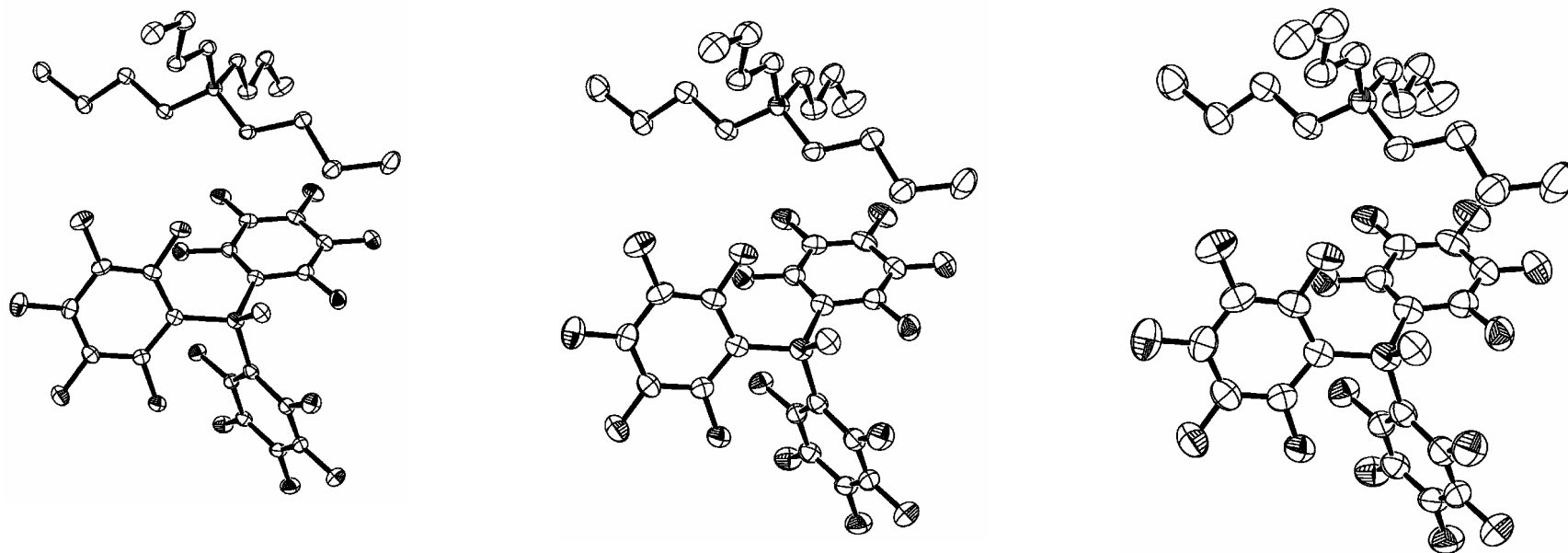


Thermal Ellipsoids

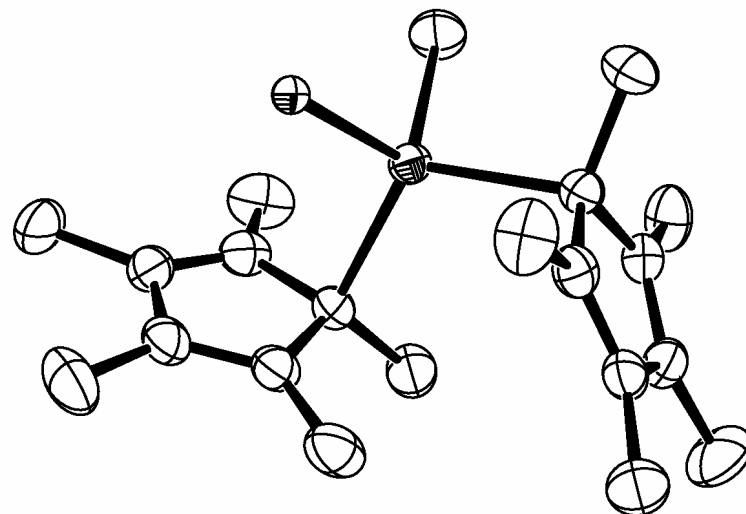
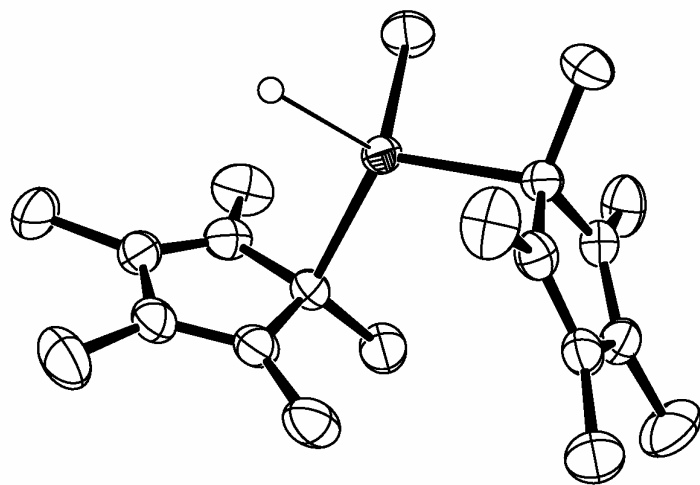
Remember that thermal ellipsoids can indicate problems with a refinement even when the R factors seem to indicate a reasonable solution. Elongated or distorted ellipsoids can indicate that something is wrong with the solution (such as disorder). It is wise to remember that the ellipsoid surfaces are indicative of a probability. You can consider the percentage assigned to a given surface as being the probability that the electron density is completely bound by the ellipsoid. Obviously, the size of the ellipsoids depend on the probability surface we choose. Shown below are thermal ellipsoid plots of a single structure at the 30%, 50% and 70% levels of probability.



