Nasty things happen to nice crystals

In March 2004 Station 9.8, the small molecule X-ray crystallography (SMX) facility, on the SRS underwent a substantial upgrade with the installation of the APEXII diffractometer, a three circle D8 goniometer with APEXII detector from Bruker-Nonius. This new hardware allowed data collection times to drop from 360 to 80 minutes for a full sphere of data, the whole unique diffraction pattern plus many equivalent reflections. This, combined with software improvements and alternative scanning modes, allows for even faster, though less commonly used, data collection methods to be employed, bringing the full sphere down to just over 14 minutes and a hemisphere, giving the unique diffraction pattern and fewer equivalents, down to approximately 11 minutes. With this increase in the data collection speed parametric and dynamic studies of systems became a reality.

In parallel, the Synchrotron Radiation Department's Seed Corn fund provided for the design and construction of an environmental gas cell. This cell allows a single crystal to be placed either under vacuum (for dehydration, solvent or guest removal) or exposed to a gas or gas mixtures. When the gas cell is combined with the high intensity and low divergence of the X-rays on Station 9.8, small crystals giving a beneficial surface to bulk ratio for the experiment can be used. The high intensity also provides for rapid data collections by reducing counting times.

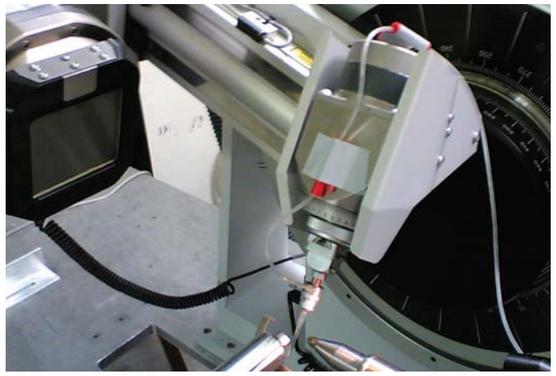


fig 1 *The environmental cell in place on the APEXII/D8 diffractometer Station 9.8*

This unique combination of apparatus and facility allows for an unprecedented view into the behaviour of guest systems in the crystal lattice. The environmental cell can be applied to the study of diverse systems such as gas inclusion complexes, hydrogen storage, auto-exhaust catalysts, zeolitic gas exchange/filter and greenhouse gas inhibitors, ranging across many branches of science. The facility is available to users of the SMX beamlines at the SRS, upon request through the existing beamtime application process.

Test Case

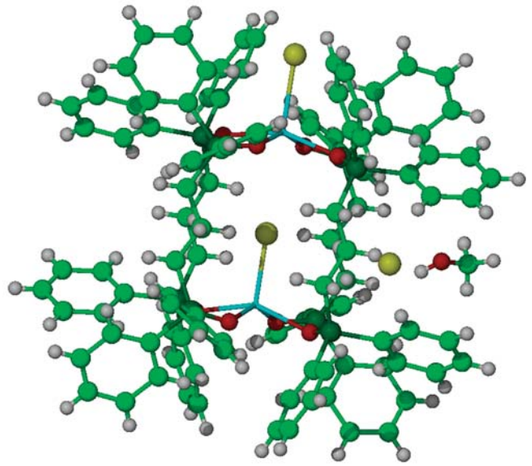
Sulphur dioxide (SO_2) is a greenhouse gas which is produced through the combustion of fossil fuels such as coal. Its uncontrolled release has potentially harmful effects on plant and wildlife through the formation of acid rain, via the reaction of SO_2 with water in the atmosphere. The corrosive rain also has an impact on man-made structures such as ancient monuments, statues and buildings. Selective removal of SO_2, from flue gases and exhausts, would be of great benefit to the environment and could potentially generate a useful end-product.

