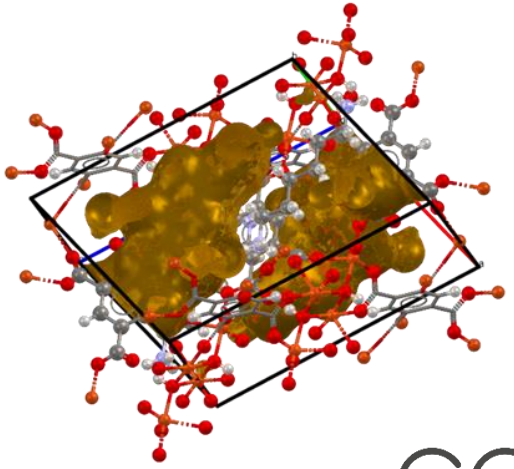
Analysing Porous Materials in Mercury (MER-006)

Developed using
2023.2 CSD Release
(CSD 5.44 + 2 data updates)



CCDC
advancing structural science

Table of Contents

Introduction 2
- Learning Outcomes 2
- Pre-required Skills 2
- Materials 2

Example 1. Analysing void space using Pore Analyser 3
- Conclusion 6
- Exercises 7

Summary 8
- Next Steps 8

Feedback 8

Exercise discussion 9

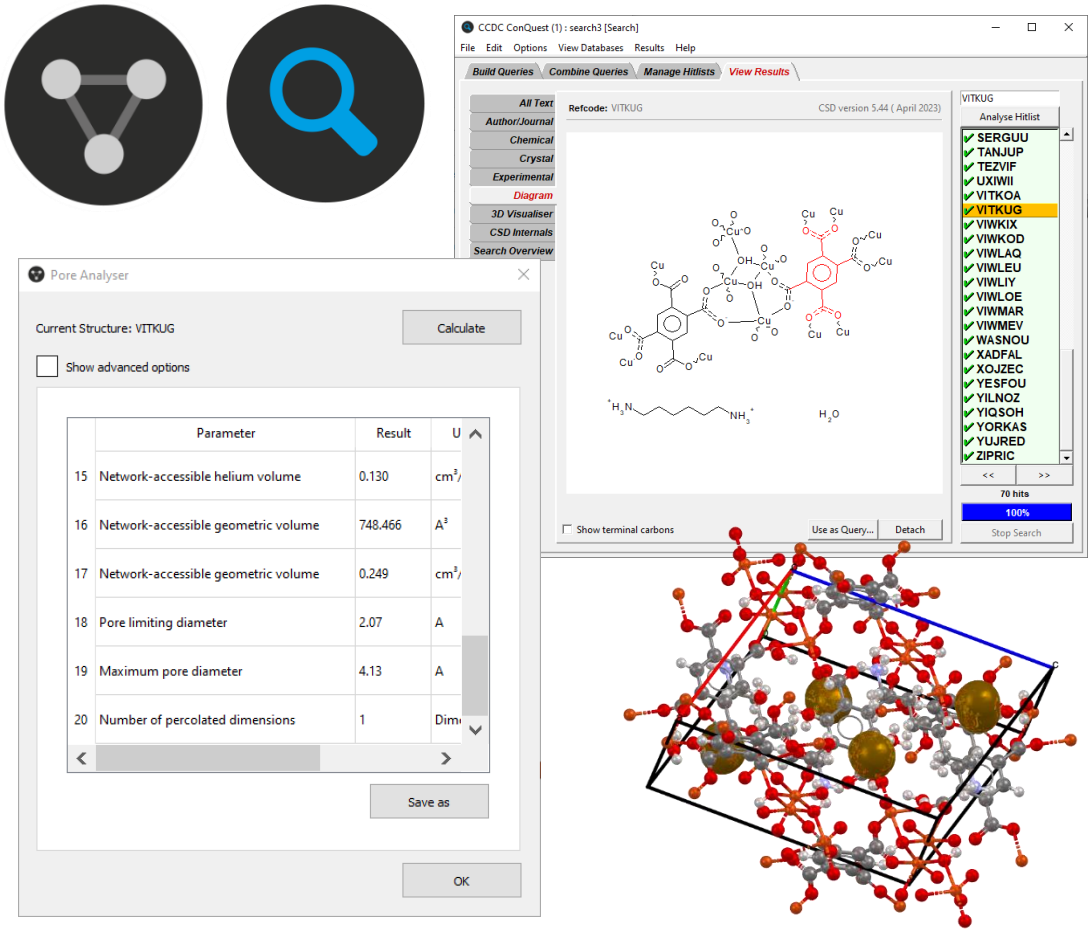
Glossary 10

Basics of Mercury Visualization 13

Introduction

Mercury is the visualisation and analysis software of the Cambridge Structural Database (CSD). Mercury not only allows for flexible structure visualisation but provides an interface to a wealth of tools for calculating structure properties. One such tool is the Pore Analyser, which facilitates calculation of pore properties, including geometric and network-accessible volumes, maximum pore and pore-limiting diameter, and network dimensionality.

In this workshop, we will use Mercury's Pore Analyser to explore the void properties of a Metal-Organic Framework structure.



Learning Outcomes

After completing this workshop, you will be able to:

- Run a Pore Analyser calculation on a structure from the CSD and interpret the results.
- Edit a structure in Mercury.
- Visualise void space in a porous material.

This workshop will take approximately ***25 minutes*** to be completed. The words in *Blue Italic* in the text are reported in the Glossary at the end of this handout.

Pre-required Skills

Basic familiarity with Mercury is required. You can find a brief summary guide at the end of the handout.

Materials

No additional materials are required for this workshop.

