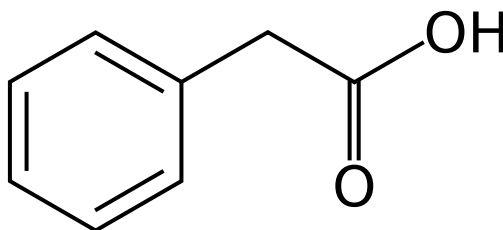


## TUTORIAL EXPO: DIRECT SPACE METHODS SOLUTION

### INSTRUCTIONS FOR EXERCISE 1

In this exercise, you will perform the crystal structure solution of phenylacetic acid ( $C_8H_8O_2$ ) by direct space methods (DSM).



Go to directory **Direct space methods solution/phenyla**. You will see the following files:

- **pd\_0009.xye** this is a file containing the experimental powder diffraction data.
- **Structure3D\_CID\_999.sdf** this is a file containing a 3D starting model of the phenylacetic acid. The file has been downloaded from the PubChem database: <https://pubchem.ncbi.nlm.nih.gov/compound/999#section=Top>
- **phenyla\_pub.cif** this is a CIF file containing the fractional coordinates of the published model (Hodgson, D. J. & Asplund, R. O. (1991). [Acta Cryst. C47, 1986–1987](#)).
- **phenyla.exp** this is an EXPO2014 input file for structure solution of phenylacetic acid ( $C_8H_8O_2$ ) by direct space methods, once cell parameters and space group have been determined.

Open and read the file **phenyla.exp**, it consists of the following lines:

```
%Structure phenyla
%Job Phenylacetic acid (C8 H8 O2)
%Data
  Cell 10.226  4.967  14.467  90  99.25  90
  SpaceGroup p 21/a
  Pattern pd_0009.xye
%fragment Structure3D_CID_999.sdf
%sannel
```

**%fragment Structure3D\_CID\_999.sdf** is the command used to import the 3D starting structure model.

**%sannel** is the command enabling the access to the graphic interface of direct space methods (DSM).

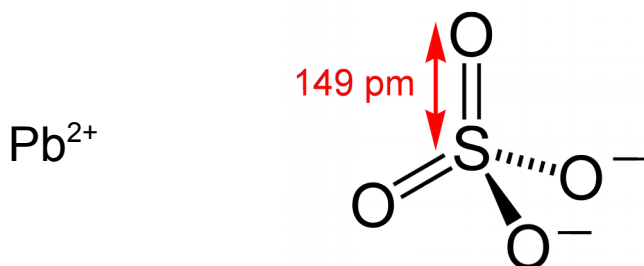
The directive `wavelength` is not necessary because the information is provided in the first line of the `pd_0009.xye` file.

**To run EXPO2014 on `phenyla.exp`:**

- Open EXPO2014 and click on **Load & Go** button in the **File** menu.
- Navigate to directory `phenyla` and load the input file `phenyla.exp`.
- Now click **GO**.
- It will open the **Global optimization dialog**. Modify the field **Resolution**: 2.5 Å is enough to obtain accurate atomic positions. This action is equivalent to add the directive `resm 2.5` after the command `%sannel` in the input file.
- Now click on **Execute** and 10 runs of the DSM procedure will be performed. For each *i*-th DSM run a CIF file (`phenyla_besti.cif`) containing the best solution is created in the `phenyla` working directory. At the end of the 10 runs, the solution corresponding to the lowest cost function is automatically selected.
- Click on the button **Solutions** to explore the 10 best structural models, ranked according to the cost function. Click on **Save**, to select one of the ten best solutions;
- To compare the selected best solution with the published model `phenyla_pub.cif` click on **Quit** (to leave the 'Global optimization dialog' window) and on **Tools→Overlay Structures** to load the `phenyla_pub.cif` file.
- Remove the published model from **Tools→Delete Model→phenyla\_pub.cif**. Check the chemical reasonableness of the structure by showing the hydrogen bonds: **View→Contacts→Hydrogen Bonds**. Use **View→Symmetry→Grow Fragments** to expand the hanging contacts.

**INSTRUCTIONS FOR EXERCISE 2**

In this exercise, you will perform the crystal structure solution of lead(II) sulfate ( $\text{PbSO}_4$ ) by direct space methods (DSM).



Go to directory **Direct space methods solution/PbSo4**. You will see the following files:

- **pbso4.dat** this is a file containing the experimental powder diffraction data.
- **9015524.cif** this is a CIF file containing the fractional coordinates and the isotropic thermal parameters of a published model, downloaded from the COD database <http://www.crystallography.net/cod/9015524.html>
- **pbso4.exp** this is a EXPO2014 input file for structure solution of PbSO<sub>4</sub> by direct space methods, once cell parameters and space group have been determined.

Open and read the file `pbso4.exp`, it consists of the following lines:

```
%structure pbso4
%job Lead(II) sulfate (PbSO4)
%data
    Pattern pbso4.dat
    Wavelength 1.54056
    Cell 6.95802 8.48024 5.39754 90 90 90
    Spacegroup p b n m
%frag tetra S O 1.49
%frag atoms Pb
%sannel
    doc
```

The command `%frag` is used to build the starting model from two independent fragment: a SO<sub>4</sub> tetrahedron (`%frag tetra S O 1.49`) and a Pb atom (`%frag atoms Pb`). 1.49 is the expected S-O distance in angstrom unit.

