



High Pressure Crystallography

STUDY OF A Pd(II) COMPLEX

The study of crystalline samples under pressure is increasing in popularity due to the capabilities of modern X-ray diffractometers and the increased availability of synchrotron facilities. Rigaku Oxford Diffraction's systems and CrysAlis^{Pro} software are particularly well-suited to high pressure crystallography, with a range of features designed to make experiments straightforward and accessible to the wider crystallographic community. In this application note, work carried out with **Prof. Sandy Blake** of the University of Nottingham is presented.

THEORY

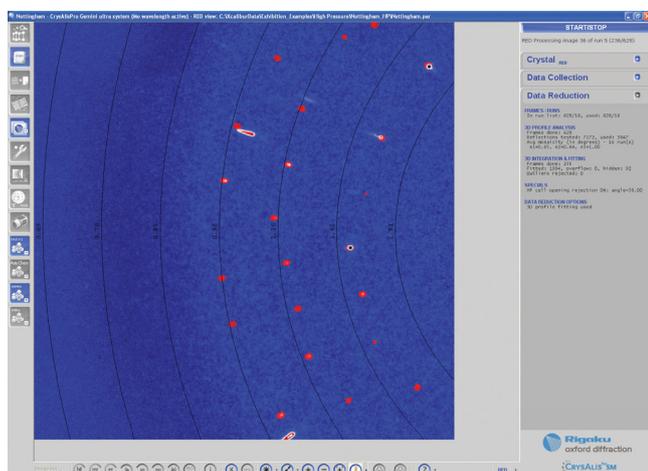
The application of pressure is capable of inducing major structural and other changes in crystalline materials. The ability to vary pressure greatly extends the scope for studies of the solid state: the behaviour of materials under pressure is relevant to areas as diverse as pharmaceutical processing, materials science and the study of life under extreme conditions.

In general, the effects of a few kbar of pressure will only be seen in the weak intermolecular contacts: as these shrink the unit cell volume reduces and rearrangement of the structural units is possible. With higher pressures of tens of kbar, changes within molecules and ions, for example in their conformation or internal geometry, become more likely, and at even higher pressures of hundreds of kbar it is possible to induce chemical reactions such as polymerisation. Across the pressure range, changes could include the appearance of new polymorphs, the restructuring of hydrogen bonding networks, new molecular conformations or forms of organisation and the close approaches between parts of the structure.



Early high pressure structural studies were typically linked to geology, and a typical measurement would have investigated the behaviour of a mineral at pressures (and possibly temperatures) at relevant depths in the Earth. The range of materials studied has since been expanded to include simple organic compounds, biologically-relevant molecules ranging in size from amino acids to proteins, and metal coordination complexes.

The most widely used design for high pressure cells is that of the diamond-anvil cell (DAC), one version of which can easily be mounted on a standard diffractometer but is capable of generating pressures of 100 kbar or higher. High pressure studies present particular experimental challenges: for example, the body of the DAC limits the proportion of unique reflections which can be measured, particularly in lower-symmetry crystal systems, and its components contribute significantly to the diffraction pattern. One of these problems can be addressed by the use of beryllium-free cells: scattering from beryllium backing plates results in significant features in the diffraction images, which can cause problems with weakly scattering samples.