Example 1. Analysing void space using Pore Analyser

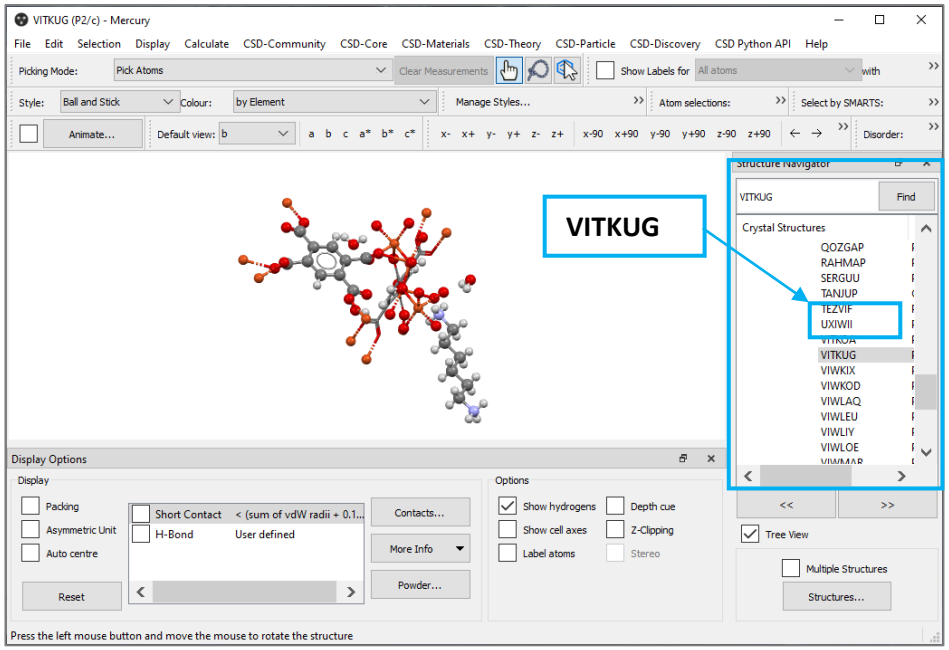
1. Open Mercury from the start menu or by clicking the Mercury icon from the desktop.

2. In the **Structure Navigator**, scroll down to CSD Entry VITKUG (a *Metal-Organic Framework* structure) and click on the *refcode* or type it into the navigator to bring up the structure. This crystal structure consists of three parts (i) the framework based on $[C_6H_2(COO)_4]^{4-}$ and OH^- bridged Cu^{2+} centres, (ii) the diammonium $[H_3N–(CH_2)_6-NH_3]^{2+}$ counterion and (iii) water of crystallisation.

3. From the top menus, select *Calculate > Pore Analyser*.

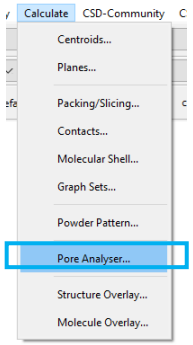
4. Press **Calculate** and allow the calculation to run. Scroll through the results of the calculations. You will notice that certain values, such as the *Network-accessible surface area* (0.00 $Å^2$) and *Network-accessible helium volume* (28.02 $Å^3$) are small.

