

INTRODUCTION

- The accumulated data in the Cambridge Structural Database provides a wealth of structural information which, with rare exceptions, can be used to determine precise and unbiased estimates of molecular dimensions and conformational preferences.
- When using experimentally determined results the ability to inspect and evaluate the underlying data is a key advantage and one that is not readily afforded by theoretical methods. In this module you will determine the preferred value of a Sb-Cl bond length and evaluate the precision of your findings using statistical criteria.

Use the < and > navigational buttons above to move between pages of the teaching module. Additional online resources can be accessed by clicking on the links on the right hand side of any page.

This module is divided into the following sections:

OBJECTIVES (see page 2)

GETTING STARTED (see page 2)

STEPS REQUIRED (see page 3)

SUMMARY OF KEY CONCEPTS (see page 10)

OBJECTIVES

- To determine the preferred value of a Sb-Cl bond length in hexachloro-antimony by generating a bond length distribution from structures in the Cambridge Structural Database.
- Evaluate the precision of the results you obtain using statistical criteria.
- To examine the outliers in the Sb-Cl bond length distribution and attempt to distinguish those due to error from those that happen to be an interesting new discovery like a very short bond length.

GETTING STARTED

- This module requires full access to the Cambridge Structural Database System. Specifically, the following software components will be used:
 - *Mogul*, a library of molecular geometry.
 - *Mercury*, for visualisation and examination of crystal structures.

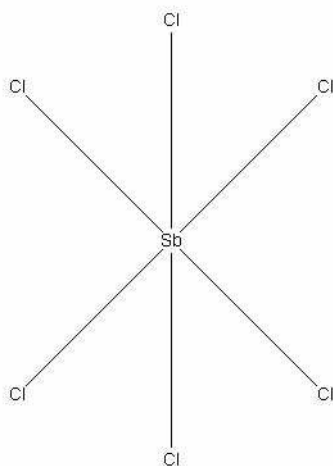
1 STEPS REQUIRED

1.1 Background

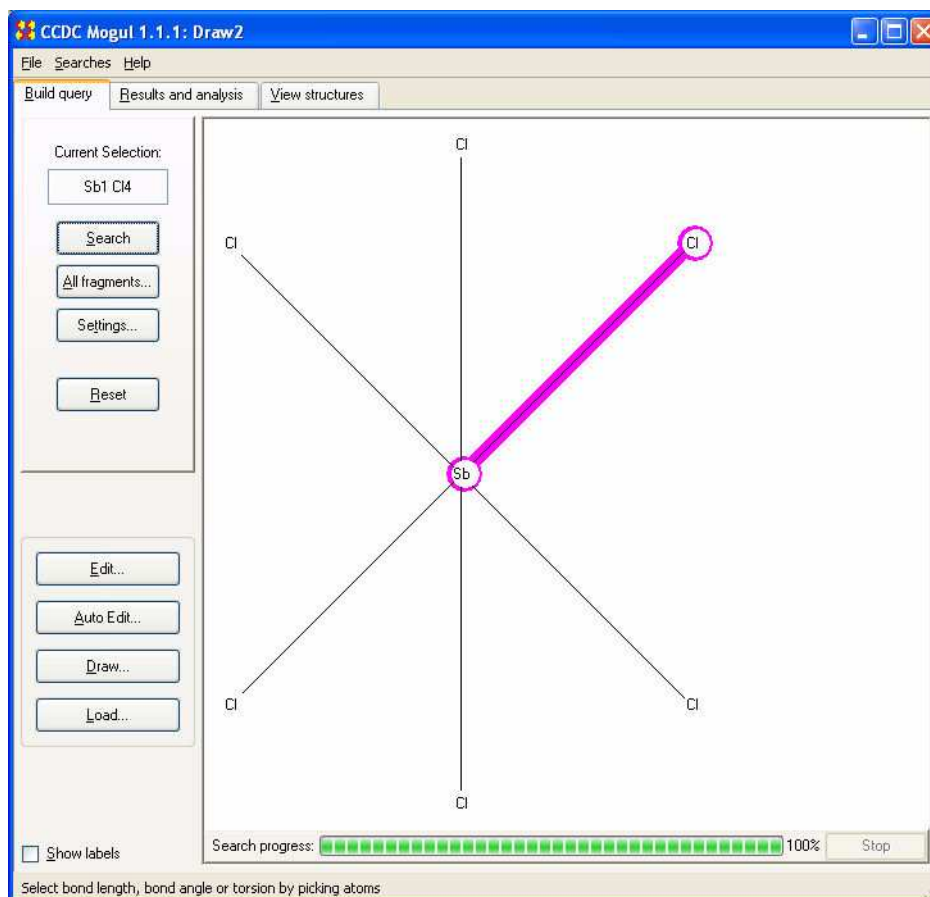
- The Cambridge Structural Database (CSD) is a primary source of experimental information on molecular geometries. For crystallographers and structural chemists, the main interest is often in bond lengths and angles. Comparison of the dimensions of a newly determined small-molecule crystal structure with the bond lengths and angles of similar structures in the CSD is useful as a check against refinement errors and to highlight unusual geometrical features.
- Indeed, CSD-based printed compilations of the means, medians, and standard deviations of organic and organometallic bond lengths have been widely used to set up dictionaries for the restrained refinement of new crystal structures.
- *Mogul* is a library of molecular geometry derived from the Cambridge Structural Database (CSD) and provides rapid access to the preferred values of bond lengths, valence angles and acyclic torsion angles.
- *Mogul* is primarily used for structure validation, e.g. checking the molecular dimensions of new crystal structures, or validating the conformations of calculated, or modelled molecules. However, *Mogul* can also be used to very quickly look up the value of e.g. a particular bond length in a given query molecule.