Note that the size of the ellipsoids will be reduced if the data collection is done at low temperature because of the reduction in the amount of atomic motion. It is thus almost always advisable to collect data at low temperatures.

Temperature Factors and Thermal Ellipsoids

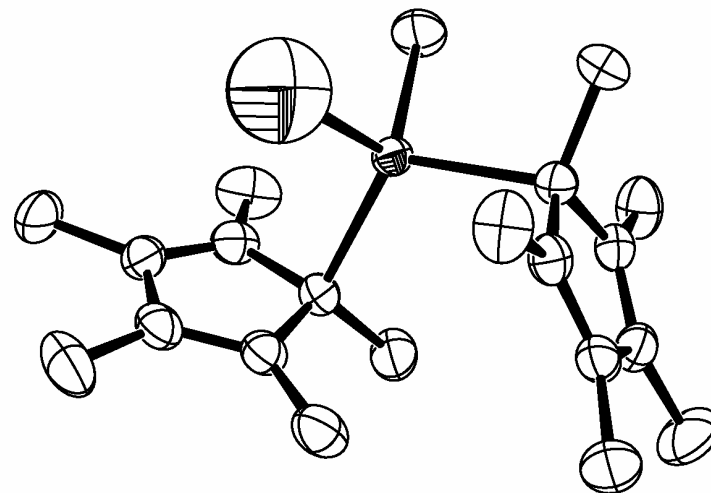
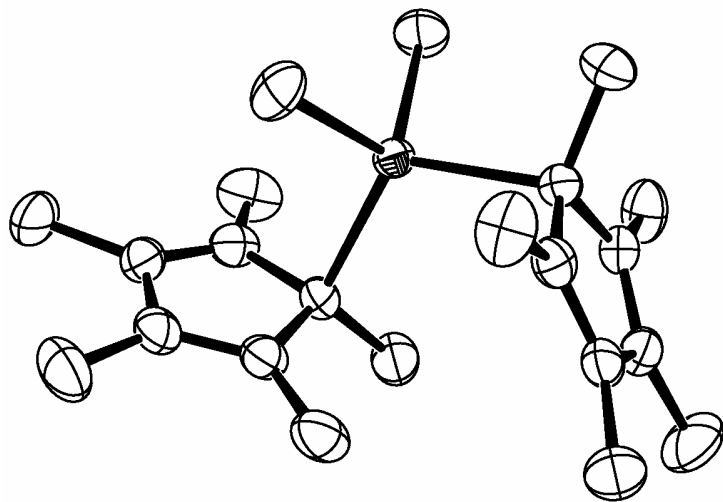
Remember that thermal ellipsoids can indicate problems with a refinement even when the R factors seem to indicate a reasonable solution. Consider the case of the molecule $\text{Cp}^*_2\text{SnMeX}$. With no H atoms attached to the Me groups, the following results were obtained when X was H, Li, C, or Cl. Notice that after a few cycles of refinement, the R1 factors for each of these solutions appears acceptable but the temperature factors and ellipsoids show that something is wrong for all of the options except X = C.



