wavelength can be chosen from the range available, though not all with equal intensity, subject to the mechanical limits of adjustment of the monochromator and other components. There may be reasons for choosing a particular wavelength, such as the exploitation of anomalous dispersion effects for distinguishing different elements or even different oxidation states of the same element (see section 5g). A longer wavelength usually gives more intensity and better angular resolution of individual diffracted beams (X-ray reflections) for samples with large unit cells. A shorter wavelength reduces absorption and extinction effects, which are causes of systematic errors in measured data, and compresses the diffraction pattern into a smaller angular spread, so that more reflections can be measured with a single position of an area detector; both of these points can be important for high-resolution charge-density studies (see section 5g) and for samples investigated at high pressure (see section 5e).

Synchrotron radiation is essentially totally polarised in the plane of the storage ring (the actual situation at the sample depends on the various optic elements in the beam). This property has to be correctly handled in the conversion of raw measured intensities into corrected data for structure determination, but its main practical effect is that diffraction data should be measured with vertical rather than horizontal deflection from the primary beam direction to avoid major intensity loss. This means that diffractometers have to be operated 'on their side' relative to standard laboratory usage, and this usually entails mechanical modifications such as counter-weights on heavy detectors, which are moved in a vertical rather than a horizontal plane.

Owing to the bunches of electrons circulating in a storage ring, SR is actually not continuous, but has a pulsed time structure, each electron bunch producing a discrete pulse of radiation as it passes a bending magnet or insertion device. The precise pulse pattern and rate are determined by the storage ring operating parameters, and tend to be in the picosecond to nanosecond range for pulse length and separation. Larger interpulse intervals can be achieved by operating with only a single bunch of electrons with a concomitant reduction in overall intensity. Such a time structure is important for some spectroscopic studies, but it is irrelevant to most chemical crystallography experiments, in which even the shortest exposure times (seconds) usually encompass huge numbers of pulses, though some special techniques have been developed for investigation of excited state structures (see section 5g). The most important time dependence for chemical crystallography is the steady, approximately exponential, decay of the SR intensity as electrons are slowly lost from the circulating beam; this needs to be monitored and corrections applied to the measured intensities.

So what is the impact of these special properties of SR on chemical crystallography? For most users, the overriding factor of importance is the incident X-ray intensity that can be obtained at the sample. With an increase of several orders of magnitude compared with conventional laboratory sources, this makes feasible experiments that would otherwise be impossible. Samples which otherwise give no observable diffraction patterns have often been found to yield full structural results every bit as precise and reliable as are routinely obtained by standard chemical crystallography with normal crystals. The causes of weak diffraction are various, the most common one being very small crystals, with dimensions measured in microns. The availability of SR facilities thus greatly extends the range of materials that can successfully be studied.

The second most important property is the essentially free selection of wavelength, though the ease with which this can be done does depend on the particular set-up for each SR facility. The polarisation and time structure of SR are not usually of interest.

3 Worldwide SR facilities for chemical crystallography

SR storage rings are generally large-scale national or international facilities; they are growing in importance and usage because of continuing improvements in their design and performance and because of their unrivalled application in diverse fields of science and engineering. Particular impetus has been given to their use in recent years because they are an essential tool in modern structural biology and particularly in genome mapping projects; macromolecular crystallography stations are rapidly growing in number on existing and new storage rings around the world. Chemists have been well able to benefit from these developments in generating access to SR facilities for spectroscopic and diffraction purposes. There is a great deal in common between macromolecular and chemical crystallography in terms of the techniques, the equipment and the computing resources needed.

There are, however, relatively few single-crystal SR facilities worldwide for chemical crystallography. Most of them are shared facilities in the sense that a single end-user station on a storage ring beam-line is designed for a number of purposes, typically chosen from single-crystal diffraction, powder diffraction, small angle scattering, and EXAFS spectroscopy.

Examples are the ID11 and ID13 beam-lines at the European Synchrotron Radiation Facility in Grenoble, France (ESRF); the DuPont–Northwestern–Dow Collaborative Access Team (DND-CAT) beam-line and the ChemMatCARS CAT beam-line at the Advanced Photon Source, Argonne, USA (APS); some beam-lines such as X3 at the National Synchrotron Light Source, Brookhaven, USA (NSLS); the D3 and F1 beam-lines at HASYLAB, Hamburg, Germany; the 14A beam-line at the Photon Factory in Japan; and the crystallography beamline at MAX II in Lund, Sweden.