2

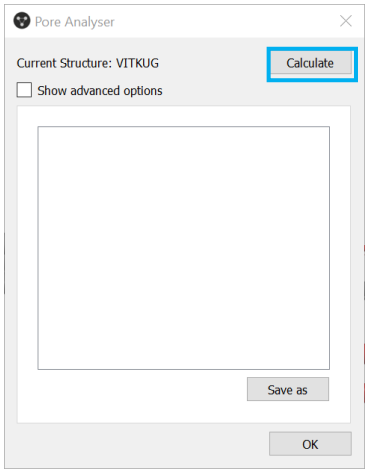


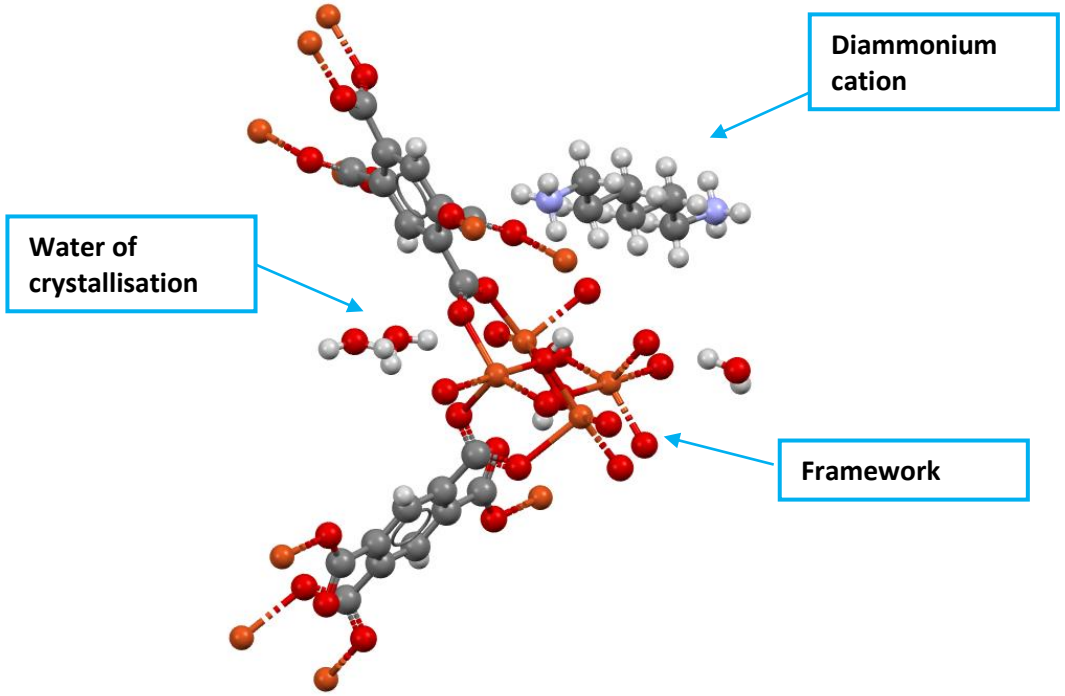
VITKUG

3



4





5. Click **Save as** to save the results as a CSV file which can be opened in a spreadsheet program such as Excel.

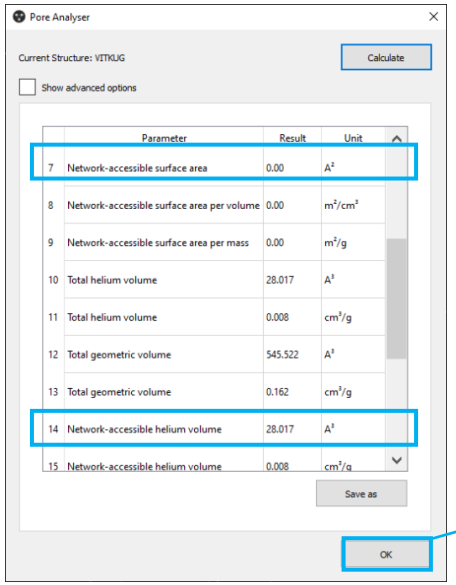
6. We can edit the structure to calculate what properties the void space might have with or without certain components. Right click on a framework atom and choose *Selection* > *Select Molecule*. The selected atoms will be highlighted yellow.

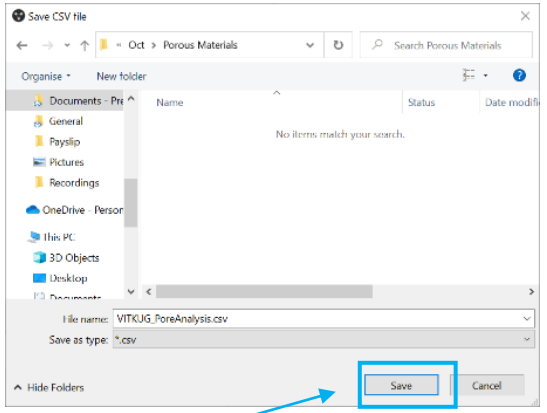
7. Right click on the selected molecule and choose *Selection* > *Invert Selection*. The diammonium cation and water will be highlighted but not the framework.

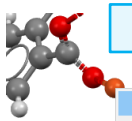
8. From the top-level menus, select *Edit* > *Edit Structure…*

9. Within the *Remove* area, click **Selected Atoms** and click Close.

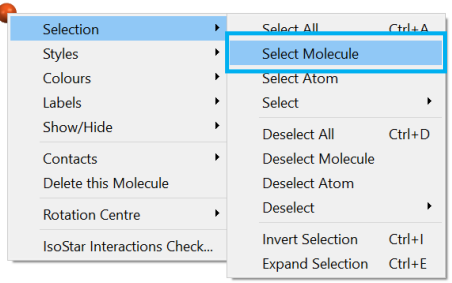
10. Repeat **Steps 3**–**5** again and explore the Pore Analyser results. You should see that the network-accessible surface areas and helium volumes have increased significantly. Make sure you save the calculation results.