R1 = 0.060: H3 2 0.591794 0.139842 0.156746 11.00000 0.00001

R1 = 0.048: LI3 5 0.592551 0.139622 0.156865 11.00000 0.01957

Temperature Factors and Thermal Ellipsoids



R1 = 0.046: C3 1 0.592026 0.139458 0.156972 11.00000 0.04659

R1 = 0.056: CL3 4 0.589217 0.139459 0.157247 11.00000 0.26295

Consider why the size of the ellipsoid varies in this way: Since it is the electron **density** we are modeling, if there is not enough electron density provided by a given atom at a certain point, the only way to increase the electron density is to “shrink” the volume of space occupied by that atom. Conversely, if an atom provides too much electron density at a position in the cell, the only way to decrease the density is to increase the volume of space occupied by that atom.

The a summary of the progress of each refinement cycle is stored in a file called name.lst (or shelxl.lst) and contains a variety of useful information. If your refinement has crashed for some reason, the list file can provide you with an indication of the cause of the problem. Likewise, if an error or warning message is provided at the end of the refinement, the name.lst file should offer information into the nature of the problem. For example, if we input a molecular formula that does not agree with the number and type of atoms found in our model, an error message will be produced. You will then find in the .lst file a statement such as:

Unit-cell contents from UNIT instruction and atom list resp.

C	140.00	140.00
H	156.00	0.00
B	4.00	4.00
N	4.00	4.00
F	60.00	60.00

Make sure that you understand why the numbers do not agree and then fix the problem. In this case, we haven't included H atoms yet so none are found in the atom list.

Other important information in the list file can be found in the correlation matrix (missed symmetry) and in the final listing of atomic positions (disorder).

One of the most important files that we must generate after refinement is completed is the crystallographic information file (CIF) name.cif, which is the type of file that we submit when we report a crystal structure. Such files are created by inserting the ACTA command in the instruction files prior to the final refinement cycle. The name.cif file contains virtually all of the information that anyone might need to determine any desired information regarding the crystal structure to which the file refers.

I have given you a copy of a cif file for the structure of the ammonium borate as well as the tabulated data that are usually generated and reported. These tables generally include:

1. Crystal data and the refinement information.
2. Atomic coordinates, isotropic U values and their errors.
3. Bond lengths and angles and their errors (if desired torsion angles must be generated by the CONF command in the name.ins file)
4. Anisotropic displacement parameters U_{ij} for the atoms.
5. Hydrogen atom positions, isotropic U values and their errors.

You do NOT usually want to generate the list of calculated and observed structure factors – this was done in the past so that people could assess the data but now there are software (e.g. PLATON) and online methods (IUCr) of doing this.

Metrical Parameters

The interatomic distances, angles between 3 atoms, torsion angles, planes and related quantities are known collectively as “Metrical Parameters”. Such parameters are readily calculated by software packages using the formulae provided in the “Derived Results” handout from Stout and Jensen. In many situations, we need to be able to compare these distances to other values that have been reported (e.g. to see if your bond lengths are typical or unusual). To do this, we must use the estimated standard deviations (ESD, σ_i) associated with each particular parameter to assess if the quantities are the same (indistinguishable) or different to a certain level of probability.