Of these, for example, the ESRF beam-lines support a range of techniques for analysis of materials, with a selection of diffractometers, detectors and sample mountings; the high brilliance of the source makes this particularly suitable for single-crystal diffraction by tiny crystals more generally thought of as powder grains, because of the special properties of such third-generation storage rings. The same applies to newer third-generation sources: the DND-CAT and ChemMatCARS facilities at APS, still being developed, include both single-crystal and powder diffraction, and the new crystal structure analysis beam-line (BL02B1) at SPring-8 in Japan has a specially designed seven-axis diffractometer with several types of detector in order to handle both powder and single-crystal samples.[5] No results other than preliminary commissioning tests have been published from these newer SR facilities yet, unlike the ESRF, which has been operating very successfully for several years and has led to numerous chemical crystallography results, some of which are given below.

Similar combinations of techniques are catered for at the other, older, sources listed above. There is a particular emphasis on high-resolution charge-density studies at NSLS (see section 5g), and this is also a significant component of the HASYLAB work. NSLS additionally includes time-resolved diffraction studies of electronically excited states.

The chemical crystallography station (9.8) at Daresbury SRS is unique in this respect, in that it is entirely devoted to single-crystal diffraction as a public-access facility, almost exclusively with routine use of a modern charge-coupled device (CCD) area detector. It was, in fact, originally designed to share its beam-line location with energy-dispersive powder diffraction, but its success and the high level of demand for it subsequently led to dedicated use; every available day of multi-bunch storage ring operation throughout the year is now allocated for this purpose, and oversubscription is likely to lead to the development of a second station, at least in part use with other techniques. It is expected that one or more equivalent stations, with appropriate updated equipment available at the time, will be included in the first set of operating stations on the new UK synchrotron source being constructed over the next few years at the Rutherford Appleton Laboratory.

This station at SRS is being used as a model for the planning and development of some other chemical crystallography SR facilities, such as on the new Canadian Light Source. There are prospects also for further chemical crystallography facility developments elsewhere, including the Swiss Light Source, Elettra (Trieste, Italy), and a possible new French storage ring Soleil.

4 The chemical crystallography facility at SRS

Station 9.8 at Daresbury SRS was designed, constructed and commissioned over the period 1993–1997. Before that, some chemical crystallography research was carried out by occasional parasitic use of one of the macromolecular crystallography stations.[6,7] The project was funded by UK research councils (EPSRC through a research grant and CCLRC through the allocation of substantial personnel and infrastructure resources) in response to a strongly expressed demand from a wide range of chemists, crystallographers, materials scientists and physicists. The design of the station was carried out by Daresbury scientists and engineers, led by Dr (now Professor) Bob Cernik, bringing together features that had successfully been developed for other SRS stations in previous years, such as the mounts for X-ray optic elements and the remote-controlled alignment table for the diffractometer. The constraints imposed by the restricted physical space available and its geometrical shape dictated some of the design features; greater optimisation will be possible in a *de novo* design for the new SR source. The scientific side of the project was led by myself, with Professor Richard Catlow of The Royal Institution as grant co-applicant, and assisted in some decision-making aspects by a management advisory panel of leading UK crystallographers. My involvement was enormously assisted by a three-year formal Joint Appointment at Daresbury, funded by CCLRC and providing effectively a 50% secondment from my University responsibilities.

The original proposal was for a conventional four-circle diffractometer to form the heart of the experimental set-up, with a choice of a high-speed scintillation detector for serial single reflection measurement and a commercial image-plate area detector for more rapid collection of many reflections simultaneously. By a happy conjunction of events and timing, the first complete commercial CCD area detector and diffractometer systems became available a little before a final decision had to be made on this aspect, and in a parallel development we had recently installed one of the first of these with a standard sealed-tube X-ray source in Newcastle and judged it a resounding success. Thus we were able with confidence to make the same equipment, with suitable minor modifications for SR use, the workhorse instrument on a more ambitious station 9.8.