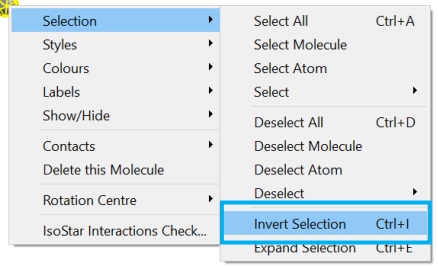




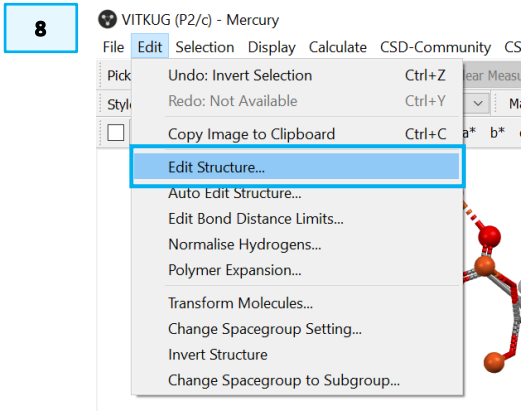
6



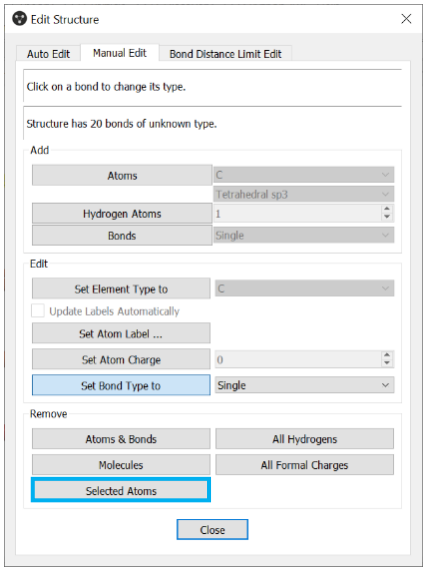
7



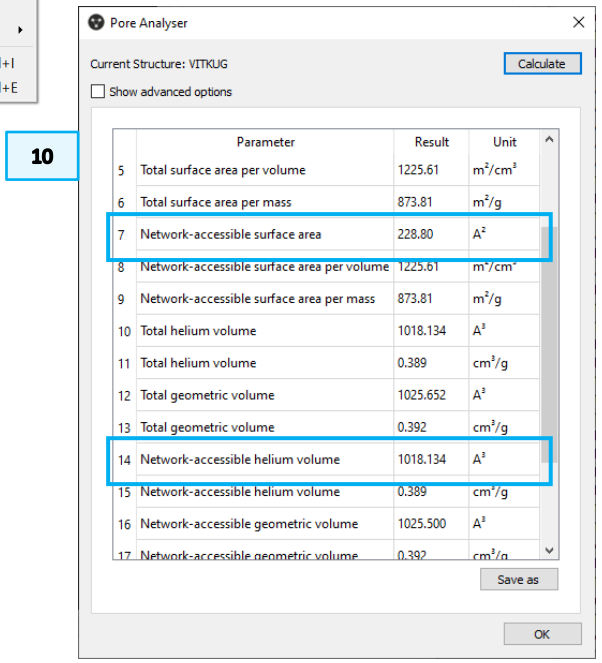
8



9



10



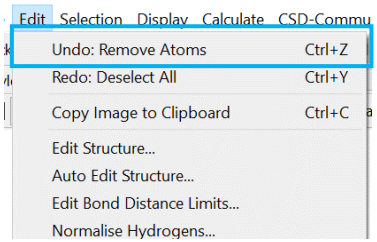
11. A cation-free structure would not be chemically possible; to undo the structure editing, press **Ctrl + Z** or select *Edit > Undo: Remove Atoms* from the top menus.

12. Click on the lasso icon  from the top toolbar and drag around the water molecules to select them.

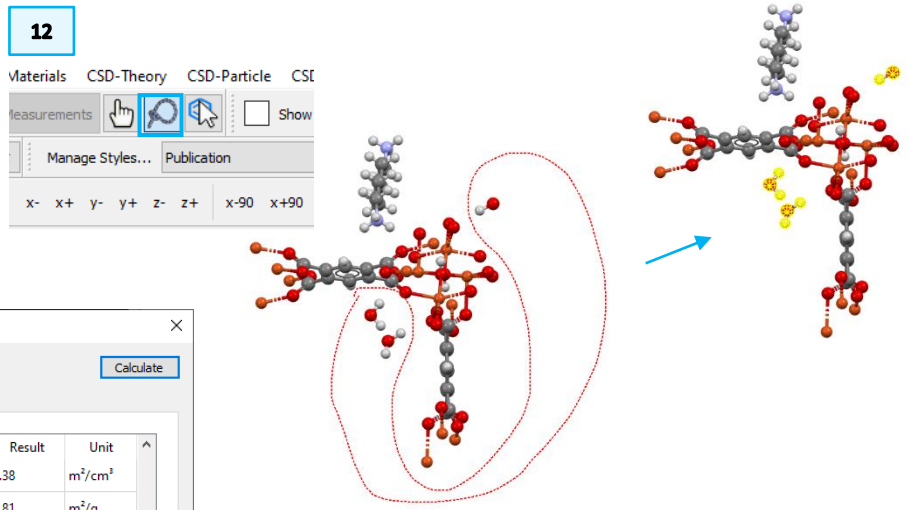
13. Repeat **Steps 8–9** to delete the 3 water molecules.

14. Run Pore Analyser again by repeating **Steps 3–5** on the edited structure. The values reported are relevant to the physical process of dehydration and may help you to understand the impact that such a process would have upon the stability of the structure.