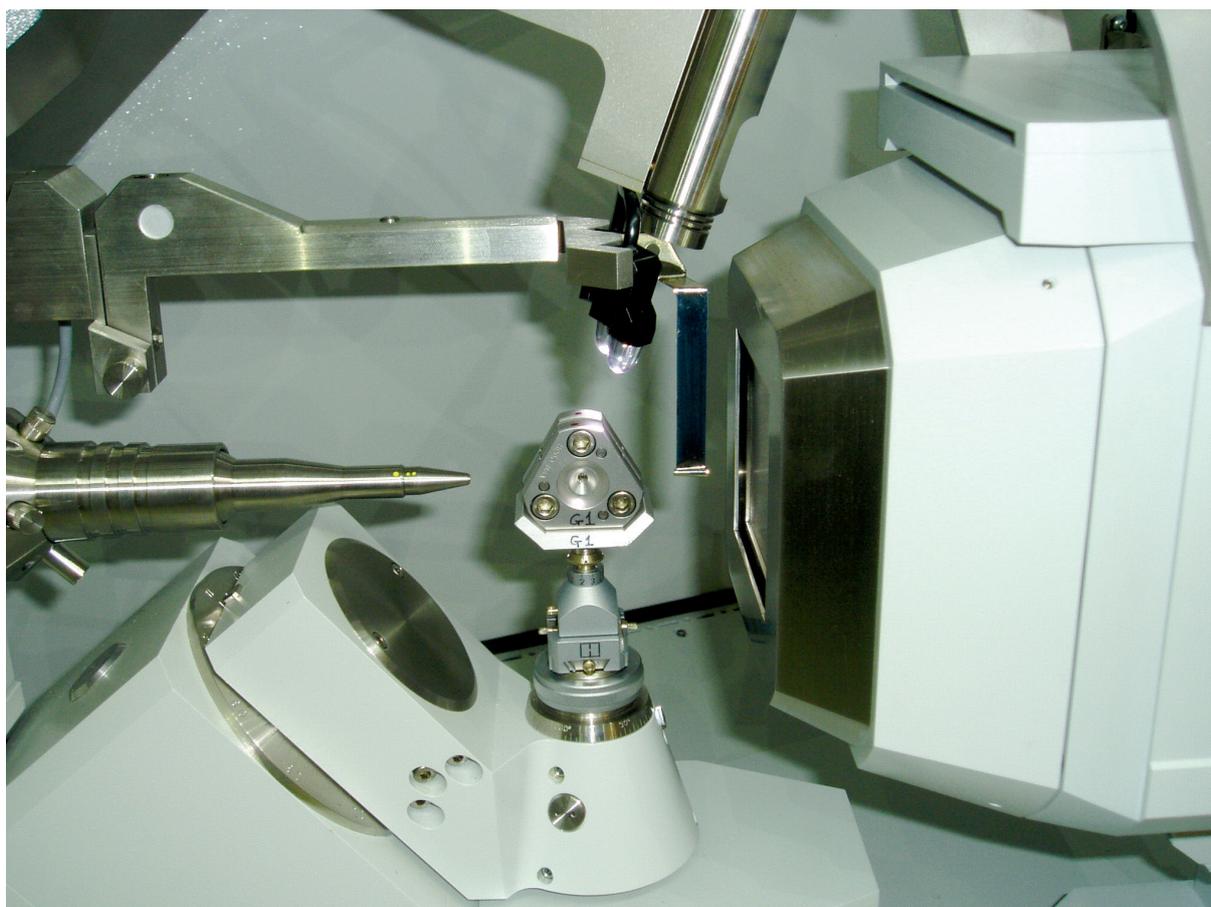


Figure 1 - Diamond anvil cell (DAC) mounted on the dedicated high pressure SuperNova E system at the University of Nottingham

EXPERIMENTAL

A high pressure experiment will usually start with the measurement of a dataset from a crystal inside the DAC but at ambient pressure. After each pressure increment, a dataset is taken, the number of these being determined by the scientific aims of the experiment, the behaviour discovered during the experiment, and limited by the pressure where the crystal or the DAC fails. The resulting structures at each pressure are examined in order to discover the details of how the material reacts to compression. Pressure inside the DAC can be measured from the pressure-dependent shift in the position of the fluorescence band of a calibrant (e.g., ruby).

At the University of Nottingham we combine use of an in-house diffractometer, an Rigaku Oxford Diffraction SuperNova E, with synchrotron beamtime to study the behavior of metal-organic complexes under pressure. The in-house instrument is dedicated to and optimized for high pressure studies: it is equipped with a single-wavelength molybdenum source, a short collimator and a long beamstop to accommodate the DAC, and a high-sensitivity Eos CCD detector (Figure 1). The instrument has three distinct roles: the first is the screening and selection of crystals, both before and after they are loaded into the DAC; the second is for complete in-house high pressure structural studies; the third is to identify pressure regions of interest which can only be effectively explored using synchrotron radiation.

Although most experiments can feasibly be conducted in-house, certain samples will always exhibit very poor diffraction, perhaps as the result of a phase change or reaching a high-pressure limit, and in these cases synchrotron beamlines provide the only practical source of diffraction data.