The main features and components of station 9.8 have been described elsewhere,[8] and only a brief summary will be given here, concentrating on the relevance of these to the interests of chemical crystallography. These features are, to a large extent, common to other SR chemical crystallography stations elsewhere. The station takes its primary beam from a wavelength-shifting wiggler of the SRS. This means that the spectrum of radiation available is shifted towards shorter wavelengths (higher energies) than the output at the storage ring bending magnets. This matters because of the greater practical value overall of wavelengths <1 Å. Shorter wavelength X-rays are more penetrating, being less strongly absorbed by most materials, and this effect is particularly important for materials containing 'heavier' elements (more strictly correct, those with more electrons); depending on crystal size, absorption effects begin to become significant in the presence of elements of the second full row of the Periodic Table (from about Si to Cl) if $\lambda > 1$ Å, the significance declining as the wavelength is reduced. Absorption of X-rays is an undesirable but inevitable process occurring simultaneously with diffraction, and it represents a systematic error for the measured intensities. Corrections are possible, but they are generally not perfect, and it is always best to minimise the effect. In addition, shorter wavelengths lead to a compression of the diffraction pattern to smaller angles ($\sin \theta \propto \lambda$ from the Bragg equation), so more reflections can be measured for a given detector position, reducing the time required for a complete experiment or increasing the data coverage for a given time. The use of particular X-ray tube target materials in conventional laboratory equipment means that a few wavelengths are especially familiar (see Table 1, which also shows the equivalent photon energies, more commonly used than wavelength as units by SR specialists). By use of convenient geometric parameters of the diffractometer, a full data set to a generally acceptable resolution, related to the maximum measured Bragg angle, can be obtained at a single CCD detector position, with a wavelength similar to that of Mo-Kα radiation ($\lambda \approx 0.7$ Å). The characteristics of the station X-ray optic components is such that the incident intensity is relatively high (about 5–6 orders of magnitude more than laboratory sources) with this choice, and effective absorption corrections can usually be made for most materials at this wavelength. More strongly absorbing samples and some specialised experiments, such as charge density studies requiring very accurately measured higher resolution data, demand shorter wavelengths, where the disadvantage is a lower available X-ray flux. Alteration of the X-ray wavelength involves movement of optic components and the whole diffractometer to a different position, with consequent alignment and calibration procedures, and takes usually 1–2 hours with the particular configuration of this station, so it is not frequently undertaken; most measurements are made with $\lambda \approx 0.7$ Å.

Table 1 Commonly used X-ray wavelengths and corresponding photon energies

Radiation	Wavelength/Å	Photon energy/keV
Cu-Kα	1.5418	8.041
Mo-Kα	0.7107	17.444
Ag-Kα	0.5608	22.103

The diffractometer is a Bruker AXS SMART instrument with the original 1K CCD detector. It is turned on its side, with the ω and 2θ axes horizontal because of the polarisation properties of SR, the substantial weight of the detector being balanced by a system of pulleys and counterweights. Most other hardware and software features of the diffractometer are the same as in conventional laboratory settings, although some alignment operations, like all other procedures involving the use of the X-ray beam, must be carried out with no personnel present in the experimental hutch and so are under remote control, with SRS-designed computer interfaces.

Unless there are reasons to do otherwise (such as undesirable phase transitions or other physical changes on cooling), data collections are routinely carried out with the sample at low temperature, typically in the range 100–150 K. The improvement in data quality, especially with increased intensities at higher Bragg angles, brought about by reduced atomic motion on cooling, is well known, and it would be a travesty to throw away some of the advantages of expensive SR facilities through failure to use such simple and relatively cheap ancillary techniques. Station 9.8 uses the highly reliable and popular Cryostream cooler,[9] which consumes modest amounts of liquid nitrogen. For some specialised experiments, a high-temperature device of very similar shape and size, operating with heated dry air, is available; this was developed in collaboration with Oxford Cryosystems. Recent trials have been made with an open-flow helium cooling device, but this is not currently on offer for routine use. Some experiments have also been performed with high-pressure diamond anvil cells provided by individual user groups, with either the SMART system or an alternative Enraf-Nonius CAD4 diffractometer for measurement of individual reflections serially.

A complete suite of software is provided for the control of the diffraction experiment and for initial processing of the measured diffraction pattern, generating computer files of intensity data corrected for effects such as absorption and SR beam decay, ready for structure solution and refinement. Data archiving facilities are available, and some limited work is possible on structure determination from the measured data, though most of this is generally done in users' home laboratories later.

With the high intensity of SR, diffraction patterns can often be obtained in a much shorter time than in a normal laboratory, although the high degree of collimation of the synchrotron X-ray beam may mean a larger number of finer slices of the pattern need to be made, adding to the overheads of detector read-out time. It should also be noted that simply using higher intensity X-rays does not necessarily improve the overall resolution of the diffraction pattern. In cases of severe disorder or other major structural faults, little or no real improvement may be achieved. Typically at station 9.8, 3 or 4 data sets can be measured in a full day, including the not insignificant time needed to screen, select and mount crystals and check their suitability with preliminary measurements.

5 Some examples of SR chemical crystallography research

From the foregoing discussion, it should be clear that SR facilities for chemical crystallography can find application right across the whole range of organic, inorganic, organometallic and materials chemistry. Although this Perspective appears in a mainstream inorganic chemistry journal, it would be unduly narrow and unrepresentative to restrict examples to this part of chemistry. The detailed application of the techniques has some dependence on the type of material being investigated, but this is relatively minor; an X-ray diffraction pattern has, at least qualitatively, much the same kind of appearance whether the sample is a natural product, a coordination complex or a zeolite.