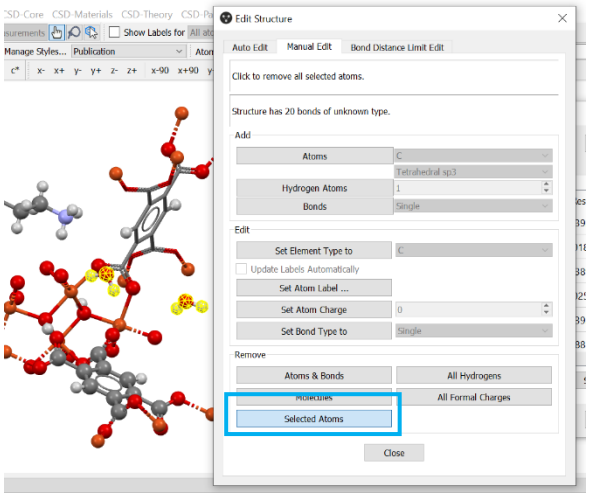
11



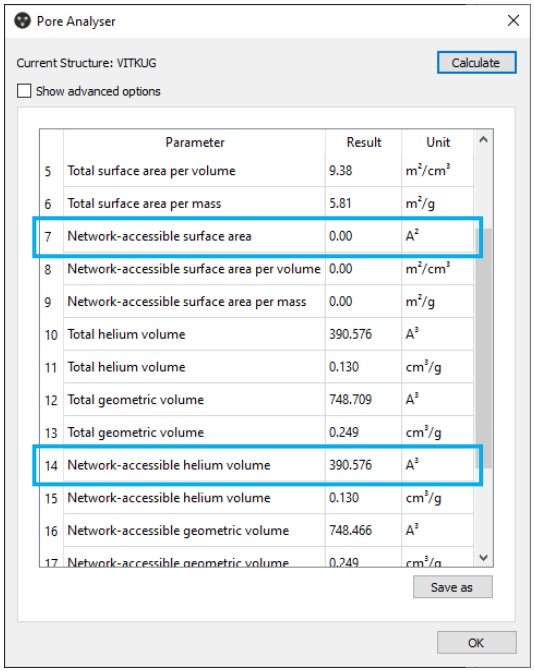
12



13

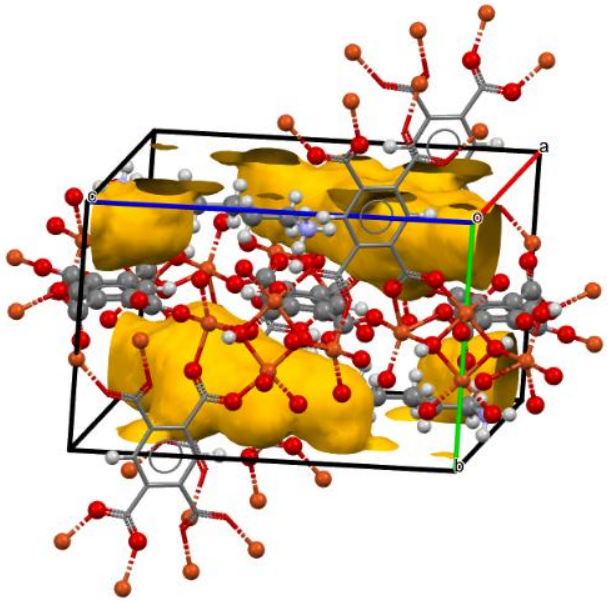


14



15. To visualise the *void* space, tick **Packing** in the *Display Options* toolbar.

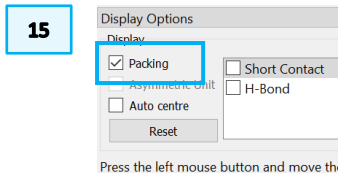
16. From the top-level menus, choose *Display > Voids…* and in the **Voids** window, click **Apply**. The result should look as shown below.

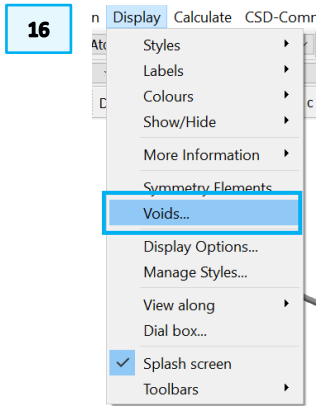


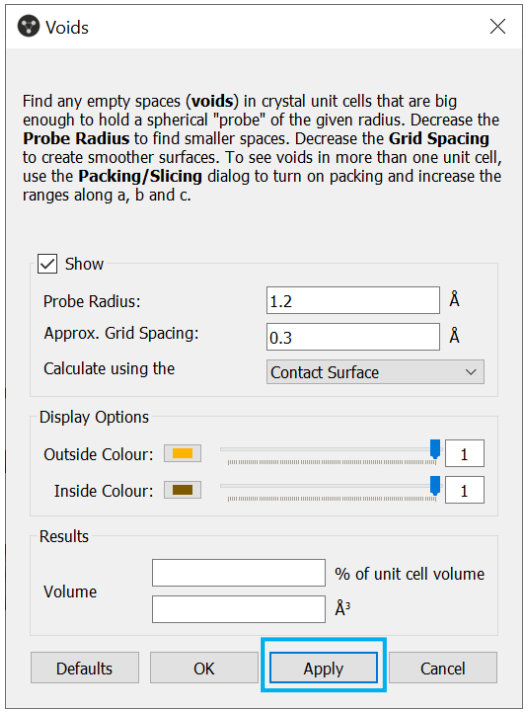
***Note**: the voids displayed in Mercury may not always reflect the result of the Pore Analyser calculation because of differences in probe definitions.*

Conclusion

In this example, we used Pore Analyser to probe the void properties of one search hit and identify changes in pore properties that are predicted to accompany dehydration. It was found that the predicted network-accessible surface area did not change upon removal of water, however, the network-accessible helium volume did change substantially, and this was accompanied by a change in void dimensionality. This might lead to increased porosity and the ability for the structure to accommodate other small molecules.