1.2 What is the typical Sb-Cl bond length in hexachloro-antimony?

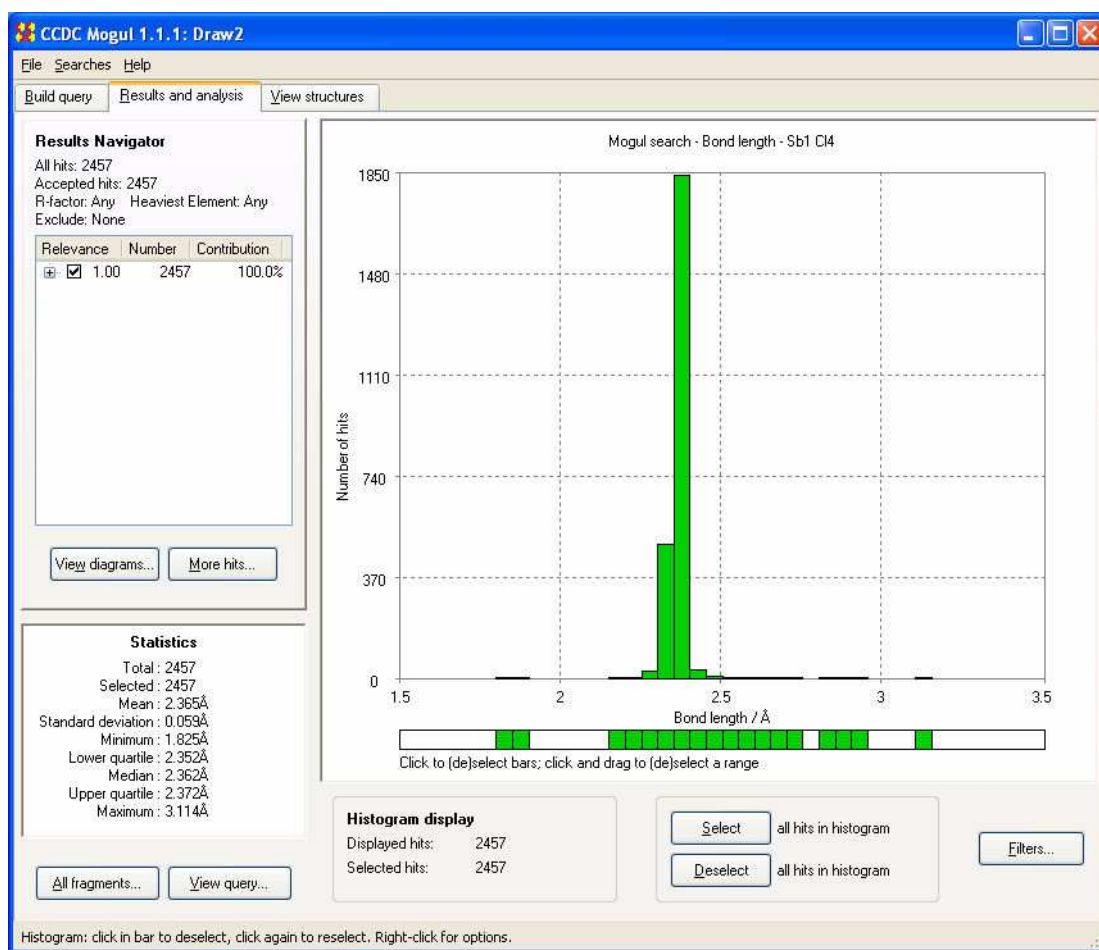
- Start *Mogul* and hit the **Draw** button to open the *Draw* window.
- Sketch hexachloro-antimony as shown below. In order to change the current element type to Sb click on the **More...** button, then select **Other Elements...** from the pull-down menu. Sb can then be selected from the Periodic Table.