Comparing a group distances or angles:

Δ = the difference in the distance or angle

$$\sigma = (\sum \sigma_i^2)^{1/2}, \quad \lambda = \Delta/\sigma$$

ρ is the probability that a quantity differs from the mean value by more than $\lambda\sigma$

ρ	λ
1.00	0.000
0.50	0.674
0.10	1.65
0.05	1.96
0.01	2.58
0.001	3.2

These statistics are derived from normal distributions, where for example 99.7% of the time your result will be within 3σ (3 standard deviations) of the mean value. Thus, a simple way to compare two values is to simply look at the range of values at $\pm 3\sigma$. Thus a bond length listed as 1.522(3) Å indicates that there is a 99.7% probability that the bond is actually between 1.513 Å and 1.531 Å. If another bond length falls within this range, you can not distinguish between the two with a high level of confidence.



Metrical Parameters

When you are reporting your crystallographic results, one of the most common points of discussion is the comparison of the metrical parameters in your structure to those of other structures. While the metrical parameters for other structures are generally given in the original literature, the best tools that we use to find the metrical parameters (and the original reports) are the various crystallographic databases.

The databases are divided into compound types:

Inorganic compounds containing no C-H bonds are found in the Inorganic Crystal Structure Database (**ICSD**). The department does not have a current license for this database but there is a free limited version available online at (<http://icsd.ill.fr/icsd/>).

Small Organic, Organometallic and Inorganic compounds are collected in the Cambridge Structural Database (**CSD**; located at the Cambridge Crystallographic Data Centre <http://www.ccdc.cam.ac.uk/>). These are searched using the ConQuest software.

Proteins and large biological molecules are collected in the Protein Data Bank (**PDB**). While most of the class does not generally search for this type of molecule, the file name.pdb is one of the most extensively used formats for the exchange of crystallographic data.

Chem 59-553 Inorganic Crystal Structure Database

The **ICSD** contains the structural information for minerals. We are attempting to obtain a current version of this database but some information is available from the free version available online at (<http://icsd.ill.fr/icsd/>). When you select the link to the demo version, the screen that appears will look like this:

Authors <input type="text"/>	Years <input type="text"/>	Journal <input type="text"/>	Title <input type="text"/>	Help <input type="button" value="Search"/> <input type="button" value="Reset"/>
Elements <input type="text"/>	Element Count <input type="text"/>	Mineral Name <input type="text"/>	ANX Formula <input type="text"/>	Pearson Symbol <input type="text"/>
System <input type="text" value="any"/>	Laue Class <input type="text" value="any"/>	Space Group <input type="text"/>	Cell Volume <input type="text"/>	Density <input type="text"/>
Remarks <input type="text"/>	Min. Distance <input type="text"/>	Distance Select <input type="text"/>	Distance Range <input type="text"/>	Co-ordin. <input type="text"/>

Welcome to the Inorganic Crystal Structure Database.

Click the blue heading links for help and examples.

Most of the search parameters are obvious – the links above each of the boxes will provide help regarding that search parameter – and the most useful ones for our use are searches based on the elements in the structure or the mineral name. For example, if we want to search for structures containing calcium an phosphate anions, we can enter “Ca P O” in the Elements box and hit search to produce:



Chem 59-553 Inorganic Crystal Structure Database

Authors	Years	Journal	Title	Help
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="button" value="Search"/> <input type="button" value="Reset"/>
Elements	Element Count	Mineral Name	ANX Formula	Pearson Symbol
Ca P O	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
System	Laue Class	Space Group	Cell Volume	Density
any <input type="text"/>	any <input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
Remarks	Min. Distance	Distance Select	Distance Range	Co-ordin.
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>

