How to perform HP single-crystal diffraction at Diamond

David R. Allan

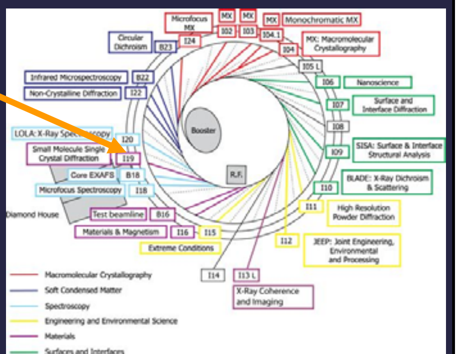
Diamond Light Source

Outline

- I19, the small-molecule single-crystal diffraction beamline
- Scientific Aims
- Beamline Requirements
- Outline Design
    - General Layout
    - Optics Hutch (Mono, Mirrors)
    - Experimental Hutches (Diffractometers/Detectors)
- High-pressure studies using Merrill-Bassett diamond-anvil cells (with some examples)
- Simultaneous high-pressure/variable-temperature studies

nd

The dedicated small-molecule single-crystal diffraction beamline I19 has high-pressure capability.



This beamline is dedicated to monochromatic studies (5-25 keV) using single-crystal techniques.

diamond

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The original science programme outlined for I19, small-molecule single-crystal diffraction, anticipated the following themes:

Underpinning the frontiers of science and technology
- micron sized crystals
- microporous and mesoporous systems, such as zeolites
- supramolecular assemblies and very large molecules
- catalysis, “smart” materials, optical devices and information storage

Charge density, from electron density to molecular properties
- understanding materials: e.g. non-linear optic systems, guest-host materials

Anomalous dispersion studies – enhanced detail at the edge
- contrast between isoelectronic species and differing oxidation states

Disorder and its relation to physical properties
- weak scattering features at high Q values
- total-scattering studies

Structure under change
- catalytic reactions, phase transitions, synthesis/degradation
- environmental cells: pressure, humidity variation, microwave radiation
- excited states/ time resolved studies

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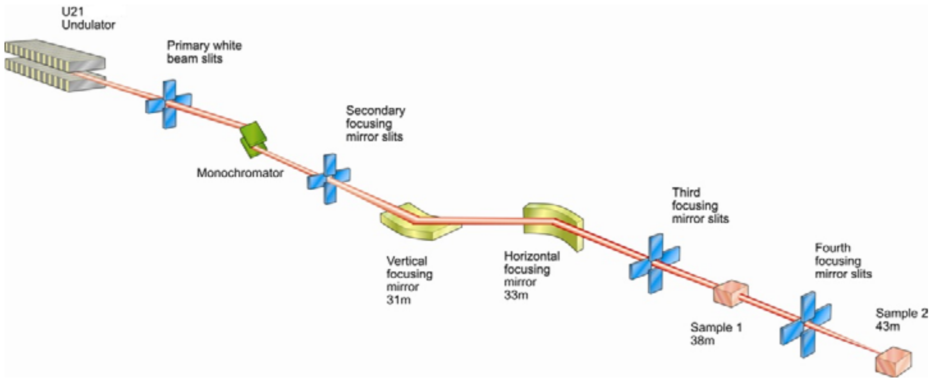
General layout



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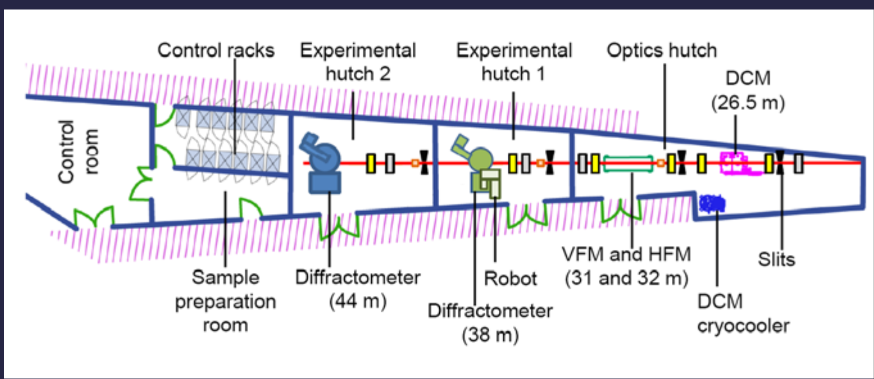
Beamline layout



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I19 diffractometer 1

- Small sphere of confusion
- Fast diffractometer
- Fast detector with large dynamic range
- Scope for upgrade
- Integration with external kit (e.g. robot) possible
- User friendly data collection and processing software

Main use is for chemical crystallography studies.

However, it can be used for high-pressure studies with no modification.

Aim is essentially similar to the ethos for the beamline's predecessor station 9.8 at Daresbury:

-require a versatile, easy to use, diffractometer that wouldn't be unfamiliar to the users (including the software).

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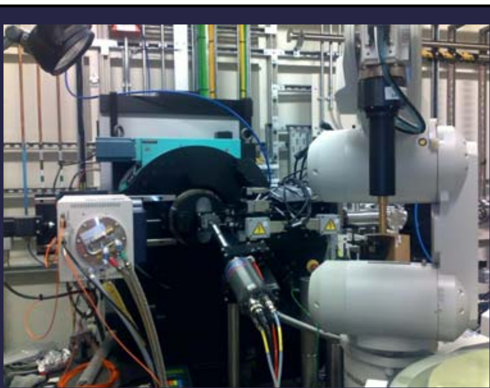

The diffractometer and robotic sample changer were supplied by Rigaku (Saturn 724+ CCD detector).

The motorised goniometer head is replaced with a standard Huber manual version.

As it is difficult to centre the cell accurately using only optical techniques the focusing mirrors are not used and beam is taken straight off the monochromator (the beam size is significantly larger but there is an appreciable decrease in flux).