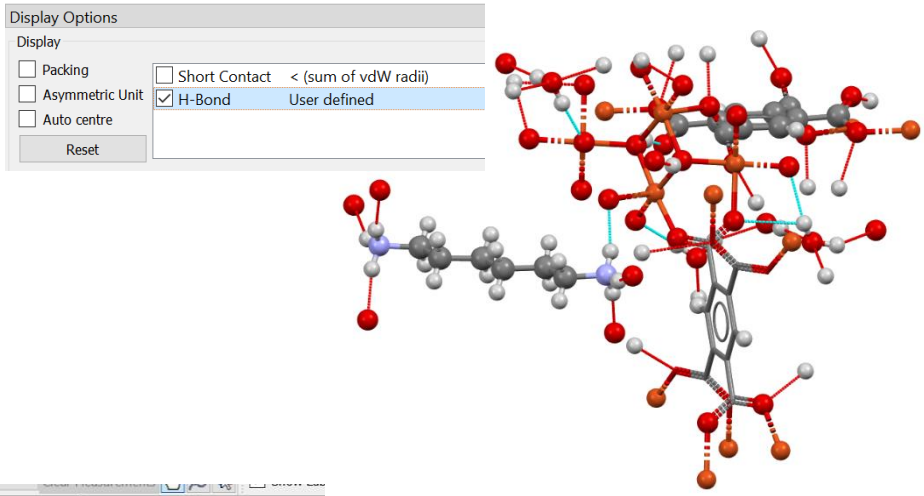


Exercises

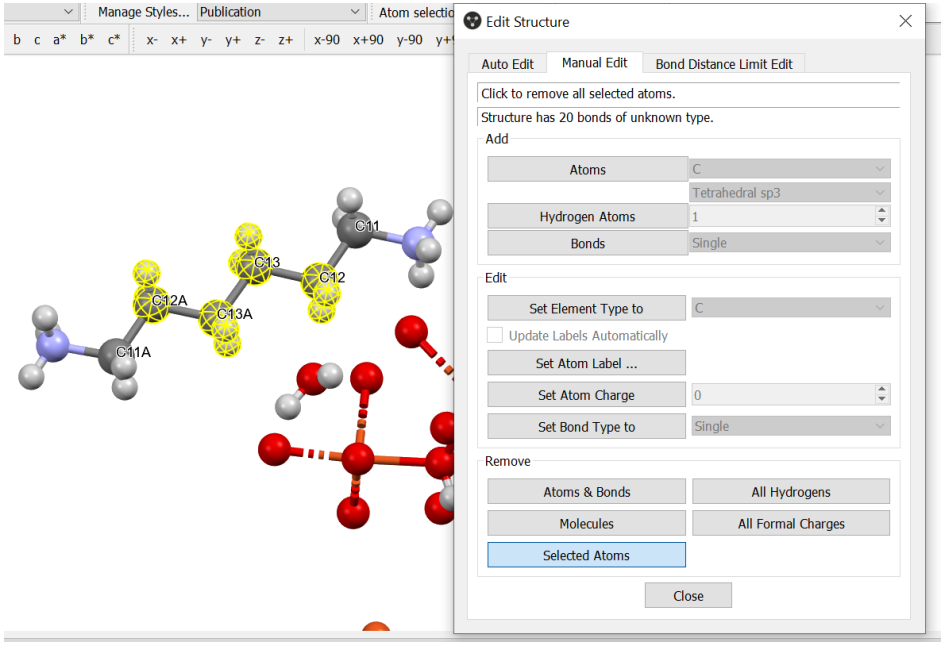
1. Investigate the hydrogen bonding interactions of the hexane-1,6-diammonium cation in the structure. To do so, tick **H-Bond** in **Display Options**, then click on the hanging red lines to expand the contacts.

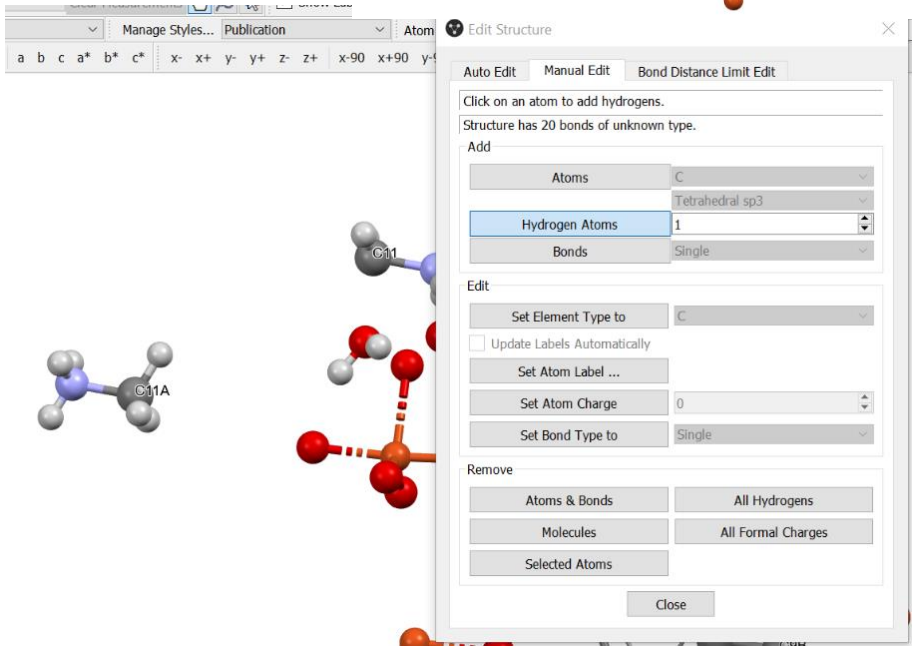
2. Investigate how the pore properties would change if the hexane-1,6-diammonium cation was replaced by two methylammonium ions, the structure being otherwise identical. *Hint: you will need to remove the highlighted atoms using Edit Structure (and add the missing hydrogen atom to each of the resulting methylammonium ions).*

1



2





Summary

In this workshop, we have learnt how to explore the void properties in a MOF using the Pore Analyser tool in Mercury. You should now be able to:

- Run a Pore Analyser calculation in Mercury.
- Edit a structure in Mercury.
- Visualise void space in Mercury.

For your reference, you can consult the Mercury user guide.

Next Steps

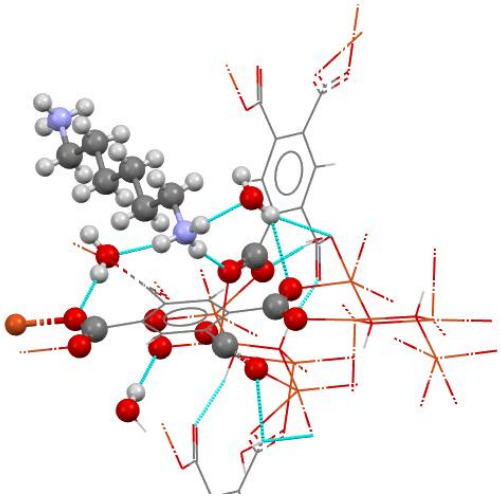
If you have enjoyed this workshop, you can find self-guided workshops on more functionality in Mercury here. In particular, you might like to try workshop CQ-005, "Searching and Analysing Metal-Organic Structures Using ConQuest and Mercury", which gives guidance on how to search for metal-organic structures of the type used in this workshop. You might also like to try our on-demand module on Visualization in Mercury or explore instructional videos on functionality such as Pore Analyser on our YouTube channel.