Select All / None 30 Results

Year	Authors	Struct. Formula	sgr	Mineral Name
<input type="checkbox"/> 2000	Kampf, A.R.	(Ca ₂ (H ₂ O) ₂) (Mn ₃ O ₂ (P O ₄) ₃) (H ₂ O)	P121/C1	Pararobertsite
<input type="checkbox"/> 1999	Wilson, R.M.; Elliott, J.C.; Dowker, S.E.P.	Ca _{10.132} (P O ₄) _{5.958} (O H) _{3.258}	P63/M	Hydroxylapatite
<input type="checkbox"/> 1999	Wilson, R.M.; Elliott, J.C.; Dowker, S.E.P.	(Ca _{3.892} Na _{0.087} Mg _{0.021}) (Ca _{5.628} Na _{0.126} Mg _{0.029}) (P O ₄) _{5.67} (C O ₃) _{0.33} (O H) _{2.01}	P63/M	Apatite
<input type="checkbox"/> 1998	Gonzalez, G.; Pina, C.; Jacas, A.; Hernandez, M.; Leyva, A.	Zn _{0.867} Ca _{0.433} P _{2.253} Al _{8.667} O ₂₄ (H ₂ O) ₁₂	R3-MH	
<input type="checkbox"/> 1997	Khan, N.; Morozov, V.A.; Khasanov, S.S.; Lazoryak, B.I.	Ca ₁₉ Cu ₂ (P O ₄) ₁₄	R3CH	
<input type="checkbox"/> 1997	Fleet, M.E.; Pan, Y.-M.	(Ca _{0.876} Na _{0.097} Ce _{0.019} Dy _{0.009}) ₄ (Ca _{0.935} Ce _{0.044} Dy _{0.021}) ₆ ((P _{5.88} Si _{0.12}) O ₂₄) F ₂	P63/M	Fluorapatite
<input type="checkbox"/> 1997	Morozov, V.A.; Presnyakov, I.A.; Belik, A.A.; Khasanov, S.S.; Lazoryak, B.I.	Ca ₉ Mg Na (P O ₄) ₇	R3CH	
<input type="checkbox"/> 1996	Jeanjean, J.; McGrellis, S.; Rouchaud, J.C.; Fedorov, M.; Rondeau, A.; Perocheau, S.; Dubis, A.	Ca _{8.8} (P O ₄) ₆ (O H) _{1.92}	P63/M	Hydroxylapatite
<input type="checkbox"/> 1993	Senbhagaraman, S.; Guru Row, T.N.; Umarji, A.M.	Ca _{0.5} (Ti ₂ P ₃ O ₁₂)	R3-H	
<input type="checkbox"/> 1993	Boudin, S.; Grandin, A.; Borel, M.M.; Leclaire, A.; Raveau, B.	Ca ₂ (P ₂ O ₇)	P41	

Pages : [1] 2 3(30 results) results per page.

Demo ICSD database copyright 2003-2004 Fachinformationszentrum (FIZ) Karlsruhe
PHP/MySQL Interface V04-02-19 copyright 2003-2004 by Peter Hewat email: hewat@free.fr

The buttons above the list of results can then be used to obtain more information on any of the structures that have been listed.

ICSD Details

1 entry selected. CC=Collection Code: ID=ID Number: [mC24]=Pearson Symbol:

CC=73712
ID =34148

Help

Title Redetermination of the β -Ca₂P₂O₇ structure.

Authors Boudin, S.; Grandin, A.; Borel, M.M.; Leclaire, A.; Raveau, B.

Reference [Acta Crystallographica C \(1993\) 49, 2062-2064](#)

Compound **Ca2 (P2 O7)** - Calcium diphosphate - β -Ca [tP88]

Cell 6.6858(8), 6.6858(8), 24.147(3), 90., 90., 90.
P41 (V=1079.37)