- Hit **Done** to transfer the sketched structure to the *Build query* pane in the main *Mogul* window.
- Select the two atoms that are needed to define one of the Sb-Cl bond lengths by clicking on them with the left-hand mouse button (if you make a mistake hit **Reset** to clear the current selection). Selected atoms will be highlighted within the query:



- Hit **Search** to run the search.
- *Mogul* will retrieve all crystal structures in the CSD that contain a Sb-Cl bond in the same chemical environment as the query molecule. The results are then presented as a histogram which shows the Sb-Cl bond length distribution calculated from those matching entries:



- What is the average Sb-Cl bond length taken over all hit structures, i.e. what is the *Mean* of the bond length distribution?
- How many Sb-Cl bond length fragments were found in the CSD, i.e. how many observations does the histogram contain?
- A single crystal structure can, of course, contain more than one Sb-Cl bond length fragment e.g. a hexachloro-antimony ion will contain six. How many different crystal structures are represented in the histogram? You can view the CSD entries contributing to the histogram by clicking on the *View structures* tab. The refcodes of hit structures will appear in the list on the right-hand side, you can use the << and >> buttons to browse the hit structures.

1.3 Evaluating the precision of the data.

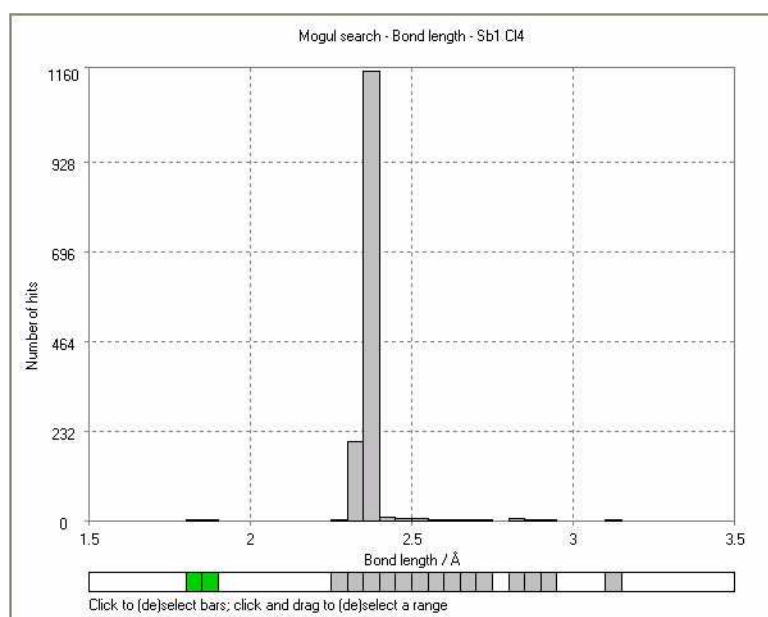
- Return to the histogram by clicking on the *Results and analysis* tab. How confident are you that the *Mean* of the bond length distribution is an accurate estimate of a typical Sb-Cl bond length? In other words, since we are dealing with real data, might the results be influenced by experimental errors in individual observations?
- The precision with which *Mogul* can predict molecular dimensions will be determined by the

dispersion of the geometry distributions it produces. The reported *Standard deviation* of the distribution therefore serves as a measure of the precision of those measurements. A large *Standard deviation* would indicate that the data points are far from the mean and a small *Standard deviation* would indicate that they are clustered closely around the mean.

- The *Standard deviation* of the Sb-Cl bond length distribution is reported under the *Statistics* listed on the left-hand side of the window. With a value around 0.06\AA , the *Standard deviation* is higher than we would like.
- The high *Standard deviation* is due to a number of severe outliers in the distribution i.e. CSD structures have unusually short or long Sb-Cl bond lengths.
- What are the minimum and maximum Sb-Cl bonds lengths observed in the CSD? Are these observations valid, or could they be from structures that contain experimental errors?