Merrill-Bassett cells are used:

- small, light and uncomplicated

- only achieve modest pressures (< 100 kbar) but this is sufficient for most studies of molecular systems.

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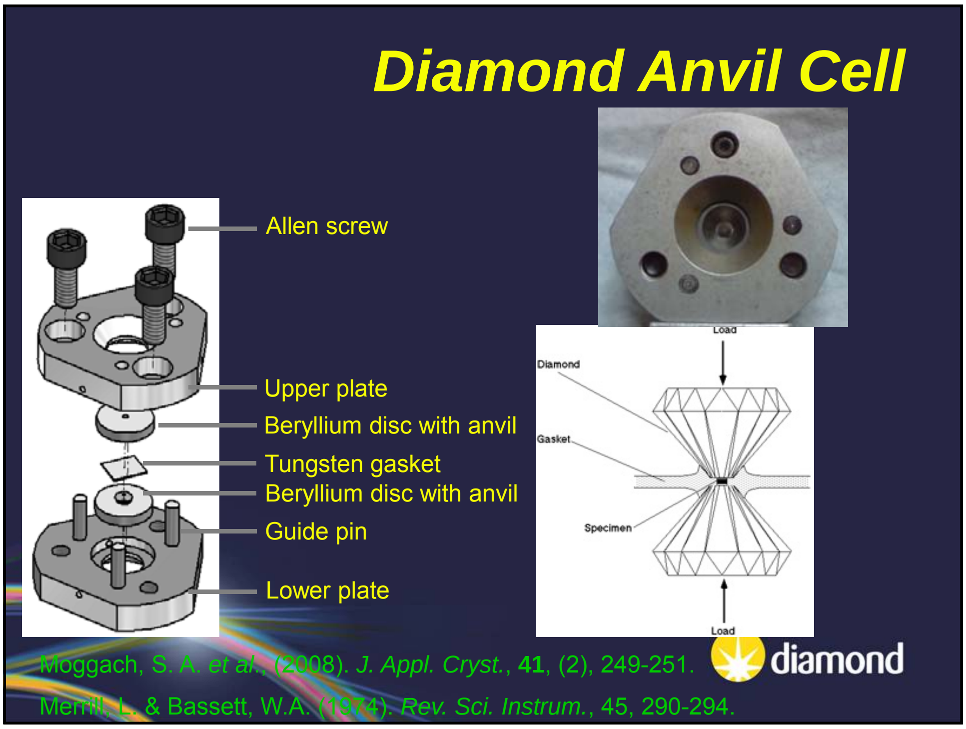
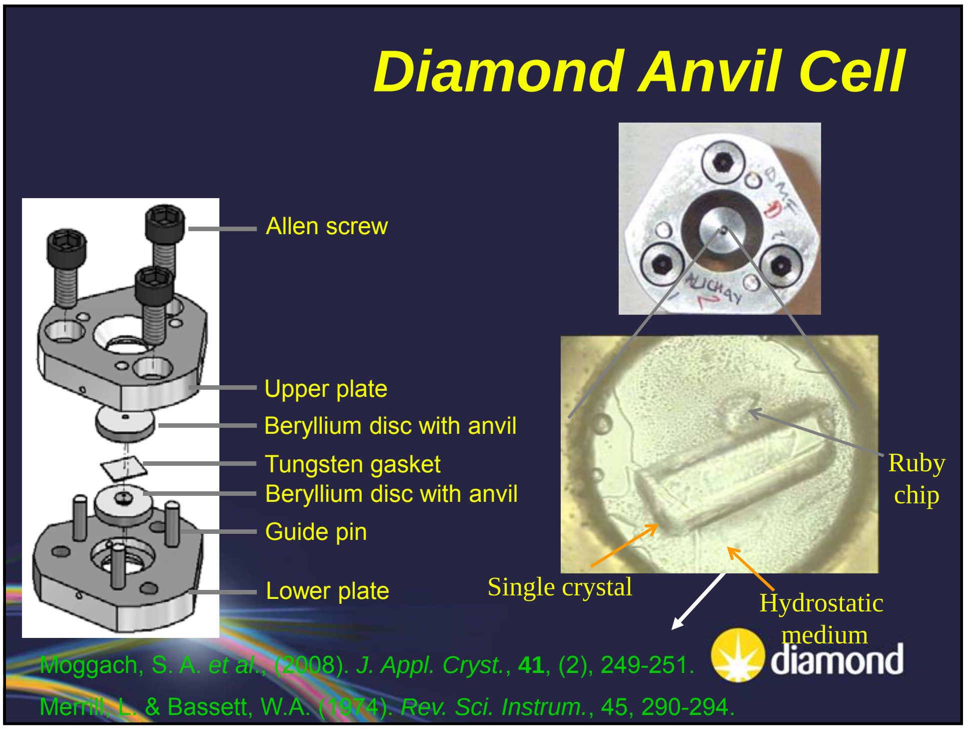
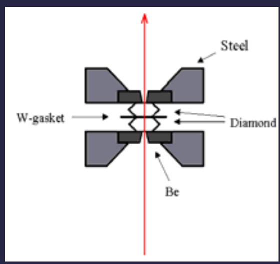
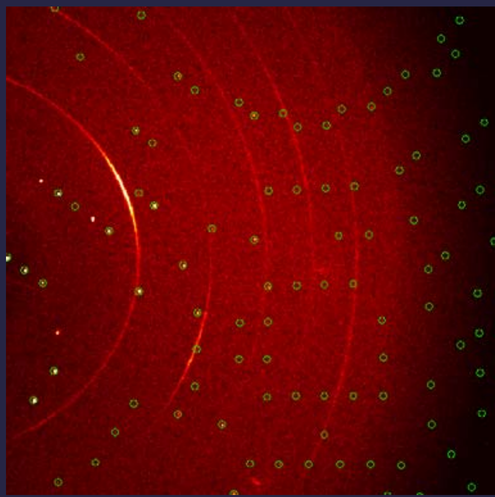

Diamond Anvil Cell
Allen screw
Upper plate
Beryllium disc with anvil
Tungsten gasket
Beryllium disc with anvil
Guide pin
Lower plate
Load
Diamond
Gasket
Specimen
Load
diamond
Moggach, S. A. et al., (2008). J. Appl. Cryst., 41, (2), 249-251.
Merrill, L. & Bassett, W.A. (1974). Rev. Sci. Instrum., 45, 290-294.