Conducting high pressure experiments can be almost as simple as routine single crystal data collections. The DAC is mounted perpendicular to the X-ray beam, then aligned both optically and by using the X-ray beam itself. A pre-experiment is conducted by scanning across the DAC opening angle in order to obtain a unit cell, which then forms the basis of a customized data collection strategy, calculated in CrysAlis^{Pro}. To avoid the inclusion of cell orientations where no data can be observed (due to the limits of the DAC), the opening angle (typically $\sim 37^\circ$) is included in the strategy calculation (Figure 2). The resulting run list is then as complete as can be achieved based on the accessible regions of reciprocal space and the symmetry of the sample. The DAC gasket partially shadows many frames in the data set, and to account for this the opening angle feature is also used in data reduction (Figures 3a and 3b). The end result is that only those areas of frames unaffected by gasket shadows are included in the data processing.

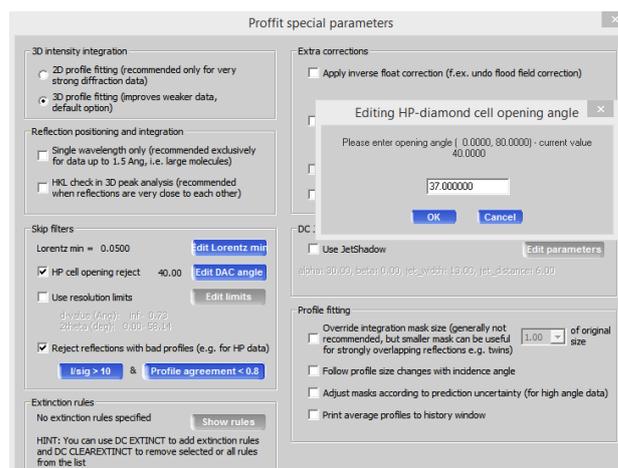


Figure 2 - High pressure opening angle rejection for strategy calculation and data reduction

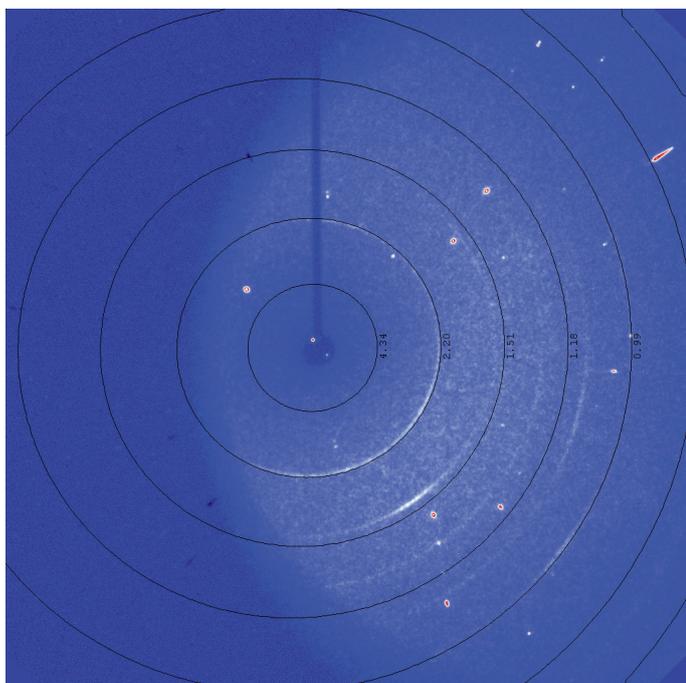


Figure 3a - A typical data collection frame shadowed by the diamond anvil cell (DAC) - the low-intensity powder rings represent scattering from the tungsten gasket

