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

Assignment 3

Due: 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.

For C2/c, the general positions are:
(1)   *x, y, z*
(2)   *-x, y, 0.5-z*
(3)   *-x, -y, -z*
(4)   *x, -y, 0.5+z*

These 4 positions are obtained using the (0,0,0) origin and the 4 additional positions obtained because of the (0.5,0.5,0) centering are identical and result in a doubling of the multiplicity of the vectors.

The vectors connecting these positions are:

Vector	Multiplicity	Label	Comment
±(2x,2y,2z)	2	a	(the multiplicity of each of the peaks is 2x from centering)
±(0,2y,0.5)	4	b	This is a Harker line
±(2x,0,0.5+2z)	4	c	This is a Harker plane
±(2x,-2y,2z)	2	d	
(0,0,0)	8	e	This is the trivial solution that gives rise to the origin peak.

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.

(question and answer courtesy of D.L.Ward at MSU)
Calculate:

1. *origin peak height;*
2. *scale factor relating the calculated origin peak height to the observed origin peak height; and,*
3. *expected scaled Cd-Cd and Cd-P peak heights.*

1. *Origin peak:*

```
         zi    zi    ni    Z
Cd1    48 * 48 *  1 * 8   = 18432.
P2     15 * 15 *  2 * 8   =  3600.
F8      9 *  9 *  8 * 8   =  5184.
O18     8 *  8 * 18 * 8   =  9216.
C54     6 *  6 * 54 * 8   = 15552.
B2      5 *  5 *  2 * 8   =   400.
H66     1 *  1 * 66 * 8   =   528.
                            ------
                     HO   = 52912.
```

2. *Scale factor:*

```
SF = 5824. / 52912. = 0.110
```

3. *Expected peak heights:*

```
            zi    zj
Cd - Cd   48 * 48 * SF =   254 (multiplicity = 1)
                           507 (multiplicity = 2)
                          1014 (multiplicity = 4)
                          2029 (multiplicity = 8)

Cd - P    15 * 48 * SF =    79 (multiplicity = 1)
                           159 (multiplicity = 2)
                           317 (multiplicity = 4)
                           634 (multiplicity = 8)
                          1268 (multiplicity =16)
(etc.)
```

Match observed peaks with expected peaks (note that the expected scaled 2x and 4x Cd-Cd peak heights are about one half of the observed peak heights so there is so **the actual scaling factor must be ca. twice as large…ca. 0.218**):

```
                                    assignment---------------
2.   0.5000 0.2149 0.5000   2011.  |  b.      0, 2Y, 1/2    1014. i.e.  4xCd-Cd
3.  -0.2248 0.0166 0.4314   2009.  |  c.   2X, 0, 1/2+2Z    1014. i.e.  4xCd-Cd
5.  -0.2756 0.2198 0.0680   1115.  |  a.      2X, 2Y, 2Z     507. i.e.  2xCd-Cd
```

Apply Patterson map space group (C2/m) symmetry operations to calculate the positions of equivalent Patterson map peaks:

```
 use  -1/2+X, 1/2+Y,   Z  with peak 2
 use      -X,    -Y, 1-Z  with peak 3
 use   1/2+X, 1/2+Y,   Z  with peak 5
```

resulting in:

```
                                   assignment--------------
 2'  0.0000 0.7149 0.5000  2011.  | b.     0, 2Y, 1/2   1014. i.e. 4xCd-Cd
 3'  0.2248 -.0166 0.5686  2009.  | c.  2X, 0, 1/2+2Z   1014. i.e. 4xCd-Cd
 5'  0.2244 0.7198 0.0680  1115.  | a.     2X, 2Y, 2Z    507. i.e. 2xCd-Cd
```

Calculate coordinates for the Cd atom:

The above gives two estimates of 2X (0.2248 and 0.2244)
- which average to 2X = 0.2246 and lead to X = 0.1123;
two estimates of 2Y (0.7149 and 0.7198)
- which average to 2Y = 0.7174 and lead to Y = 0.3587; and
two estimates of 2Z (0.0680 and 0.0686)
- which average to 2Z = 0.0683 and lead to Z = 0.0342.