Diamond Anvil Cell
Allen screw
Upper plate
Beryllium disc with anvil
Tungsten gasket
Beryllium disc with anvil
Guide pin
Lower plate
Ruby chip
Single crystal
Hydrostatic medium
diamond
Moggach, S. A. et al., (2008). J. Appl. Cryst., 41, (2), 249-251.
Merrill, L. & Bassett, W.A. (1974). Rev. Sci. Instrum., 45, 290-294.





If the incident beam passes through the optical ports in the cell,
the Be is not illuminated and the diffraction pattern is relatively clean.

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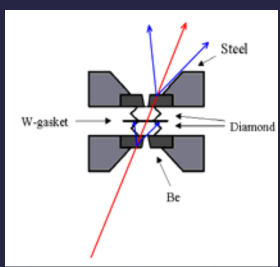

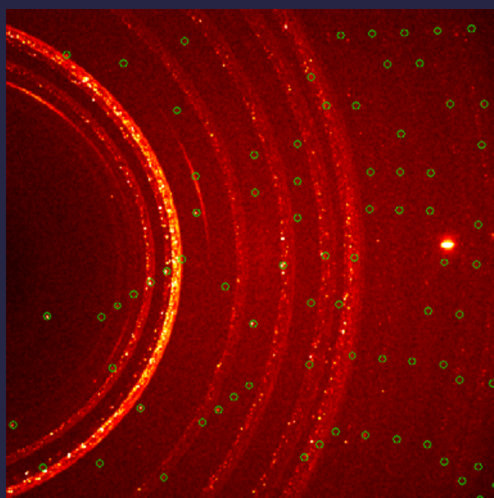

If the incident beam passes through Be then diffraction pattern is contaminated with Be powder pattern:

- spottiness exacerbated by low-divergence of synchrotron beam
- for larger systems: greater density of predicted reflections; intensities comparable

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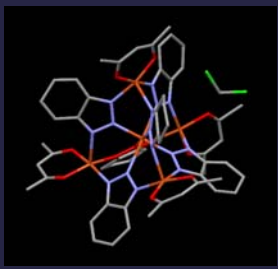
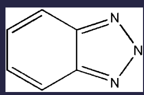
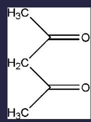
Studies of systems with relatively large structures reveal that the textured background introduced by the cell can lead to considerable problems with intensity integration.



In the small-molecule magnet $Cu_5(bta)_6L_4$

bta = benzotriazolate, L = β-diketonate





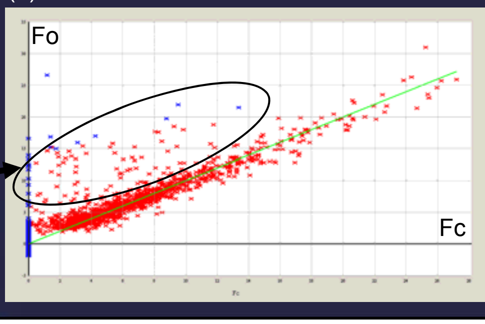
Pbna

a = 16.7334(3)Å, b = 19.8171(3)Å, c = 19.9186(3)Å

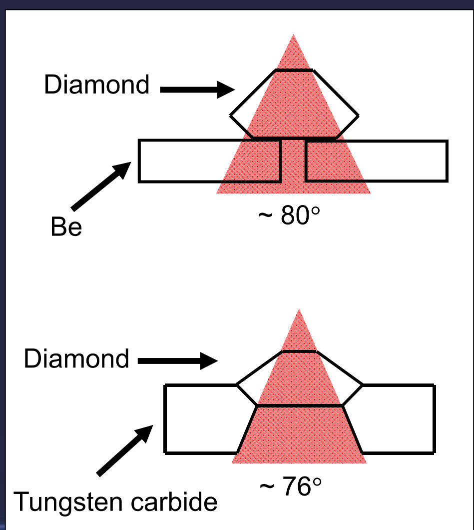
V = 6605(1)$Å^3$

Dr E. Brechin, Edinburgh

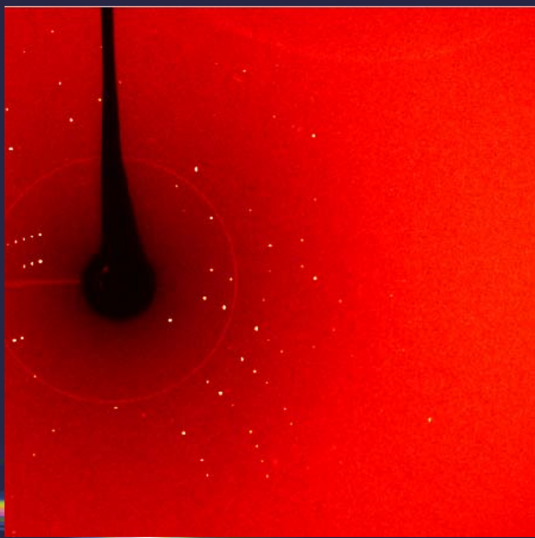
The high-pressure data set has a large number of outliers – reflections appear to be too strong



Boehler-Almax anvils



Pancreatic elastase



Ambient Pressure,
V = 223608(41) Å^3
Resolution: d ≈ 1.5 Å
R_{int} = 0.0506
99.6% complete