A number of examples are shown here, chosen to illustrate the wide range of application and the essentially universal impact of SR chemical crystallography across our subject, and to highlight some of the special features that can not be addressed by other techniques. Inevitably, given the unique nature of SRS station 9.8 as a dedicated single-crystal diffraction station and my own involvement in it, the majority of these examples are drawn from its output, particularly those that are illustrated graphically. There are, however, a number of results from other SR facilities, included particularly where these are unrivalled in some respect by the SRS work.

(a) Microporous materials

Microporous materials, whether of natural or synthetic origin, are of interest for their catalytic and shape-selective properties among other features. They include zeolites and aluminophosphates and are characterised by a relatively rigid and stable framework, usually of oxygen atoms alternating with atoms of other elements, enclosing pores, channels and other voids that may be empty or occupied by molecules and/or ions. Framework atoms may be ordered or may be subject to substitutional disorder. Synthesis is often by solvothermal methods, with a variety of small molecules present to act as templates directing the size and shape of voids and hence the framework structure.

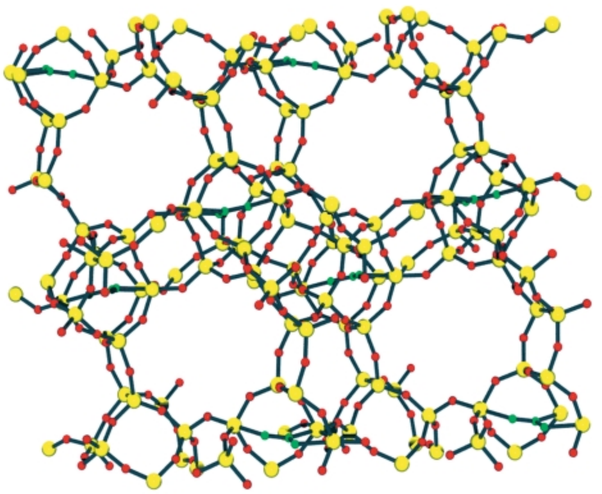

Fig. 3 SSZ23, an unusual zeolite as an example of microporous materials. The structure contains disordered fluorides in the framework and (not shown) organic template molecules in the cavities.

Such materials are commonly available only as very small crystals or in microcrystalline powder form. Structural characterisation often relies on X-ray and neutron powder diffraction, and this can be rendered more difficult by space-group ambiguities and pseudo-symmetry problems, as well as by the complexity of some structures. As such, they are ideal candidates for study by SR single-crystal diffraction; in many cases X-ray scattering efficiencies are quite high compared with molecular organics, because of the presence of reasonably electron-rich elements and rigidity of the structural framework, and relatively strong diffraction patterns can be obtained from crystals only a few microns in size.

In this context, it should be noted that diffraction intensities are proportional to $I_0 \cdot \Sigma f^2 \cdot V_{crystal}/V_{cell}^2$ for a given X-ray wavelength, where I_0 is the incident X-ray intensity, $V_{crystal}$ the sample crystal volume, and V_{cell} the volume of the crystallographic unit cell; f is the atomic scattering factor for X-rays by each atom in the unit cell. At zero Bragg angle this is equal to the atomic number (the number of electrons). The Σf^2 term in this expression is a reasonable approximation to a more rigorous treatment.[6] Microporous materials generally have only moderate unit cell volumes and have relatively high average f values for the framework atoms. Essentially the very high I_0 for SR X-rays compensates for the small crystal size $V_{crystal}$ to produce adequate diffracted intensities. For very simple small inorganic structures and for some minerals, the high value of the inherent X-ray scattering efficiency as measured by the term $(\Sigma f^2)/V_{cell}^2$ means that extremely small crystals can successfully be studied. Classic examples are LiF[10] and the mineral kaolinite,[11] which demonstrate the advantages of third generation SR sources for such extremely tiny crystals, sub-micron in some cases.

A good example of the application of SR for microporous materials is the discovery of the unusual structure of SSZ-23,[12] the first example of a zeolite containing rings with odd numbers of SiO_4 tetrahedra, in this case 9 and 7 (Fig. 3). Without the availability of this technique, it is unlikely that the structure of SSZ-23 could be established; it had already remained unsolved for a decade.

