University of Windsor
Chemistry and Biochemistry
Chemistry 59-553, Winter Term 2017

Assignment 3

Due: Tuesday, April 4

1. Derive the Patterson peak locations (and multiplicities) that would be observed for an atom located at a general position in the space group *C2/c*. Indicate the positions of any Harker lines and planes.

2. A molecule with the formula $C_{54}H_{66}B_2Cd_1F_8O_{18}P_2$ crystallizes with Z = 8 in *C2/c*. A Patterson synthesis was computed and showed peaks with approximate intensities (I) as follows:

	u	v	w	I	d (distance from origin)
1.	0.0000	0.0149	0.0000	5824	0.17
2.	0.5000	0.2149	0.5000	2011	18.13
3.	-0.2248	0.0166	0.4314	2009	20.14
4.	0.0014	0.0137	0.0768	1172	2.46
5.	-0.2756	0.2198	0.0680	1115	12.54
6.	0.2191	0.0121	0.4896	726	13.51

Please note: a) the molecule is expected to have a linear P-Cd-P fragment with a Cd-P distance of around 2.4Å; b) the origin peak is peak 1; c) the distances (d) of peaks from the origin can be useful in assigning them.

Calculate the Cd and P atom positions. Show your work clearly and account for each peak in the Patterson synthesis.

3. Draw a reasonable Patterson map for the molecule AsC_5H_5 (arsabenezene, the arsenic analogue of pyridine – for simplicity, assume that the molecule is a regular hexagon with a bond distance of around 1.4 Å) located at a general position in the plane group *p1* (this is the 2D equivalent of the space group *P1* and is meant to simplify the problem) with a = 10 Å , b = 8 Å and γ = 80º. Be sure to indicate the relative intensities of each peak.

4. You have determined the structure of the pentabromocuprate(II) ion by X-ray diffraction. The coordination geometry appears to be that of a trigonal bipyramid. Ionic dimensions are Cu-Br1 2.446(3) Å, Cu-Br2 2.454(3) Å, Cu-Br3 2.509(5) Å, Cu-Br4 2.519(4) Å, Cu-Br5 2.532(5) Å. Angles at the Cu atom in degrees formed by Br atoms are given as follows:

3,4 119.7(3)	1,3 90.4(3)	2,4 90.3(3)
3,5 120.1(3)	3,2 89.5(4)	2,5 90.3(3)
4,5 120.2(3)	1,4 89.5(3)	1,5 89.4(4)

By calculating mean values and determining the standard deviations on the mean values, (a) show the

coordination geometry does (or does not) deviate significantly from that of an ideal trigonal bipyramid. (b) compare the equatorial bond lengths with the axial values. (c) suggest an explanation for any significant differences.

5.

(a) Use the ICSD to search for compounds containing Na, Mn and O. Print out a screen shot of the first page of results and please indicate the number of the "hits" you obtained.

(b) For the compound $MnNa(VO_4)$, export the structural data into Diamond and use it to make a picture of structure that highlights the "columnar" nature of the crystal structure. In addition, determine the Na-O and Mn-O distances for the oxygen atoms closest to each metal (4 for Na and 6 for Mn).

6.

(a) Use the CSD (ConQuest) to search for structures containing any type of bond between a pentamethylcyclopentadienyl (C_5Me_5, Cp*) group and a gallium atom. Provide me with a printout of your search parameters and print out a screen shot of the first page of results and please indicate the number of the "hits" you obtained. Note: Use the "Write PDF to view/print results" selection under the File menu and select the "list" option.

(b) Use a 3D search in the CSD to determine the average C-Ga distance **for Cp* groups that are sigma bonded to the Ga atom.** I.e. the carbon atom attached to the Ga should formally sp^3 hybridized and the other carbon atoms in the ring should be sp^2 hybridized. Provide me with a printout of your search parameters and results.

(c) Export the data for structure RAHBEH (Cp*Ga) into ORTEP-3 and make me diagrams that illustrate (i) the structure of the asymmetric unit and (ii) the hexameric nature of the packing.