0.15 GPa,
V = 219774(18) Å^3
Resolution: d ≈ 2.0 Å
R_{int} = 0.0893
45.5% complete

CCD image collected on Station 9.8 at SRS Daresbury

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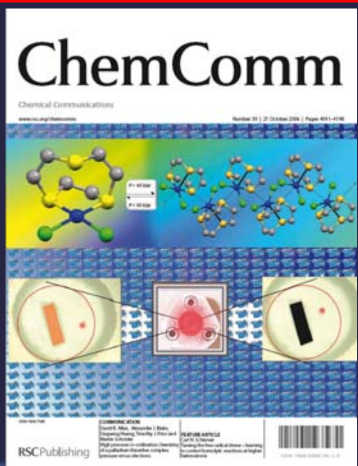
Dr S. Moggach, Edinburgh

Results for the palladium thioether complex $[PdCl_2([9]aneS_3)]$

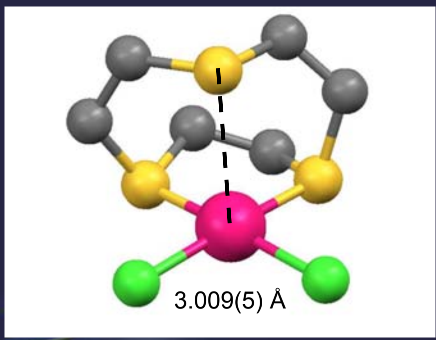
an example from 9.8 at SRS

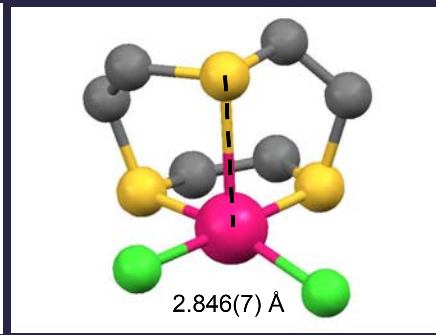


D.R. Allan, A.J. Blake, D. Huang, T.J. Prior, M. Schröder, *Chem. Commun*. 2006, 4081–4083.

$[PdCl_2([9]aneS_3)]$

- axial Pd—S1 distance contracts



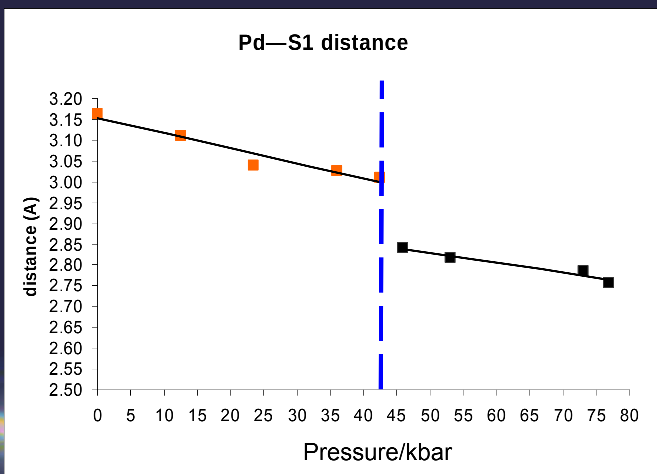


42.5 kbar

46 kbar

$[PdCl_2([9]aneS_3)]$

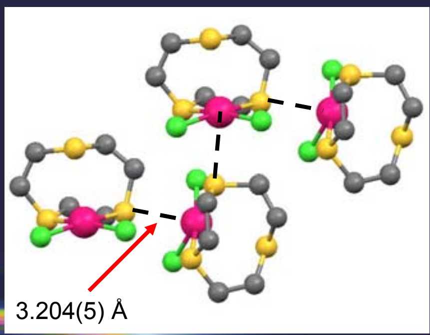
- axial Pd—S1 distance



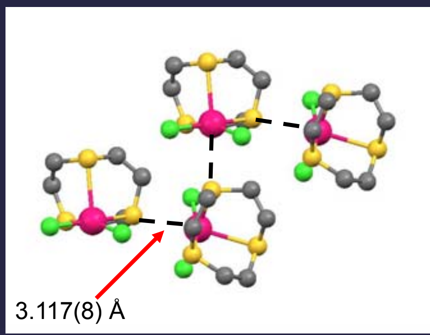
20

[PdCl$_2$([9]aneS$_3$)]

- intermolecular Pd...S contracts
- distorted octahedral coordination
- chain polymer formed



42.5 kbar



46 kbar

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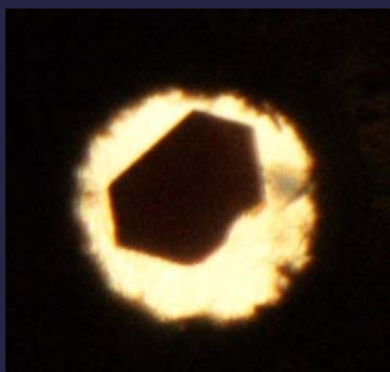
[PdCl$_2$([9]aneS$_3$)]

- dramatic but reversible colour change

42.5 kbar



46 kbar

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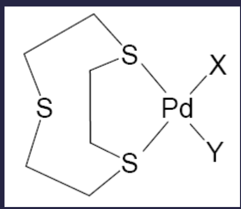
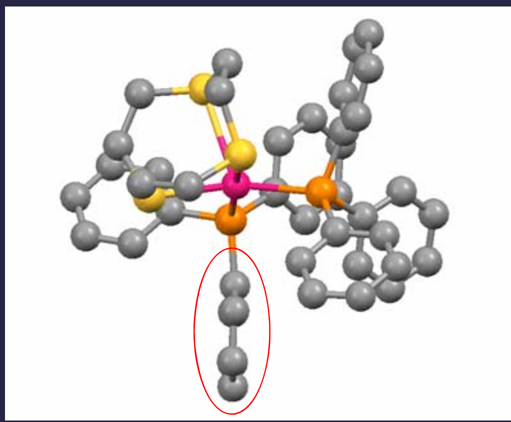
More recently we have continued these studies on the structurally more complex system $[Pd([9]aneS_3)(PPh_3)_2](PF_6)_2$ on I19.