Work by McAuliffe and Pritchard led to the discovery of a range of 'Chinese Lantern' complexes which showed the interesting property of reversible SO_2 capture. Understanding how the SO_2 is reversibly held in the lantern structure could lead to a system which would actively react and produce new commercial products via reversible uptake and release in a catalytic manner, turning harmful waste into a new commercial product. These systems were reported to absorb reversibly six equivalents per lantern of SO_2 when measured by thermogravimetric analysis (TGA). However, due to the reversible and therefore "transient" nature of the SO_2 adsorption it had not previously been possible to characterise crystallographically the preferential sites in the lattice for SO_2 occupation.

This system was therefore an ideal candidate for Warren and co-workers to study with the newly-developed environmental cell. An experiment was designed to reproduce the TGA environment used to measure the bulk sample with the added step of *in vacuo* heating.

The work reported here is still on-going and the structures shown have been refined to moderate residual factor (Rf) values, which give a mathematical comparison between the structural model and the actual data. The lower the value the better. Further work is required to study disorder, which is not shown here. The structures constitute snapshots at key stages of the experiment.

A single crystal, approximately 0.02 x 0.04 x 0.04mm^3, produced a diffraction pattern of sufficient quality for the experiment and provided enough information for full structure solution and refinement, structure A, shown in **fig 2**.



Atom Colour Key:

Green	=	Carbon
White	=	Hydrogen
Red	=	Oxygen
Cyan	=	Manganese
Yellow	=	Bromide
Dark Green	=	Phosphorus
Magenta	=	Sulphur

Crystal Information – Generic

All 'Chinese Lanterns' form as body centred tetragonal (a=b=14 c=26 Å), space group I4/m with the cation centred on crystallographic C4h sites.

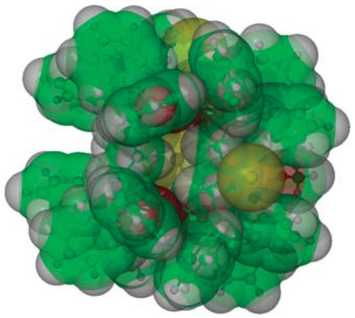
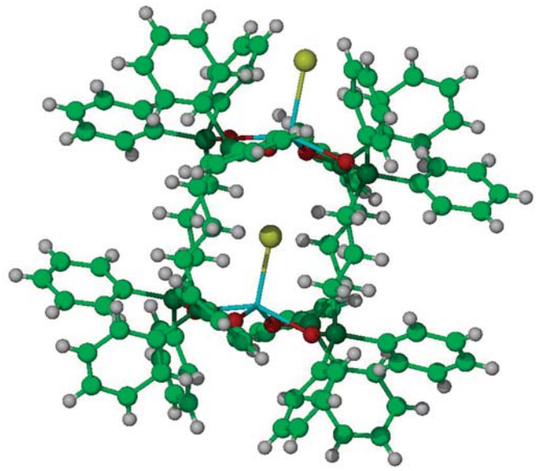


fig 2 *Starting structure shown in 'ball and stick' representation for clarity. Data collected at 10°C in gas cell. Disordered methanol shown and H_2O omitted. Rf at current stage of processing 5.56%. Also shown is a 'spacefill' representation of crystal structure to allow for a more realistic interpretation of the molecules.*

The sample was then heated for two hours on a ramping gradient from 10° to 130°C, under vacuum *in situ* and six data sets were collected to monitor the removal of solvent. Once the solvent looked to be sufficiently removed the sample was cooled back to 10°C and a further data set was collected. The data were used to produce structure B, shown in **fig 3**.

An SO_2 and argon (Ar) mixed gas atmosphere was then slowly introduced into the cell. During this process a total of 18 data sets were collected to monitor the SO_2 uptake. The structure displayed was solved and refined structure C, **fig 4**, from the final data set collected. Data produced from this study is still being processed but initial unit cell parameters have been included for comparison.

Examination of a plot of the unit cell length of the a-axis in Å and the unit cell volume in Å^3, clearly shows changes across the range of conditions to which the crystal was exposed, **fig 5**.