#### To run EXPO2014 on PbSO<sub>4</sub>:

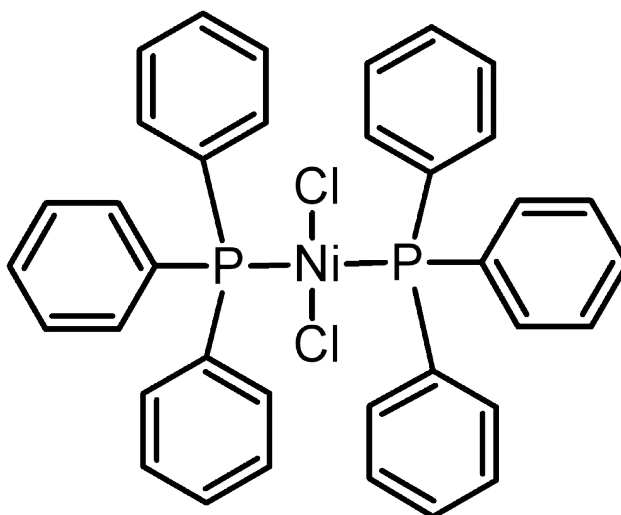
- Open EXPO2014 and click on **Load and Go** button in the **File** menu.
- Navigate to directory `pbso4` and load the input file `pbso4.exp`.
- Now click **GO**.
- It will open a the **Global optimization dialog**. Since atoms in special positions are expected, it is advisable to carry out the structure solution process applying the dynamical occupancy correction (DOC). In this case the DOC is also used to merge the excess of atoms introduced in the starting model. It can be activated by adding the directive `doc` after the command `%sannel`. Alternatively, to activate the DOC click on the tab **Internal DOF**

button, then on the button **Atomic Parameters and Dynamical Occupancy Correction**, and finally on the check button **D.O.C.**, that enables to apply DOC to all the atoms.

- Now click **OK**.
- Click on the button **Execute**, in the dialog window, to run DSM. 10 runs of the DSM procedure will be performed. For each *i-th* DSM run a CIF file (pbs04\_best*i*.cif) containing the best solution is created. At the end of the 10 runs, the solution corresponding to the lowest cost function is automatically selected.
- Click on the button **Solutions** to explore the 10 best structural models, ranked according to the cost function. Click on **Save**, to select one of the 10 best solutions.
- Click on **Quit** to leave the 'Global optimization dialog' window.
- On the **JAV** molecular viewer, click on **Modify**→**Delete Duplicate Atoms** and then on **OK** to remove the oxygen atom in excess.
- The correctness of the obtained final model provided by DSM can be verified comparing it with the published model in the file 9015524.cif: **Tools**→**Overlay Structures** to load the 9015524.cif file.

### INSTRUCTIONS FOR EXERCISE 3

In this exercise, you will perform the crystal structure solution of trans-Dichlorobis(triphenylphosphine)nickel(II) ( $C_{36}H_{30}Cl_2NiP_2$ ) by direct space methods (DSM).



Go to directory **Direct space methods solution/nickel**. You will see the following files:

- **nickel.xy** this is a file containing the experimental powder diffraction data.
- **Conformer3D\_CID\_11776.sdf** this is a file containing a 3D starting model of the triphenylphosphine molecule. The file has been downloaded from the PubChem database: <https://pubchem.ncbi.nlm.nih.gov/compound/11776#section=3D-Conformer>.
- **nickel\_pub.cif** this is a CIF file containing the fractional coordinates of the published model (Brammer, L. & Stevens, E. D. (1989). [Acta Cryst. C45, 400–403](#)).
- **nickel.exp** this is an EXPO2014 input file for structure solution of the compound by direct space methods, once cell parameters and space group have been determined.

Open and read the file `nickel.exp`, it consists of the following lines:

```
%Structure nickel
%Job trans-Dichlorobis(triphenylphosphine)nickel(II) (C36 H30 Cl2 Ni P2)
%Data
    Cell      11.638  8.197  17.388  90  107.03  90
    Pattern    nickel.xy
    Wavelength 1.54056
    space P 2/c
%frag Conformer3D_CID_11776.sdf
    deletehydro
%frag atoms Ni Cl
%sannel
    doc Ni
    resm 2.5
```

In this crystal structure the asymmetric unit is half a molecule and the Ni atom is expected to lie in a special position. The command `%frag` is used to build the 3D starting model of the asymmetric unit from 3 independent fragments: a triphenylphosphine molecule (`%frag Conformer3D_CID_11776.sdf`), Ni and Cl atoms (`%frag atoms Ni Cl`). The directive `deletehydro` deletes the hydrogen atoms from the molecule in the file `Conformer3D_CID_11776.sdf`.

**To run EXPO on nickel:**

- Open EXPO2014 and click on **Load & Go** button in the **File** menu.
- Navigate to directory `nickel` and load the input file `nickel.exp`.
- Now click **GO**. It will open a the **Global optimization dialog**.

- Click on the button **Execute**, in the dialog window, to run DSM. 10 runs of the DSM procedure will be performed. For each *i-th* DSM run a CIF file (`nickel_besti.cif`) containing the best solution is created. At the end of the 10 runs, the solution corresponding to the lowest cost function is automatically selected.
- Click on the button **Solutions** to explore the 10 best structural models, ranked according to the cost function. Click on **Save**, to select one of the 10 best solutions.
- Click on **Quit** to leave the ‘Global optimization dialog’ window.
- On the **JAV** molecular viewer, click on View→Symmetry→Grow Fragment to expand the asymmetric unit and display an entire molecule of Dichlorobis(triphenylphosphine)nickel.
- The correctness of the obtained final model provided by DSM can be verified comparing it with the published model in the file `nickel_pub.cif`: **Tools**→**Overlay Structures** to load the `nickel_pub.cif` file.