Although there were no significant geometric changes around the metal centre to to ~5 GPa we did observe significant changes in one of the intermolecular phenyl-phenyl interactions.

There appears to be a transition at ~2 GPa due to an encroaching π - π interaction.

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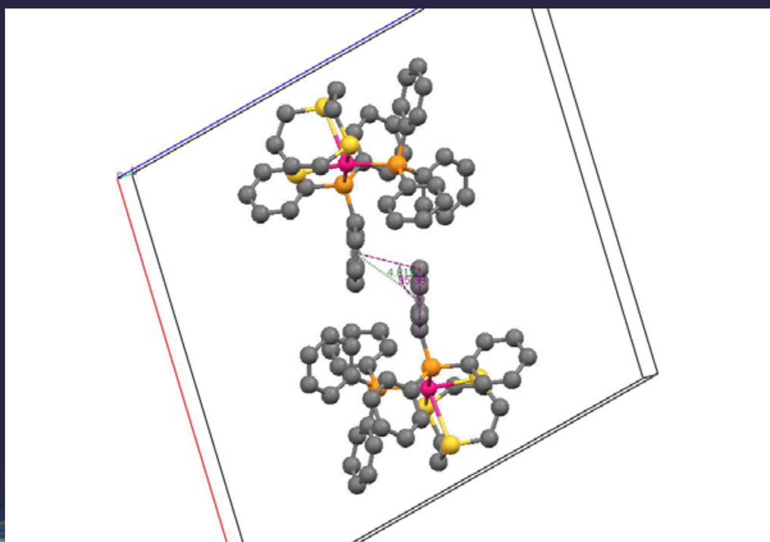

The P – Ph bond is initially approximately co-planar with the phenyl ring and starts to “kink” at ~2 GPa.

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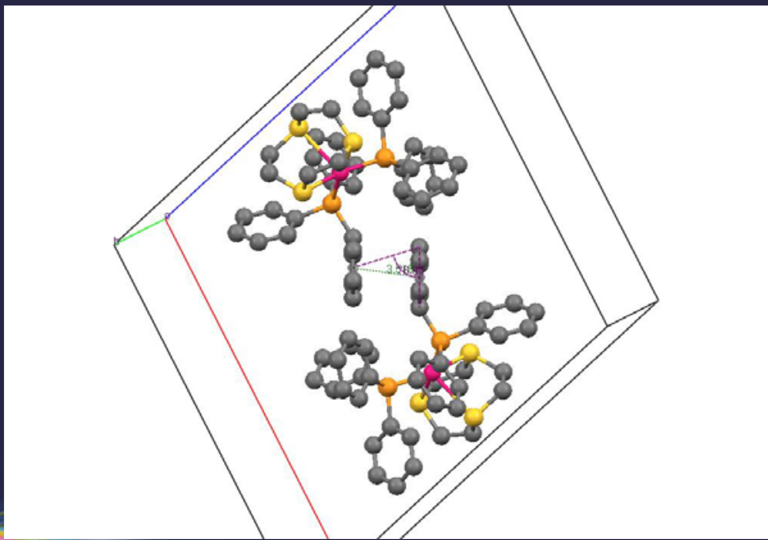

The P – Ph bond is initially approximately co-planar with the phenyl ring and starts to “kink” at ~2 GPa.

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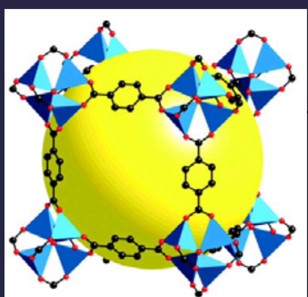
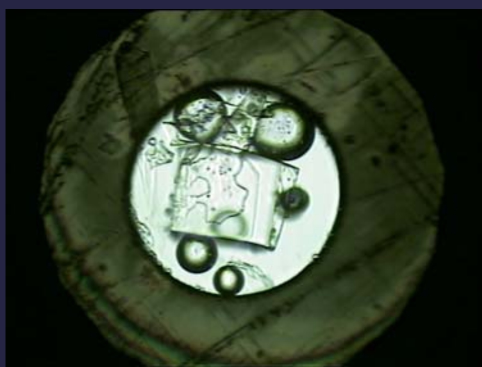
Effect of Pressure on MOF-5





Alexander Graham and Stephen Moggach,
The University of Edinburgh

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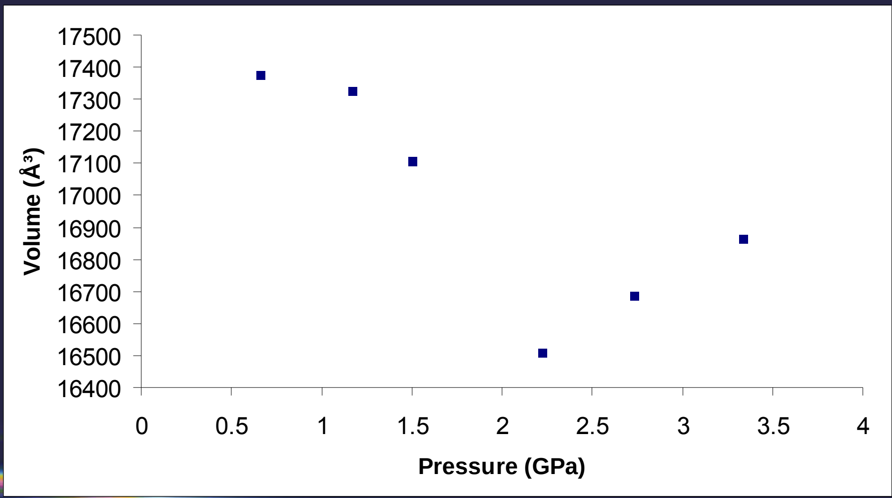
Effect of Pressure on MOF-5



Alexander Graham and Stephen Moggach,
The University of Edinburgh

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The high-pressure data can be processed using the software provided by the three main small-molecule single-crystal diffraction suppliers:

Rigaku: a modified version of CrystalClear (operating with d*trek)

Oxford Diffraction: the CrsAlisPro software can read in the images directly

Bruker: the images can be converted to the Apex II format

All of these methods produce excellent results though some testing is still required.