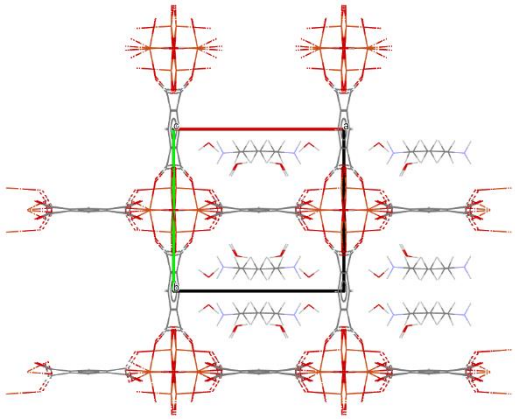
Feedback

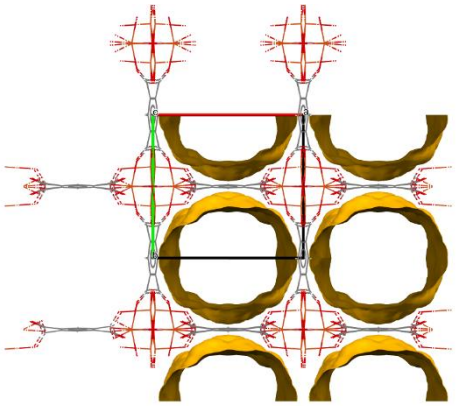
We hope this workshop improved your understanding of Mercury's Pore Analyser and you found it useful for your work. As we aim to continuously improve our training materials, we would love to hear your feedback. Follow the link on the workshop homepage and insert the workshop code, which for this self-guided workshop is *MER-006*. It will only take 5 minutes and your feedback is anonymous. Thank you!

Exercise discussion

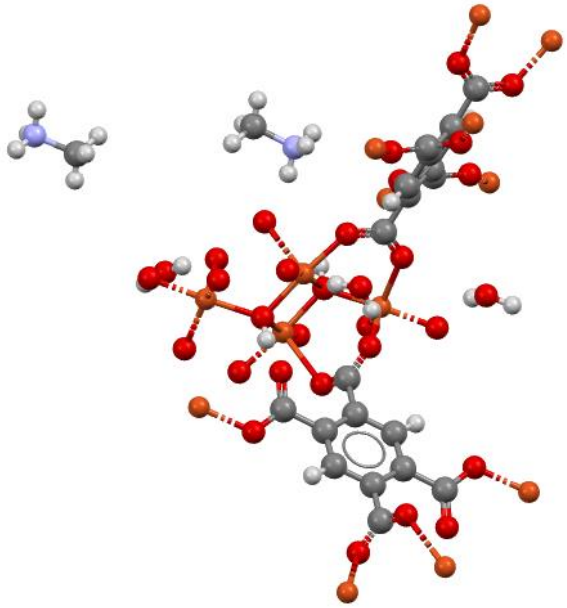
1. A close look at the structure shows that each N-H hydrogen is involved in a hydrogen bond; two of these are to water molecules and the third is to an oxygen of the carboxylate group of a linker molecule. Both ammonium groups of the di-cation are involved in this way, spanning the channels.







2. Overall, editing the structure to replace hexane-1,6-diammonium with two methylammonium ions has no effect on the surface areas, which still remain at zero. On the other hand, the network-accessible helium volume has increased nearly 10-fold, to 279.882 $Å^3$.



Glossary

Metal-Organic Frameworks (MOFs)

A metal-organic framework, abbreviated to a MOF, is a coordination network with organic ligands containing potential voids. In the CSD MOF subsets, each subset with a particular dimensionality (1D, 2D or 3D) also includes coordination polymers and coordination networks of the same dimensionality. In these subsets, the identified MOFs are not restricted to adsorption applications; therefore, 1D, 2D, and 3D MOF and MOF-like structures with all kinds of pore sizes as well as nonporous structures are included. Further information can be found in S. R. Batten, N. R. Champness, X-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh and J. Reedijk, *Pure Appl. Chem*., 2013, **85**, 1715-1724, and P. Z. Moghadam, A. Li, S. B. Wiggin, A. Tao, A. G. P. Maloney, P. A. Wood, S. C. Ward and D. Fairen-Jimenez, *Chem. Mater*., 2017, **29**, 2618-2625.