Remarks R=0.031000 : TEM=294

Atom (site)	Oxid.		x, y, z, B, Occupancy				
Ca1	(4a)	2	0.1374(2)	0.2313(2)	0	0	1
Ca2	(4a)	2	0.1591(2)	0.5447(2)	0.24262(5)	0	1
Ca3	(4a)	2	0.7895(2)	0.7337(2)	0.13802(4)	0	1
Ca4	(4a)	2	0.3627(2)	0.1054(2)	0.13548(4)	0	1
P1	(4a)	5	0.6213(2)	0.3078(2)	0.02345(6)	0	1
P2	(4a)	5	0.8673(2)	0.2534(2)	0.12431(5)	0	1
P3	(4a)	5	0.0463(2)	0.7148(2)	0.01863(6)	0	1
P4	(4a)	5	0.2873(2)	0.6462(2)	0.12074(5)	0	1
O1	(4a)	-2	0.4607(6)	0.1584(6)	0.0426(2)	0	1
O2	(4a)	-2	0.7727(6)	0.1984(6)	-0.0133(2)	0	1
O3	(4a)	-2	0.5303(7)	0.4921(6)	-0.0001(2)	0	1
O4	(4a)	-2	0.7395(6)	0.3776(6)	0.0789(2)	0	1
O5	(4a)	-2	0.7364(6)	0.0873(6)	0.1469(2)	0	1
O6	(4a)	-2	0.0519(6)	0.1769(6)	0.0953(2)	0	1
O7	(4a)	-2	0.8994(6)	0.4088(6)	0.1695(2)	0	1
O8	(4a)	-2	0.8537(6)	0.7907(6)	0.0433(2)	0	1
O9	(4a)	-2	0.1855(6)	0.8795(6)	-0.0011(2)	0	1
O10	(4a)	-2	0.0229(6)	0.5542(6)	-0.0249(2)	0	1
O11	(4a)	-2	0.1582(6)	0.5873(6)	0.0666(2)	0	1
O12	(4a)	-2	0.3450(7)	0.4526(6)	0.1474(2)	0	1
O13	(4a)	-2	0.4622(6)	0.7756(6)	0.1015(2)	0	1
O14	(4a)	-2	0.1474(6)	0.7722(6)	0.1572(2)	0	1

Atom (site)	Oxid.		U11, U22, U33, U12, U13, U23					
			0.0044(2)	0.0043(2)	0.00027(1)	0.0025(3)	-0.00010(8)	0.00036(8)
Ca1	(4a)	2	0.0035(2)	0.0034(2)	0.00038(1)	-0.0002(3)	-0.00003(8)	-0.00004(8)
Ca2	(4a)	2	0.0040(2)	0.0038(2)	0.00027(1)	0.0020(3)	-0.00026(8)	0.00014(8)

For example, the “Reference” button will provide you with the article in which the data was reported and the “Details” button will give you most of the information you would likely want for the structure. You can also download various file types (such as CIF and RES) so that you can examine and manipulate the structure with one of the viewing programs that we have seen or will see (e.g. Diamond, ORTEP-3, GRETEP, PowderCell, WebLab viewer, etc.).

The “Pattern” button can be used to generate the powder X-ray diffraction pattern of the compound you have selected. We will talk about powder XRD later but this feature can obviously be used to confirm the composition of a solid you have studied using XRD.

ICSD Diffraction Pattern

1 entry selected.

Edit the data then click on **Plot** to see the pattern. You can plot up to **3 patterns** on the same axes. You may need help setting up to **view PDF and postscript files**. Most problems with the **data format** are due to an incorrect **Space Group**, but try switching off the **gzip option** if it is selected below. **Please check the symmetry operations in the print-out !! (button below)**.

<pre>TITLE *-Ca2(P2O7)-[P41] Boudin, S.; Grandin, A.; Borel, M.M.; L[1993] CELL 6.685800 6.685800 24.147000 90.000000 90.000000 90.000000 SPCGRP P 41 ATOM CA 1 0.137400 0.231300 0.000000 0.000000 0.000000 ATOM CA 2 0.159100 0.544700 0.242620 0.000000 0.000000 ATOM CA 3 0.789500 0.733700 0.138020 0.000000 0.000000 ATOM CA 4 0.362700 0.105400 0.135480 0.000000 0.000000 ATOM P 1 0.621300 0.307800 0.023450 0.000000 0.000000</pre>					
Technique: X-Ray Diffractometer		Wavelength Custom		Custom Wave. 1.5418 Å	
Width Parameters u 0.05 v -0.06 w 0.07		Plot Type 2Theta		2Th.Zero 0 Step 0.1 2Th.Range 0 to 40	
<input type="checkbox"/> Labels <input type="checkbox"/> Dispers <input checked="" type="checkbox"/> PDF plot <input type="checkbox"/> Color <input checked="" type="checkbox"/> Gzip		Plots/Page 1		<input type="button" value="Defaults"/> <input type="button" value="Plot"/>	

After plotting, or the plot file, or the profile file, or the listing.

If MSIE won't display a plot, use [Mozilla](#) instead, or these direct links to the [PostScript](#) or [PDF](#) files.
 Postscript plotting using Klaus Yvon et al's [Lazy Pulverix](#) (Benjamin Nunes, MIT).