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I19 diffractometer 2

- relatively small sphere of confusion despite its size
- Fast detector with large dynamic range
- Scope for upgrade
- capable of carrying large sample environment cells including a closed-cycle cryostat.

Although the EH2 diffractometer and collimation setup is still being optimised (in many senses the collimation needs to be tailored for each experimental setup) it has supported a number of user groups.

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The 4-circle diffractometer was supplied by Newport and has kappa geometry.

The detector was supplied by Oxford Diffraction (Atlas) who also provided software integration.

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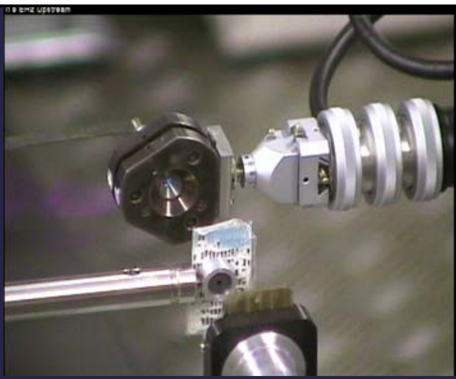
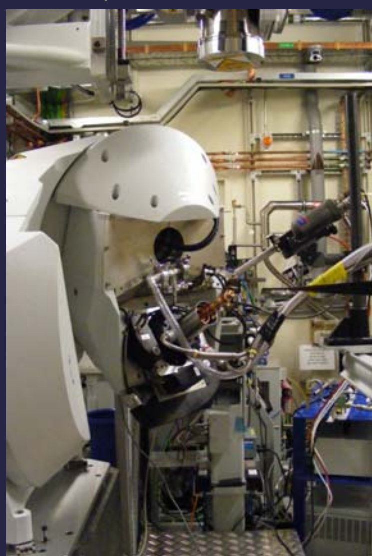


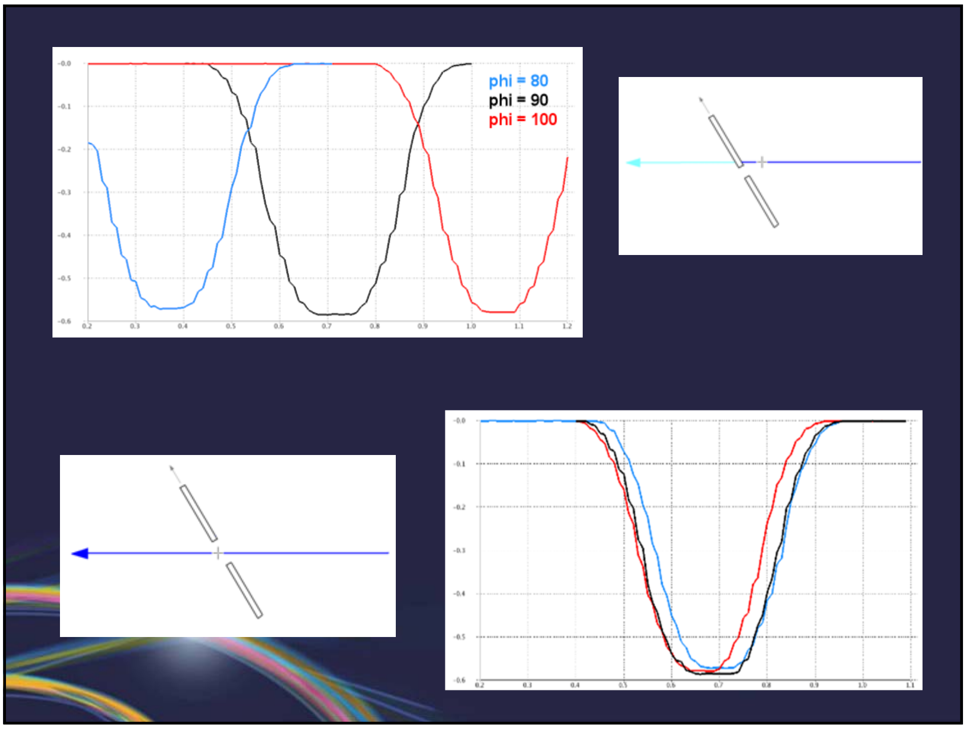
As the diffractometer has a motorised x,y,z-stage within the phi axis it is possible to use scanning techniques to accurately centre the sample (as we'll see in a moment).

The ability to accurately centre the sample allows the focusing mirrors to be used with an appreciable increase in the flux available at the sample.

The sample stage, within the phi axis, contains an x,y,z-stage which is capable of carrying 20 kg (repeatability < +/- 2μm).



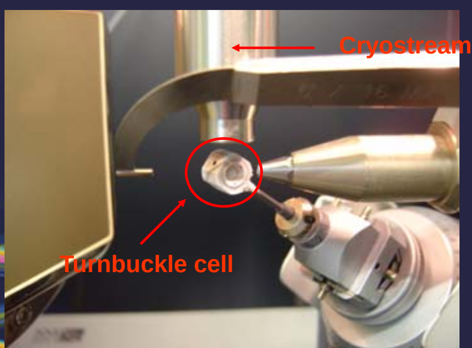
This allows a closed-cycle cryostat to be mounted on phi and positioned extremely accurately for sample centring.