Template molecules in microporous materials are often disordered over various sites or different orientations, for example

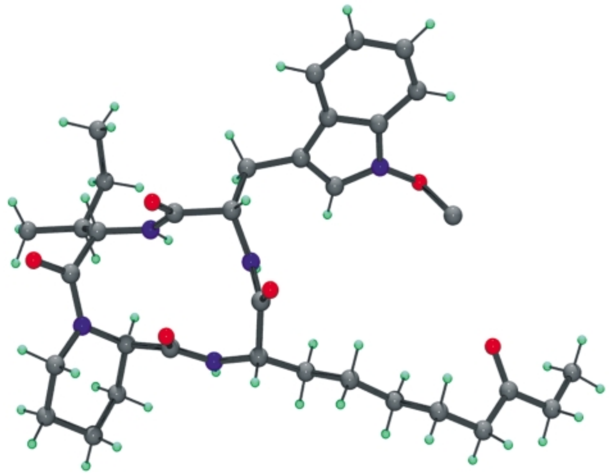

Fig. 4 The antiprotozoal natural product Apicidin as an example of pharmaceutical compounds. Only one of four crystallographically independent molecules is shown here.

a piperidylpiperidine molecule on a site of $\bar{3}$ (S_6) crystallographic symmetry in the aluminophosphate DAF5.[13] In favourable cases, however, ordered templates may be located precisely from good quality data obtained from microcrystals, even when they are twinned,[14] and many other examples of microporous structures have been reported from SR single-crystal data.[14]

(b) Pharmaceuticals

For patent and drug registration purposes it is essential to identify not only the chemical composition but also the crystal structure (or at least the unit cell parameters and preferably the space group) of a solid pharmaceutical material, because different polymorphs are considered to be different materials. It is, therefore, not surprising that pharmaceutical companies have been among the users of SR chemical crystallography facilities through the industrial DARTS service. Most of the commercial results are proprietary and can not be published prior to granting of patents. One example of a valuable structural result in connection with molecular modelling approaches to drug design is Apicidin (Fig. 4).[15] This structure was determined from tiny crystals giving relatively weak diffraction effects that were not measurable with laboratory equipment. In common with a number of other oligopeptides, the structure contains several chemically identical but crystallographically independent molecules in the asymmetric unit as well as some disorder, and this reduces the overall diffraction intensities according to the equation given earlier; even with SR data the structure proved difficult to solve.

Paracetamol (acetaminophen or *p*-hydroxyacetanilide) is one example of a pharmaceutical material that is known in more than one crystalline modification. Two forms have fully been characterised by crystallography.[16] Some very small crystals found in a commercial sample of paracetamol recrystallised from water were believed to be a previously unidentified third polymorph, but structure determination from SR diffraction data showed them to be instead an oxidatively coupled dimer, crystallised as a hydrate (Fig. 5).[17] The identification of this minor impurity would be difficult by other methods.

Another case involving very small crystals arose from an organised 'round-robin' exercise in *ab initio* structure determination from X-ray powder diffraction data.[18] One of the sets of data offered to aspiring structure solving practitioners was measured (by SR powder diffraction techniques) from a commercial sample of the antibiotic tetracycline hydrochloride. In order to provide a benchmark for comparison of results, one micro-crystal (*ca.* 0.02 × 0.03 × 0.04 mm) was selected from the powder sample and its single-crystal diffraction pattern was measured; it was important for this exercise to use precisely the same sample rather than a recrystallised one. The result was a well determined structure in which it was possible to refine all the hydrogen atoms freely, so that the tautomeric form of the protonated molecule, and its hydrogen bonding interactions, could be established unambiguously and without prejudice.[19]

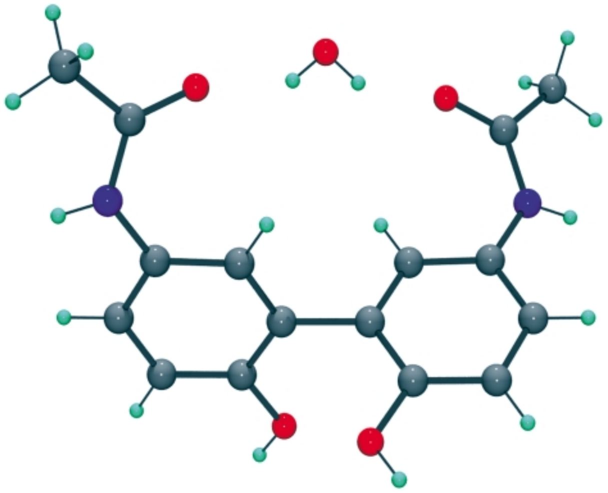

Fig. 5 An oxidatively coupled dimer of paracetamol, obtained in microcrystalline form as its monohydrate.