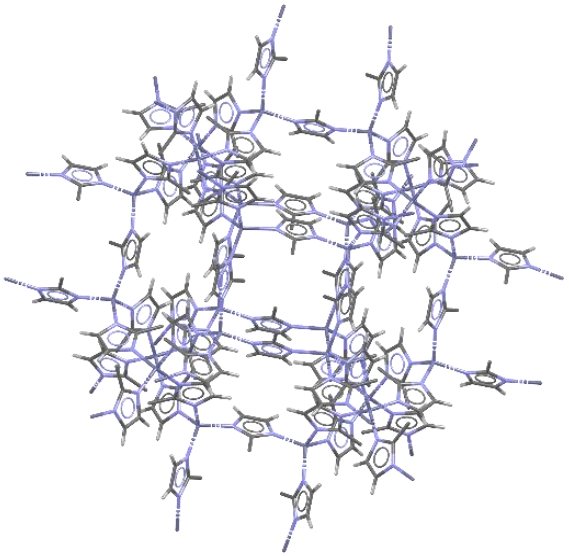
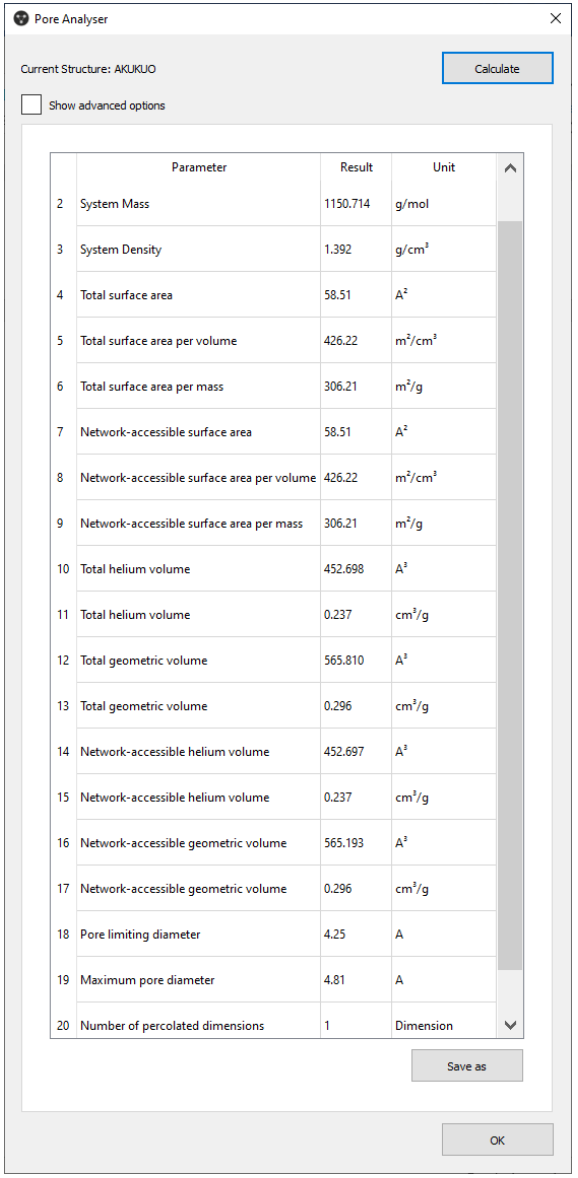


Figure of a MOF, FAWCEN03, ZIF-8.

Pore Analyser

Pore Analyser is the CSD tool for void space analysis. A pore analyser calculation reports several results including:

- System volume, mass, and density.
- Surface area, given as both total and network-accessible parameters.
    - The network accessible value considers if the probe can access the void space within a structure.
    - The total surface area will include isolated void space (closed porosity).
- Volume parameters: helium and geometric volumes differ by considering the size and interactions of the probe atom.
- Pore sizes:
    - The Pore limiting diameter value describes the largest sphere than can percolate through the void network.
    - The maximum pore diameter gives the diameter of the largest sphere that can fit in void space of the structure.
- The number of percolated dimensions:
    - Values range from 0 (isolated pores) to 3 (network of channels or layers).



	Parameter	Result	Unit
2	System Mass	1150.714	g/mol
3	System Density	1.392	g/cm³
4	Total surface area	58.51	A²
5	Total surface area per volume	426.22	m²/cm³
6	Total surface area per mass	306.21	m²/g
7	Network-accessible surface area	58.51	A²
8	Network-accessible surface area per volume	426.22	m²/cm³
9	Network-accessible surface area per mass	306.21	m²/g
10	Total helium volume	452.698	A³
11	Total helium volume	0.237	cm³/g
12	Total geometric volume	565.810	A³
13	Total geometric volume	0.296	cm³/g
14	Network-accessible helium volume	452.697	A³
15	Network-accessible helium volume	0.237	cm³/g
16	Network-accessible geometric volume	565.193	A³
17	Network-accessible geometric volume	0.296	cm³/g
18	Pore limiting diameter	4.25	A
19	Maximum pore diameter	4.81	A
20	Number of percolated dimensions	1	Dimension

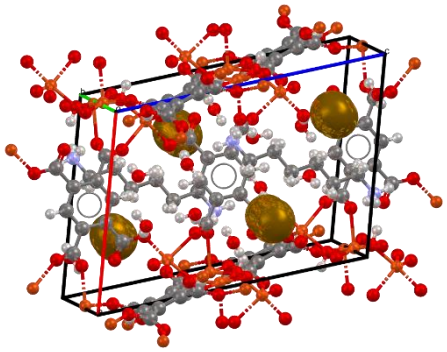
The Pore Analyser results table.

Refcode

A refcode is a CSD entry identifier comprising six letters e.g. ABACOF. Two digits identifying additional structure determinations e.g. ABACOF03.

Voids

The overall volume of a crystal structure can be partitioned into occupied 'network' and unoccupied void space. The Voids feature in Mercury displays any empty space that is big enough to contain a spherical 'probe' of a given radius.



A metal-organic framework structure, VITKUG, with voids displayed.

Basics of Mercury Visualization

Mercury is the CCDC's visualization software to view 3D structures of small molecules, generate images, and animations of molecules.

In the following we will see some of the basics of navigation and visualization in Mercury that you will find helpful to support your analysis.

In the **Mercury interface** we find:

- **At the top**: list of menus from which we can access visualization and analysis options, and other CSD components such as CSD-Materials.
- **On the right-hand side**: the **Structure Navigator**, with the database loaded (depending on your licence). The Structure Navigator allows you to select a refcode to visualize in the main Mercury window.
- Beneath the main display window: Display options toolbar. You can quickly view a packing diagram, display Hydrogen bonding and detailed information about the molecule using the More Info option.

Using the **mouse to enhance visualization**:

- Left mouse button and move – rotate molecules.
- Middle Mouse wheel – move molecules up and down.
- Right mouse button and move up and down – zoom in and out of molecules.
- Shift + Left mouse button and move - rotate in the plane molecules.
- Ctrl + Left mouse button and move - translate molecules.

Right click:
a) Near a molecule and
b) Away from a molecule