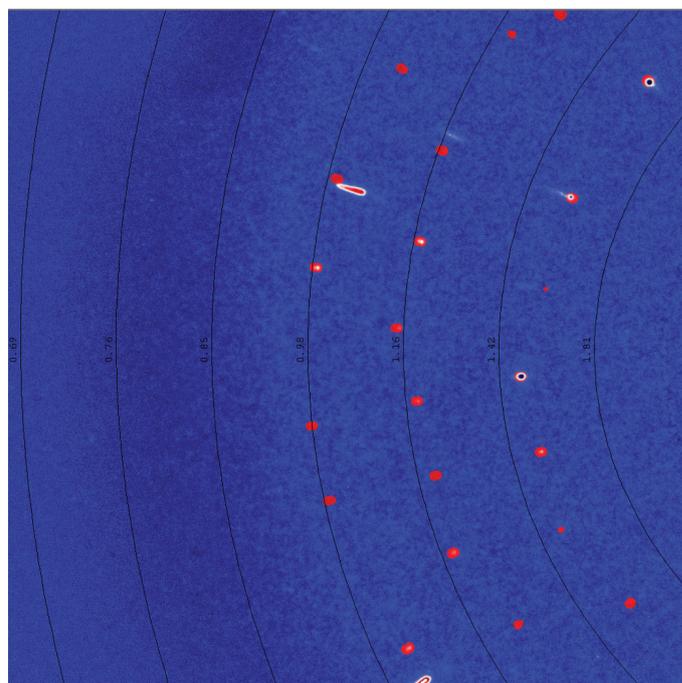


Figure 3b - Integration masks overlaid on a frame during data reduction. The shadowed region is ignored and therefore contains no masks as determined by the opening angle set in the dialog in Figure 2.

The high pressure tools in CrysAlis^{Pro} are not only relevant to in-house Rigaku Oxford Diffraction systems. Data in a number of other formats can be imported and processed using all the features available in the software. This is a particular advantage for synchrotron users such as ourselves: we use CrysAlis^{Pro} to process data obtained during high pressure experiments at the Diamond Light Source synchrotron facility in the UK.

RESULTS

Our group in Nottingham has discovered unprecedented structural, optical and electronic changes in a variety of metal coordination complexes, including examples of molecular deformation and π - π stacking of aromatic units, all induced by pressure.

One study¹ revealed a number of such changes occurring in the same sample: at 44 kbar the mononuclear square-planar Pd(II) complex $[\text{PdCl}_2([\text{9}]ane\text{S}_3)]$ (Figure 4a) converts to a chain polymer (Figure 4b) via close intermolecular Pd...S contacts of 3.117(8) Å; the metal now adopts an unusual distorted octahedral geometry as the axial Pd...S distance contracts from 3.159(10) Å at ambient pressure to 2.846(7) Å at 46 kbar; a vivid colour change (orange to deep black) indicates a major electronic reorganisation at the metal centre; finally we observe a unique conformation for the $[\text{9}]ane\text{S}_3$ ligand.

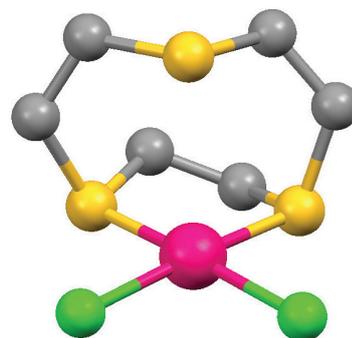


Figure 4a - The mononuclear complex $[\text{PdCl}_2([\text{9}]ane\text{S}_3)]$ at ambient pressure.

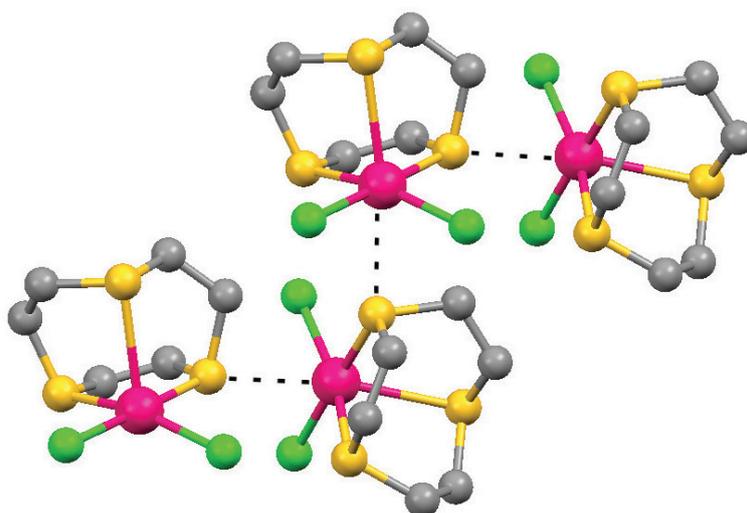


Figure 4b - The chain polymer at 46 kbar

REFERENCES

1. D.R. Allan, A.J. Blake, D. Huang, M. Schröder, T.J. Prior, Chem. Comm., 2006, 4081-4083; SRD Annual Report 2007-2008, pp. 18-19.

ACKNOWLEDGEMENTS

We would like to thank Prof. Sandy Blake from the University of Nottingham for contributing data, analysis and text to this application note.

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