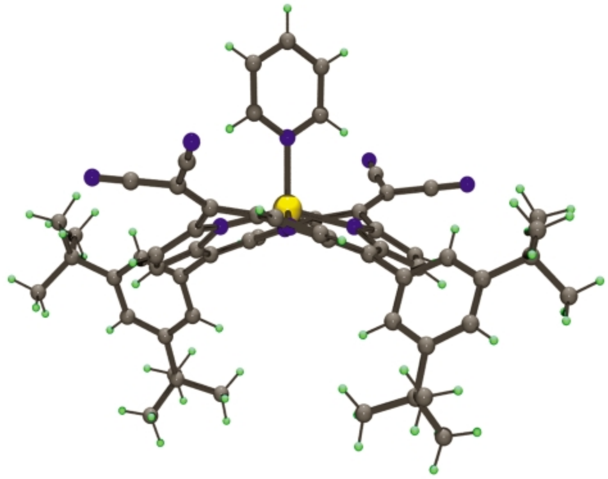

Fig. 6 A zinc porphyrin complex with a highly non-planar ring geometry.

These examples are typical of problems in pharmaceutical research, with various problems of small crystals, structural defects, and multiple molecules in the asymmetric unit, and show what can be achieved.

(c) Supramolecular chemistry

In the investigation of supramolecular assemblies and the interest in intermolecular interactions, structural disorder and the incorporation of significant amounts of solvent, itself often disordered, are recurring features. Very small and weakly diffracting crystals appear frequently, and the impact of SR chemical crystallography has particularly been marked and successful in this field of research.

Numerous porphyrin complexes prepared by several different research groups have been studied at Daresbury. Examples include uncomplexed porphyrins, complexes with various metals, and multiporphyrin arrays (Fig. 6).[20] Calixarene complexes have included a variety of metals, both main group and transition series (Fig. 7 and 8).[21] Complexes with ligands derived from nucleobases have conventional (in DNA terms) and unusual hydrogen-bond interactions.[22]

The non-covalent linking of molecules through mutual recognition leads to catenanes and rotaxanes with novel

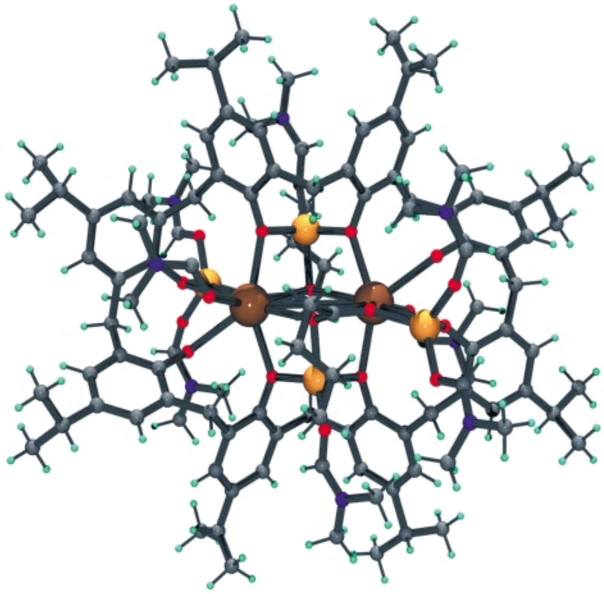

Fig. 7 A complex of *p*-isopropylcalix[8]arene encapsulating two strontium and four lithium ions. Minor disorder components of peripheral substituents are not shown.

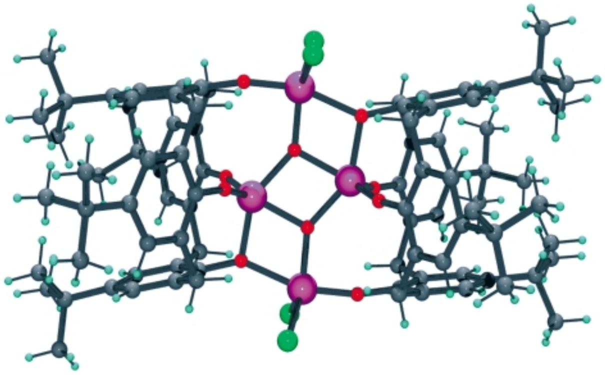

Fig. 8 A titanium oxo ladder structure stabilised by *tert*-butylcalix[4]-arene ligands.