Together these give the fractional coordinates for the Cd atom:
```
  Cd   0.1123 0.3587 0.0342
```

Calculate coordinates for two P atoms:

Assign peak 4 as the Cd-P vector (because of the Patterson vector length and the observed peak height):

```
  4.    0.0014 0.0137 0.0768  1172. This must be a 8xCd-P vector (i.e. 4xCd-P combined
with linear "centro-symmetric" P-C-P fragment, which will double peak intensity)!
```

As we expect a linear P-Cd-P fragment, we first add peak 4 coordinates to the Cd coordinates to get one P position:
```
  Cd   0.1123 0.3587 0.0342
  4.   0.0014 0.0137 0.0768
       ------ ------ ------
  P1   0.1136 0.3724 0.1110
```

Then we subtract peak 4 coordinates from the Cd coordinates to get the other P position:
```
  Cd   0.1123 0.3587 0.0342
  4.  -.0014 -.0137 -.0768
       ------ ------ ------
  P2   0.1109 0.3450 -.0426
```

This results in a P-Cd-P fragment with 180° P-Cd-P angle and 2.46Å Cd-P distances. The above is consistent with, and correctly assigns, the strongest four non-origin peaks in the Patterson map.

*Thus three atom positions that you have identified are:*
```
  Cd   0.1123 0.3587 0.0342
  P1   0.1136 0.3724 0.1110
```

Given its intensity, the final peak probably corresponds to a Cd-F vector (8x).

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 $\gamma = 80°$. Be sure to indicate the relative intensities of the each peak.

Although each map may be different depending on the orientation you chose for the molecule, your map should look something like this (from the answer of one of the students in the class):
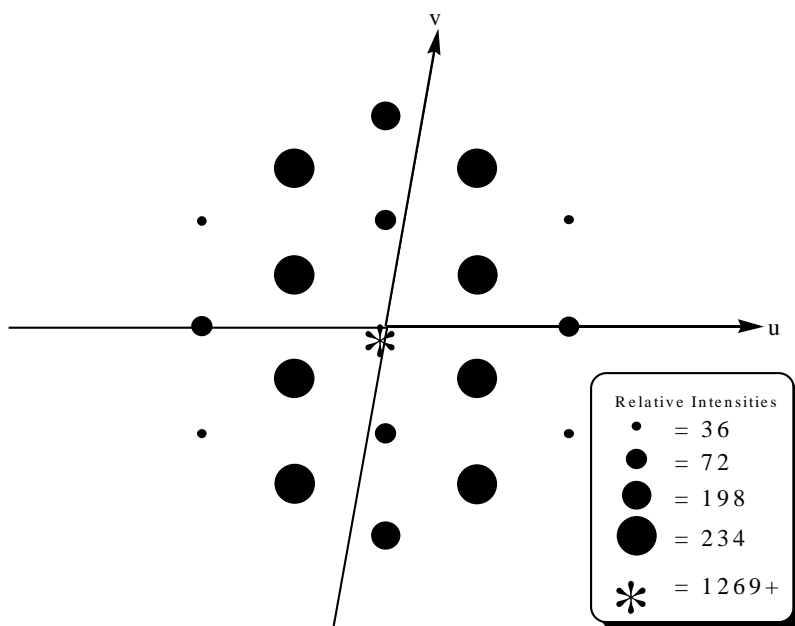
Drawing the complete unit cell is readily accomplished by translating this pattern. Please note that the peak intensities are obtained from the sum of the products of the atomic numbers for the two atoms forming the vector: e.g. the peak with an intensity of 234 results from the coincidence (overlap) of As-C vectors (33·6 = 198) and one C-C vector (6·6 = 36), etc.

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.