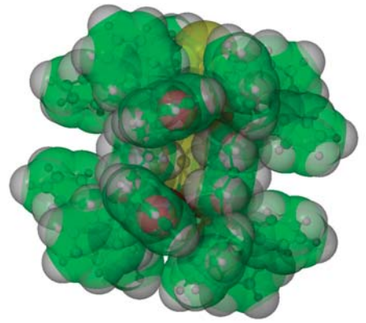
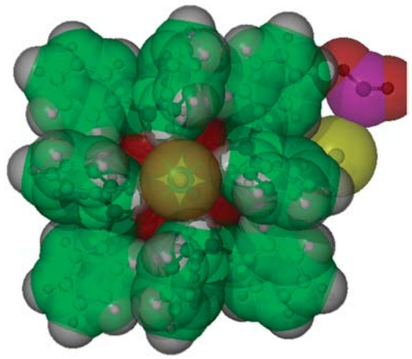


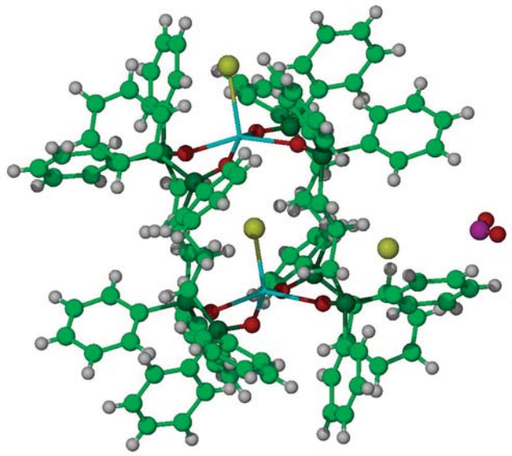
fig 3 *Data collected following cooling from 130°C to 10°C. Largest Q-peak (residual modelled data) located above axial external Br in a similar position and relative magnitude as found for solvated structure. Rf at current stage of processing 4.29%. Spacefill plot included for comparison with **fig 2**.*

Furthermore, these changes clearly map to logical changes within the unit cell. With the volume change of the cell perhaps most markedly showing the effect of removing solvent (Run 1 to 2) inserting guest molecules (Run 2 to 3) and the removal of guest molecules (Run 3 to 4).

Examination of the unit cell packing diagrams, **fig 6**, clearly indicate that on going from A-PACK to B-PACK the methanol moiety has been removed leaving a cavity which could host the incoming SO_2. This is corroborated by a reduction in the unit cell volume of approximately 110 Å^3. The uptake of the SO_2 moiety in C-PACK and the location of the cavities generated in the crystallography computer program PLATON, do not look to be coincidental and when combined with the apparent volume change of approximately 187 Å^3, uptake of SO_2 would appear to be confirmed. Thus constituting the first single crystal X-ray diffraction structure of a 'Chinese Lantern' complex in which the location of the SO_2 moiety has been determined.

Nasty things happen to nice crystals – Continued





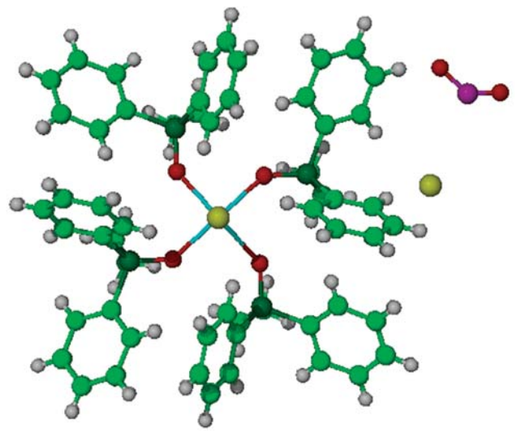


fig 4 *Data collected at 10°C under an atmosphere of Ar and SO_2. Rf at current stage of structure refinement 7.25%. SO_2 moiety located with refined occupancy factor of 84%. Additional residual electron density is also present in the structure however work to determine its structural characteristics is on-going. Inset shows the same structure when viewed down the c-axis and comparison between the 'ball and stick' and 'spacefill' representations allows for a possible interpretation of why the SO_2 is located in this particular cavity.*