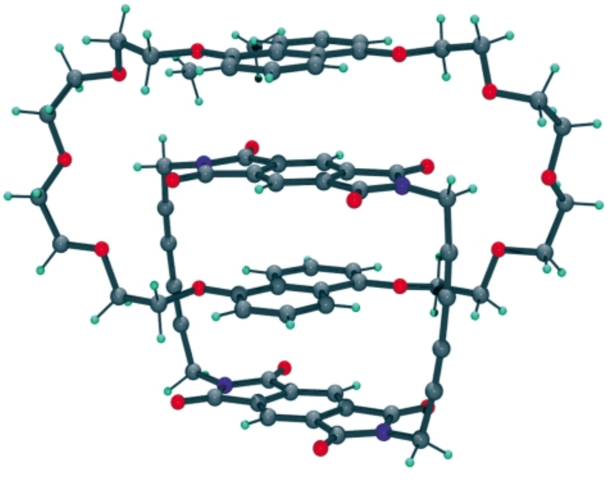

Fig. 9 A [2]catenane generated through the intermediacy of π-stacking interactions, which are maintained in the intermolecular packing right through the crystal. Disordered solvent molecules are not shown.

architectures, which would remain unknown or unconfirmed without access to SR facilities by a number of different research groups (Fig. 9).[23]

Hydrogen bonding has been found to act as a means of linking together simple metal complexes with counter ions in polymeric chains, as well as its more commonly observed role in organic structures.[24]

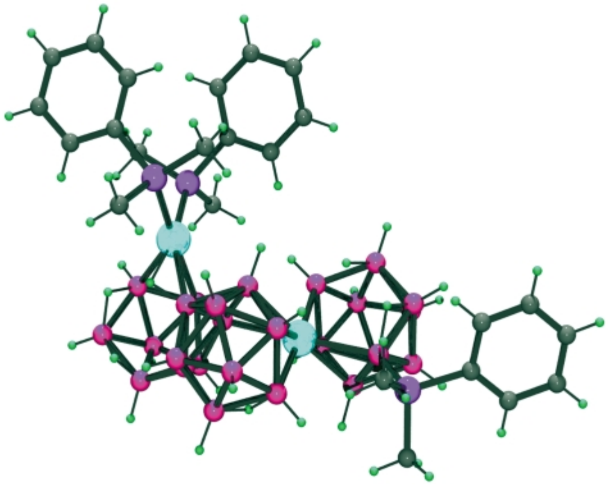

Fig. 10 A platinum-containing macropolyhedral borane complex obtained in extremely low yield.

Stacked charge transfer complexes have also been studied. A particularly impressive example is from work carried out at ESRF with a crystal of only 12 × 10 × 2 μm[25] in size for an organic superconductor.

(d) Low yield products, *etc*

Sometimes the small size of available single crystals is partly a consequence of the minute quantities produced in reactions leading to very low yields of products. Not only are the crystals very small, they are also few in number, so that the choice is limited and shortcomings in the crystal quality have to be accepted. We have had particular success in a whole series of macropolyhedral borane clusters incorporating metal atoms (Fig. 10),[26] sometimes with no more than one obvious single crystal available and that one a very fine and fragile needle with cross section only a few microns. Many compounds, not just in this area of chemistry, grow as fine needles (more appropriately described as whiskers) or as extremely thin plates (essentially invisible when viewed on edge). Reasonable size in one or two dimensions does little to boost the extremely low intensity scattered by such low-volume crystals, for which secure mounting while minimising X-ray scatter by mount, adhesive and protecting oil is itself a major challenge.

Similar situations, with minute quantities of material available in only micron-sized crystals, is found in the study of rare minerals[27] and of pigments.[28]

(e) Studies under non-ambient conditions

The most common non-ambient condition for data collection is low temperature. Indeed, at SRS station 9.8, data collection in the range typically of 100–150 K is the rule rather than the exception and is considered completely routine. The advantages of reduced temperature for X-ray crystallography are well known and its benefits are important if data quality is to be optimised, especially for weakly scattering samples. Apart from the marked reduction in atomic displacement parameters, leading to enhanced intensities and more precise structural results, cooling also helps to reduce or eliminate sample decomposition in the high intensity X-ray beam.

Sample heating is rarely a deliberate operation. At Daresbury it has been used in studies of microporous materials, for monitoring the decomposition and removal of template molecules during calcinations of products,[29] and for investigation of phase transitions between normal crystalline and liquid crystalline forms.[30]

SR brings particular benefits in high-pressure single-crystal diffraction studies. One of the most convenient means of generating controlled high pressures is a diamond anvil cell. This brings problems in the form of mechanical restrictions (only a limited angular access to the sample is available through the cell for the incident and diffracted X-ray beams), and significant absorption of X-rays by the cell materials. Both of these problems are much reduced if shorter wavelength X-rays are used, giving lower absorption and a compression of the diffraction pattern to smaller Bragg angles. Here both the high intensity and the wavelength selectability of SR are important. Owing to the high intensity, smaller crystals can also be used, reducing the likelihood that they will suffer damage at high pressure.[31]

(f) Unstable species

The high intensity of SR can give very rapid data collection from crystals that show only weak diffraction intensities on conventional sources. This is obviously an advantage for materials that are chemically unstable or that show significant decay in an X-ray beam. Examples include highly reactive alkali and alkaline earth metal complexes[32] and the first example of a Sn^{II}–Sn^{IV} covalent bond.[33] On the other hand, decomposition can be more rapid in the synchrotron beam, especially if the sample is not cooled. My own first experience with SR crystallography included an attempt to study a very unstable bismuth alkoxide, which survived only one exposure to the beam of a few seconds before the diffraction pattern disappeared completely; with present-day equipment and routine sample cooling facilities, this would probably be successful.