1.4 Evaluate the outliers in the Sb-Cl bond length distribution.

- In order to inspect just those CSD structures that contain unusually short Sb-Cl bond lengths: first deselect all hits in the histogram by clicking on the **Deselect** button, then highlight the two histogram bins located around 1.85\AA using the horizontal bar located directly under the histogram:

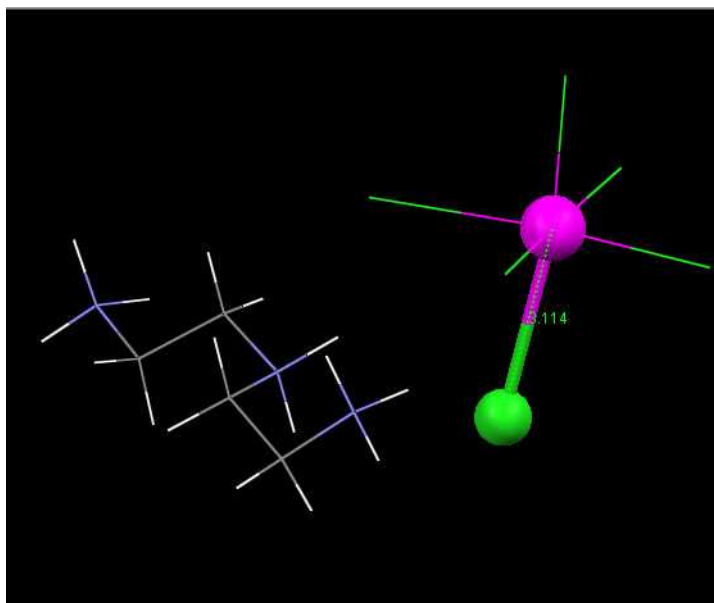


- Click on the *View structures* tab to see the CSD entries that contribute to the selected bins. You will notice that all of the selected observations come from a single crystal structure: (CSD refcode: *NARLEY*).
- Use the **Information**, **Diagram** and **3D_Visualiser** buttons on the left of the *View structures* tab to examine the structure. Can you account for the unusually short Sb-Cl bonds?

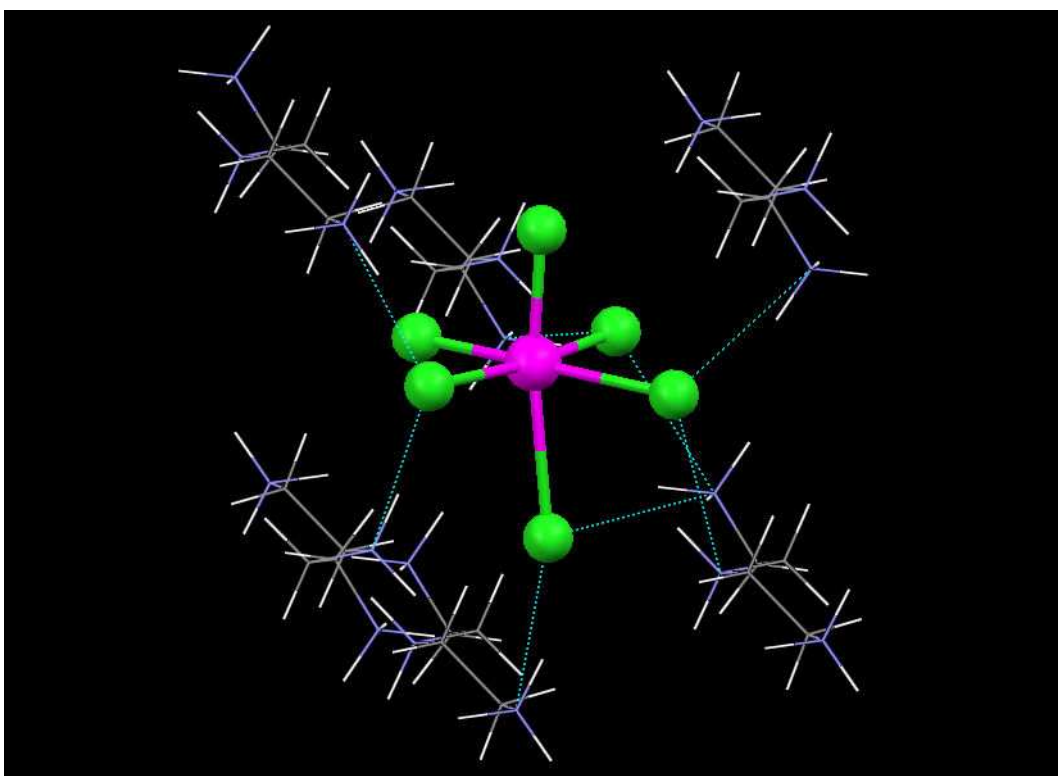
- After an initial inspection the structure looks reasonable, further investigation is clearly needed. To view the original publication reporting the crystal structure, click on the **Information** button, then click on the Digital Object Identifier (DOI) hyperlink in the *Literature Reference* field. Note that a subscription to the publication in question will normally be required to view the on-line article.
- The structure in question is referred to as *8b* in the publication. Does the information given in the *Results and Discussion* section provide any clues to the reason for the unusually short Sb-Cl bond lengths?
- The structure is reported as containing a SbF_6^- counter-ion, not SbCl_6^- . It is possible that the structure was incorrectly deposited with the database as the hexachloro-antimony ion, where, in fact, it should be a hexafluoro-antimony ion. Are the reported bond lengths of around 1.85 Å more consistent with that expected for a Sb-F bond? Check this by running a *Mogul* search on SbF_6 . Should this structure (CSD refcode: *NARLEY*) be included in our Sb-Cl bond length analysis?