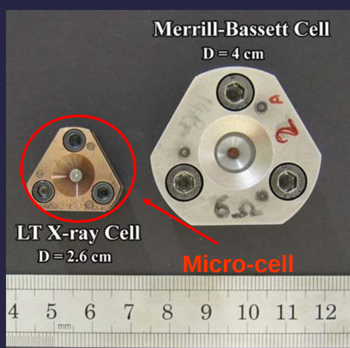


Much of the high-pressure variable-temperature work has been conducted in collaboration with members of CSEC at The university of Edinburgh.

They have developed novel diamond-anvil cell designs for studies using open-flow cryostream devices and cryostats.

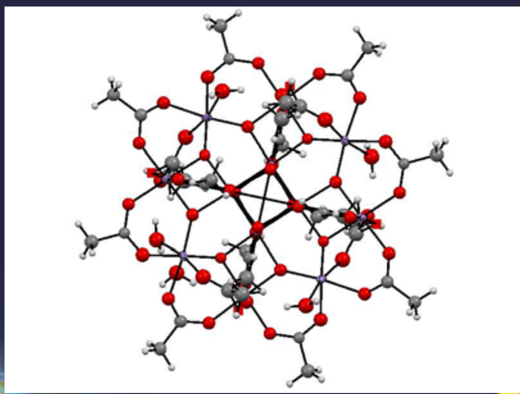
- Smaller cells constructed from copper-beryllium alloy.
- Turnbuckle cell designed for open-flow systems - calibrated in region 300 – 137 K.
- Micro-cell designed for closed-cycle systems.
- Designed by Dr Konstantin Kamenev and Dr Gaetan Giriat.





Mn_{12} Acetate

- Mn_{12} acetate $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ - first single molecule magnet discovered.
- Magnetic properties a function of Jahn-Teller axis parameters and temperature.



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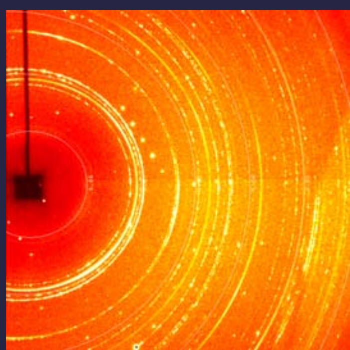
Sieber, A. *et al.*, *Angew. Chem.*, **2005,** 44, 4239-4242; Pascal, P. *et al.*, *Chem. Commun.*, **2010**, 46, 1881-1883

Data Processing

- Use of beryllium shroud leads to powder rings in diffraction pattern.
- Movement of beryllium powder rings prohibits exclusion.
- Paraffin appears to remain hydrostatic under low temperatures.



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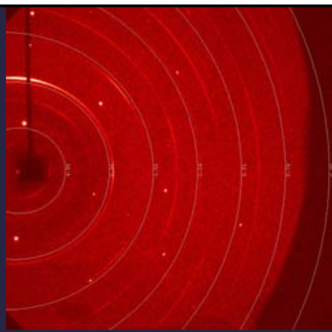
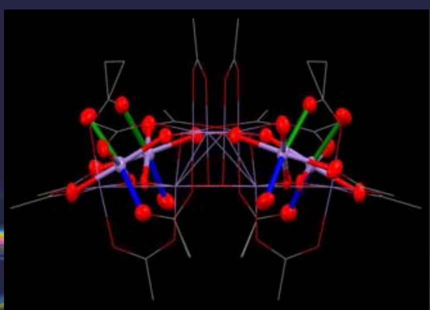


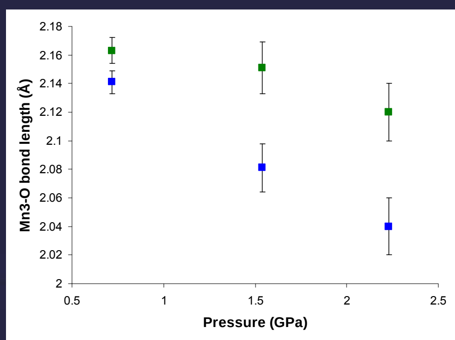
Location	Edinburgh	Diamond	Diamond
Pressure (GPa)	2.00	1.84	1.84
Temp (K)	**300**	**300**	**<300**
Resolution (Å)	**0.8**	**0.8**	**0.8**
Completeness	67	74	78
Redundancy	5.37	4.1	6.57
R	0.0441	0.0522	0.0384
Data/Param.	**5.37**	**5.81**	**8.51**

Structural Analysis - Jahn-Teller Bonds

Only one of the Jahn-Teller bonds undergoes any significant change in length.

More data are required to allow anything definitive to be concluded about the correlation of changes in the structure with those observed in the magnetic properties.





We have been collaborating with Dr Craig Bull of The University of Edinburgh to implement a high-temperature stage for the EH2 diffractometer. This will be fully tested within the next few weeks and we expect to achieve temperatures in the order of 300°C initially.

Craig has also been developing a ruby fluorescence spectrometer for the hutch which will allow in-situ pressure measurements for both the high-temperature stage and the cryostat.