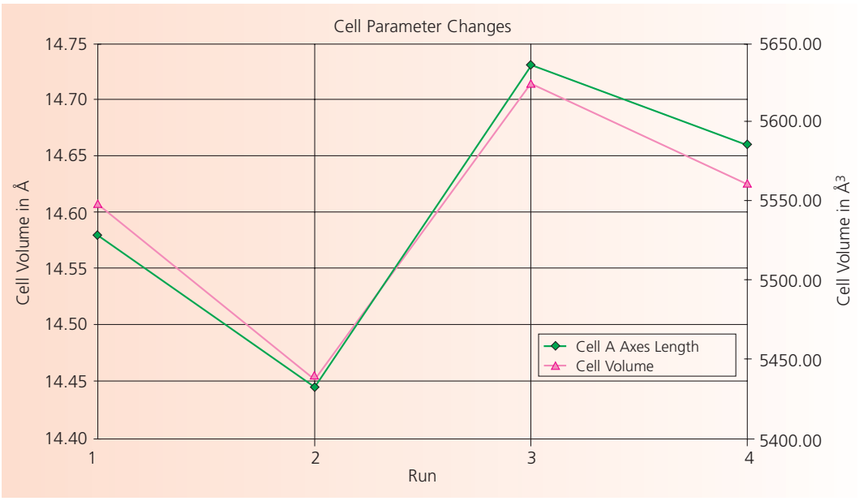


fig 5 *Plot of cell parameter change with condition: Run 1) Starting crystal, Run 2) Crystal following solvent removal, Run 3) Crystal with SO_2 gas guest, Run 4) Crystal after small vacuum applied to structure to encourage SO_2 removal.*

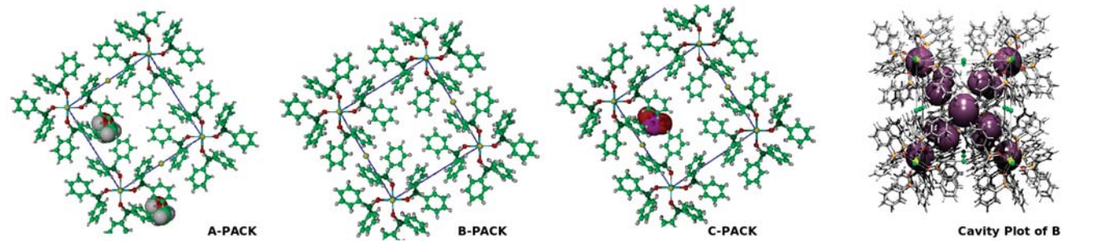
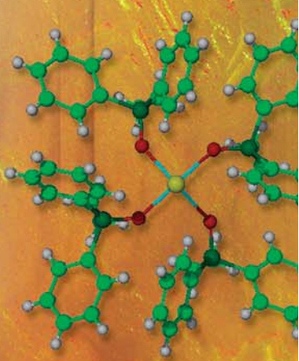


fig 6 *Three packing diagrams (unit cell in blue) for each of the systems studied (A-, B- and C-PACK respectively) plus PLATON cavity plot using crystal data from B. Cavities shown as purple sphere.*

The environmental gas cell is a departure from the traditional SMX experiment and is part of the many new advances to the experimental arsenal now available to the scientist. Whilst SMX is perhaps unique as a technique for giving 3-dimensional structural information when it is combined with the ability to change the crystals environment dynamically (be that temperature, atmosphere, pressure or to expose a crystal to external stimulus, lasers, magnetic fields or electricity). SMX becomes a truly unrivalled precision scientific tool.

General References:

WI Cross, SM Godfrey, CA McAuliffe and RG Pritchard
Crystal engineering of microporous 'Chinese-lantern' compounds to improve their ability to reversibly adsorb sulfur dioxide.
Chemical Communications 2001, 1764-1765



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