1.5 Evaluate the structure that contains the longest observed Sb-Cl bond length.

- We have already determined that the shortest observed Sb-Cl bond lengths (~1.85 Å) are in error. The hit structure containing these bond lengths is actually a hexafluoro-antimony ion.
- Return to the Sb-Cl bond length distribution by selecting **Searches** from the top level menu, followed by **Draw1: Sb1 Cl2**.
- The longest Sb-Cl bond length is reported to be 3.1 Å. Could this unusually long bond length also be due to error?
- Examine the CSD structure that contains the long Sb-Cl bond (CSD refcode: *CUMMON*). Use the **Information**, **Diagram** and **3D_Visualiser** buttons on the left of the *View structures* tab to examine the structure in detail.
- Using the **3D_Visualiser** you will see that the SbCl_6^{3-} anion has a strongly distorted octahedral geometry:



- The structure contains three short (2.41 - 2.52Å) and three long (2.83 -3.11Å) Sb-Cl bonds.
- The angles involving atoms which are mutually *cis* range from 81.73 (Cl6-Sb1-Cl5) to 97.97 (Cl4-Sb1-Cl5), while the *trans* angles are 174.47, 173.3 and 170.50, the last involving Cl3 and Cl6. The deviations of these bond angles from the ideal values of 90 and 180 are consistent with the presence of the long bonds, the largest deviations from 90 degrees involve the more weakly bonded chlorine atoms, Cl4-Sb1-Cl5 = 97.97, Cl5-Sb1-Cl6 = 81.7.
- To investigate the reason for this strongly distorted octahedral geometry open *Mercury* and read in the file *bond_lengths.gcd*. Click on the refcode *CUMNON* in the *Structure Navigator* on the right hand side of the main *Mercury* window to view the structure.
- Click on the tick box next to the words **H-Bond Default definition** in the list box underneath the 3D display. This finds all the hydrogen bonds formed by the two molecules that are currently displayed. Some of the hydrogen bonds are shown as broken red lines. Place the cursor anywhere on one of the broken red lines and left-click. This causes the complete molecule at the other end of the hydrogen bond to be shown. Repeat this process to build up a picture of the hydrogen bonding in this structure:



- It is reasonable to conclude that the presence of multiple hydrogen bonds, mainly involving the three long-bonded chlorine atoms is responsible for the octahedral distortion.
- Diethylenetriammonium hexachloroantimonate(III) (CSD refcode: *CUMNON*) is an unusual and interesting structure. However, the reported Sb-Cl bond lengths are not in error.

SUMMARY OF KEY CONCEPTS

- The CSD tries to report objectively what is presented in the literature. Therefore, in order to guarantee that the CCDC do not impose their idea of what is right or wrong but leave this judgement up to the crystallographers and the peer review process, suspicious crystal structures are not usually actively corrected without the authors consent. Inevitably this will mean that a small number of CSD entries will contain errors.
- It is extremely important, for any scientist, to question the validity of any results or data they might obtain or be provided with.
- When using experimentally determined results the ability to inspect and evaluate the underlying data is a key advantage and one that is not readily afforded by theoretical methods.
- The accumulated crystal structure data in the CSD provides a wealth of structural information which, with rare exceptions, can be used to determine precise and unbiased estimates of molecular dimensions and conformational preferences.