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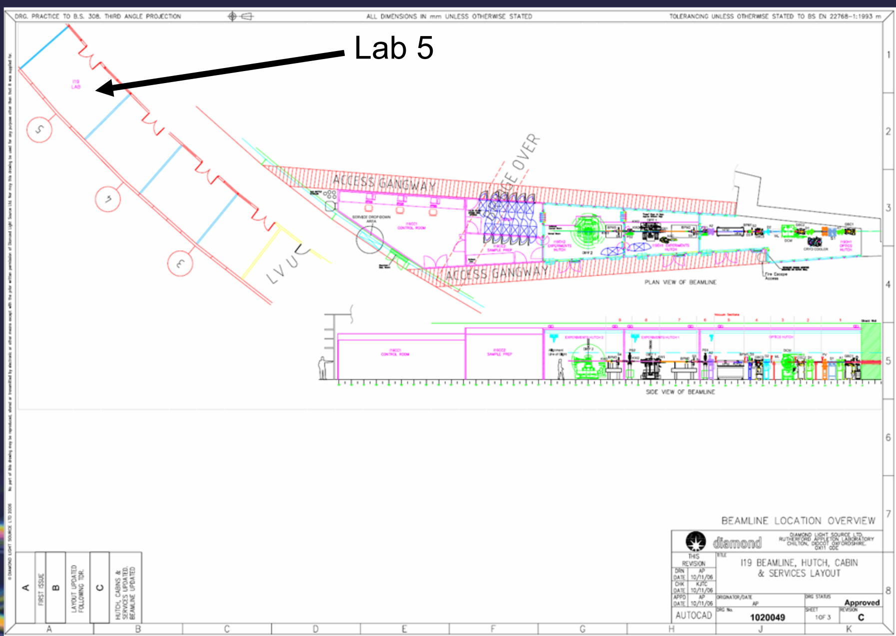
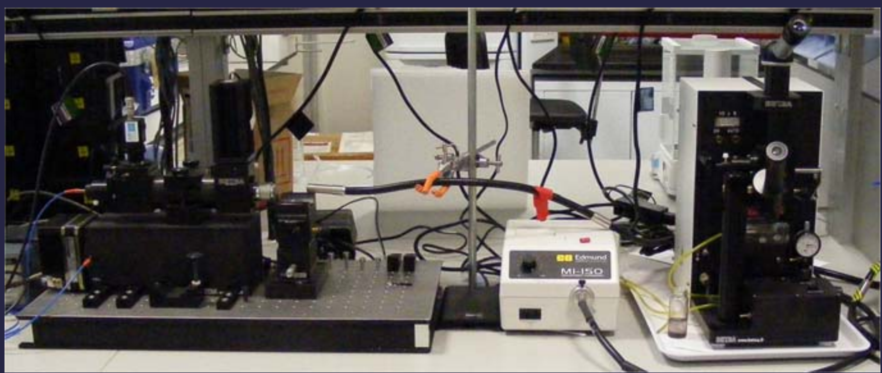
Beamline layout and peripheral lab

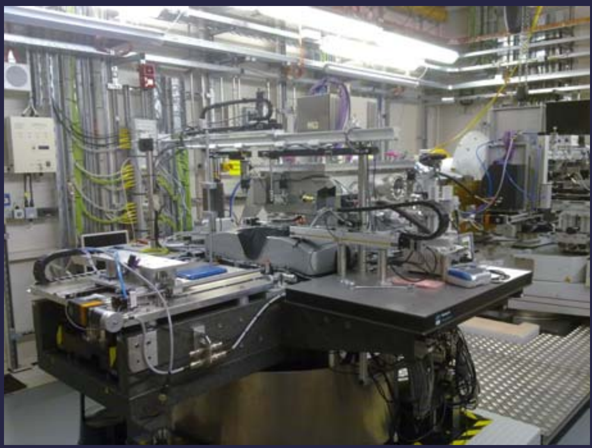



Edmund
MI-150

I15 Extreme Conditions

Beamline I15 is situated on a wiggler source and is capable of reaching very much higher photon energies (shorter wavelengths) than I19.

The Newport 6-circle, situated at the front of the experiments hutch, has been used mainly for power-diffraction studies – the images show it set up in this mode with the MAR 345 image plate detector.



At the back of the hutch there is a newly installed optical table which will provide a more dedicated facility for powder-diffraction studies, including a microfocused beam (~10 μm) via a set of KB mirrors housed on a vessel on the table, which will free up the Newport for single-crystal studies. The Newport will also have a less restricted motion.

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I15 Extreme Conditions

- Single-crystal experiments on Newport 6-circle device, using four circles
- ”Atlas” CCD detector fully integrated in the controls software and available for selected (monochromatic) energies:

  20 keV < *E* < 80 keV

  - High pressure work with DAC (p < 40 GPa); 228 reflections for 7 parameter, R1<7%,
  - Inclusions in natural diamonds, E=60 keV; minimum d-spacing of 0.25 Å; more than 500 unique reflection against only 10 parameters to be refined; agreement factor below 4% (inclusions are under pressure)

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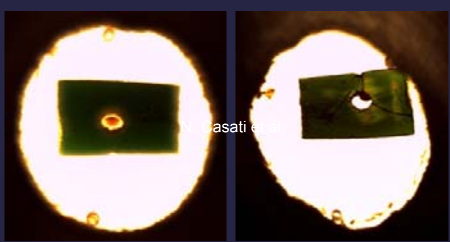
Potential problem: ‘Radiation damage’

(Metal-organic compound)

P = 20 GPa P = 0 GPa

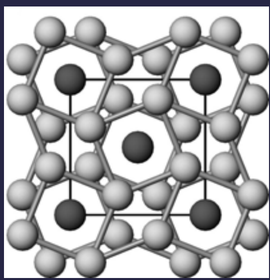


0.2 mm

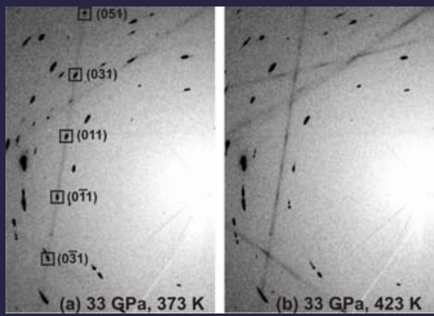
diamond

I15 Extreme Conditions

Incommensurate host-guest structure in K at high pressure and temperature



Above 20 GPa, K-III has 1-D chains of guest atoms (dark grey).



Heating a crystal above 373 K results in "melting" of the guest chains – Bragg peaks turn into diffuse discs as a result in the reduction in correlation length.

More information:
O. Narygina et al. Phys. Rev. B 84, 054111 (2011)
DLS highlights

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Acknowledgments

Diamond Light Source
Dr Harriott Nowell
Dr Sarah Barnett
Dr Claire Wilson
Dr Mark Warren
Mr Adrian Wilcox
Dr Kirsten Christensen
Dr Anna Warren

The University of Edinburgh
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