The “Structure” button can be used to display the arrangement of the atoms in the structure either as a PDB/Chime (this is easier) type file or as a VRML file.

ICSD Structure Display

1 entry selected.

Edit the CCSL data, select the **Atoms** and **Bonds** model, and click on **Display**. Choose 2 or more structures to compare them. You may need help with the **3D display** or with special **drawing options**. Most **problems** are due to the **Space Group** representation. **Please check the symmetry operations in the print-out !! (button below)**.

<pre>N *-Ca2(P2O7)-[P41] Boudin, S.; Grandin, A.; Borel, M.M.; Lecla(1993) C 6.685800 6.685800 24.147000 90.000000 90.000000 90.000000 S GRUP P 41 A Ca1 0.137400 0.231300 0.000000 0.000000 0.000000 A Ca2 0.159100 0.544700 0.242620 0.000000 0.000000 A Ca3 0.789500 0.733700 0.138020 0.000000 0.000000 A Ca4 0.362700 0.105400 0.135480 0.000000 0.000000 A P1 0.621300 0.307800 0.023450 0.000000 0.000000</pre>					
<input type="checkbox"/> PDB/Chime	<input type="checkbox"/> VRML2	<input checked="" type="checkbox"/> Cell	<input type="checkbox"/> At.Names	<input type="checkbox"/> Transparent	<input checked="" type="checkbox"/> Black B/G
<input checked="" type="checkbox"/> Perspective	<input checked="" type="checkbox"/> Axes	<input type="checkbox"/> Shaded	<input type="checkbox"/> Title	<input type="checkbox"/> Wireframe	<input checked="" type="checkbox"/> Gzip file
Blink time <input type="text" value="1"/>	Atoms <input type="text" value="Small Spheres"/>	Bonds <input type="text" value="Coord Polys"/>			
Reference Plane <input type="text" value="0.0 0.0 0.0"/> <input type="text" value="0.0 0.0 0.0"/> <input type="text" value="0.0 0.0 0.0"/>	Multiple Cells: x: <input type="text" value="1"/>	y: <input type="text" value="1"/>	z: <input type="text" value="1"/>		
Bonded atoms		Min Bond: <input type="text" value="0.75"/>	Max Bond: <input type="text" value="2.75"/>		
Defaults				Display	

After Displaying,

Re-display

Save

VRML structure

Print

CCSL output

Valence-Sum



The **CSD** contains the structural information about most of the small molecule structures that most of you make or study. We have a site license for the software and the computer on which it is located is found in the room adjacent to the room containing the single-crystal diffractometers. It is possible to purchase additional licenses (as I do) so that you can use the CSD on a computer in your office – talk to your supervisor if you would find this useful. The CSD contains more than 300,000 structures and is updated every few months. There are a number of TUTORIALS found under the “Help” menu and **you should become familiar with most of the standard searching techniques.**

You can search the CSD by:

- Structure - drawing
- Peptide - name
- Author/Journal information
- Compound Name
- Elements
- Formula
- Space Group
- Unit Cell
- Z/Density
- Experimental
- All Text
- Reference Code (CSD number)



If you are searching metrical parameters, the best search method is by structure drawing because you can draw the type of structural details that are required. While the best way to learn how to use this software is practice (as always) I have a few hints for you and I'll show you a few important things to remember.

1. Be aware of the bond-types you insert in your search structure – you may get false negative results if the CSD has it drawn differently! Draw your structure with as much flexibility as possible (e.g. “any” type of bond) when you are in doubt.
2. Use templates wisely (for the same reason as above).
3. Select multiple elements carefully to avoid too many hits.
4. Remember that you can put 2D and 3D restrictions on the model!
 - 2D restrictions include the number of atoms bonded to a selected atom, the charge on a particular atom etc.
 - 3D definitions let you search for distances, angles, planes, centroids etc.
5. Remember that you can look at the 3-D structures of the molecules in ConQuest or Mercury and you can export desired structures as CIF, SHELX, PDB and many other file types for viewing in other software.