(g) Specialised experiments

Most of the examples so far could be described as basic crystal structure studies. The objective is the same as in a standard chemical crystallography experiment with conventional laboratory equipment, the determination of a crystal structure and hence a geometrically precise description of the molecular, or non-molecular, structure for whatever purpose, but with SR because of the need for that in order to achieve a result at all. The use of SR opens up other, more unusual, possibilities for experiments.

In so-called charge density studies more than a basic geometrical structure is the aim. Experiments seek to reveal and model the valence electron density in a material, including both bonding contributions and non-bonding features such as lone pairs of electrons. In order to refine the much larger number of parameters needed to describe the non-spherical distribution of electrons in an atom produced by its valence behaviour, and to provide an effective decoupling of this from the non-spherical dynamic distribution due to atomic displacements, the temperature of the sample must be as low as possible and data of significant intensity are required to a much higher resolution (lower d spacings, equivalent to higher $(\sin\theta)/\lambda$ in the Bragg equation) than for standard structure determinations, unless complementary neutron diffraction data are also available. With conventional laboratory X-ray equipment and Mo-Kα radiation, this involves measuring data to a considerably higher maximum 2θ angle; this is very time-consuming and such high-angle data are relatively weak, so experiments take many days with a modern area detector, and weeks or months with a four-circle diffractometer. Ag-Kα radiation, with a shorter wavelength, can be used to compress the diffraction pattern to lower angles, but it is intrinsically much weaker in intensity. SR brings considerable advantages here, through the use of high intensity short wavelength radiation. Thereby, the diffraction pattern is compressed to lower angles, so that more reflections are measured at once on an area detector, greatly speeding up the process, and intensities can still be high. The shorter wavelength also means reduced systematic errors from effects such as absorption and extinction, and these are further reduced because the high intensity means smaller crystals can be used. A high quality full set of data for a charge density study, with high redundancy of symmetry-equivalent data, can be achieved within 1–2 days, depending on particular circumstances. A number of results have been published, obtained from various SR facilities.[34]

Wavelength selection can also lead to minimisation or deliberate maximisation of anomalous dispersion effects by tuning the wavelength relative to absorption edges of elements present in the sample. In macromolecular crystallography the main use of this is in obtaining information to help solve the phase problem in determining large structures, with particular recent developments in multiple-wavelength anomalous dispersion (MAD) techniques, but in chemical crystallography there are other uses. In particular, anomalous dispersion effects can be used to produce significant differences in the scattering factors of atoms having similar electron density, thereby enabling a clear differentiation between these atoms in a structure.[35] Examples include distinguishing Zn and Ga in microporous materials where these atoms may be ordered or disordered,[36] and similar problems in minerals and alloys (*e.g.* Al *versus* Si, Zn *versus* Cu). In favourable cases, it can even be possible to distinguish atoms of the same element in different oxidation states, a technique known as valence-difference contrast.[35,37]

Recently, experiments at NSLS in Brookhaven have used synchronised laser and X-ray pulses to study structures of electronically excited states of molecules. Notable examples are changes in the orientation of NO ligands in metal nitrosyl complexes.[38]

6 Conclusions and future prospects

These examples, selected from many more, give some indication of the impact of SR chemical crystallography in the last few years and the hugely significant extension it represents for the already well-established technique of crystal structure determination. Many experiments are now possible that were unthinkable a few years ago, and the equipment and applications are rapidly being further developed. The construction of more third-generation sources worldwide and the completion of commissioning of appropriate beam-lines on existing storage rings will open up these facilities for greater numbers of chemists. In the UK, a new synchrotron source is to be constructed by about 2005, and a dedicated chemical crystallography facility is likely to be among the first stations in operation, in view of the enormous success and current oversubscription of SRS station 9.8. The advent of new types of rapid and large area detectors in coming years will also decrease experimental times, improve sensitivity, make even smaller crystals viable, and enable further new types of experiments. Mechanisms of access, particularly for chemists without training in crystallography or uses of SR, including service modes of operation, are being explored and developed at various synchrotron sources. Like the SR itself, the future for chemical crystallography is very bright!

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