(a)

Ax	Value	ESD	Avg	SD	Composite ESD	SD
	2.446	3	2.450	0.005657	0.004243	no requirement
	2.454	3				
Eq						
	2.509	5	2.520	0.011533	0.008124	no requirement
	2.519	4				
	2.532	5				
Ax						
1,3	90.4	3	89.9	0.477493	0.8246	90
3,2	89.5	4				
1,4	89.5	3				
2,4	90.3	3				
2,5	90.3	3				
1,5	89.4	4				
Eq						
3,4	119.7	3	120.0	0.264575	0.5196	120
3,5	120.1	3				
4,5	120.2	3				

Thus the geometry does not deviate significantly from that of an ideal trigonal bipyramid – keeping in mind that a TBP has D_{3h} symmetry and there are no requirements for the axial and equatorial bond lengths to be the same.

(b) The axial and equatorial bond lengths are significantly different – note that even the shortest equatorial bond length 2.509(5) Å using 3 times the ESD gives a minimum value of 2.494 Å while the longest of the axial bonds 2.454(3) Å has a maximum value of 2.466 Å so the ranges are not even close to overlapping.

(c) No answer was really required here so I would accept anything reasonable that you suggested. From a crystallographic point of view, the fact that there are no significant distortions from the ideal structure indicates that there are no significant intermolecular (inter-ionic, in this case) interactions, such as H-bonding or other close contacts, that change the metrical parameters.
When there are no unusually close contacts in a structure, then chemical reasons must cause the distortions. For main group elements, one usually expects the axial bonds to be longer than the equatorial bonds in a TBP (the reasons being either the use of 3-center-2-electron bonding (reasonable) or the participation of the more diffuse d orbitals in sp^3d hybrids (less reasonable)). In the case of this transition metal complex, since all of the bonds are formed using d-orbitals, the cause of the differences in bond lengths is a Jahn-Teller distortion caused by orbital mixing.

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.

I found 1347 hits – there is enough detail in the screenshot below.

Results: List View   **# of Hits: 1347** ℹ️

Select All   Deselect All   Show Detailed View   Show Synoptic View   Export Selected Data   Back to Query

Coll. Code ▲	HMS	Struct. Form.	Struct. Type	Title	Authors	Reference	☆
5187	C 1 2/m 1	(K1.97 Na.03) (Fe4.76 Al.70 Li.16 Mn.16 Ti.24) (Al1.813 Si6.187 O20) (O H).32 F2.174 O1.489	Mica#-(1M)- C12/M1	Crystal chemical variations in Li- and Fe- rich micas from Pikes Peak batholith (central Colorado)	Brigatti, M.F.; Lugli, C.; Poppi, L.; Foord, E.E.; Kile, D.E.	American Mineralogist (2000) 85, p1275-p1286	☆ 💾
5315	R -3 H	(Pb0.61 Sr0.39) (Mn0.8 Zn0.2) (Mn0.54 Fe0.34 Na0.09 Zn0.03)2 (V7.78 Ti7.03 Fe0.37) O38		Paseroite, Pb Mn2+ (Mn,Fe)2 (V,Ti,Fe,[])18 O38, a new member of the crichtonite group	Mills, S.J.; Bindi, L.; Cadoni, M.; Kampf, A.R.; Ciriotti, M.E.; Ferraris, G.	European Journal of Mineralogy (2012) 24, p1061-p1067	☆ 💾
5330	R -3 H	(Sr.53 La.18 Pb.10 Na.03 Ca.03) (U.41 Ce.10 Y.21 Mn.07) Fe2 (Ti12.42 Fe3.35 Cr1.62 V.126) O38		Mapiquiroite, (Sr,Pb) (U,Y)Fe2(Ti,Fe3+)18O38 a new member of the crichtonite group from the Apuan Alps, Tuscany, Italy	Biagioni, c.; Orlandi, P.; Pasero, M.; Nestola, F.; Bindi, L.	European Journal of Mineralogy (2014) 26, p427-p437	☆ 💾
5331	R -3 H	(Sr.31 Pb.25 Na.019 Ca.014 La.001) (U.86 Y.07 Ce.021 Mn.005) Fe1.70 Zn.30 (Ti12.07 Fe4.99 V.37 La.009) O38		Mapiquiroite, (Sr,Pb) (U,Y)Fe2(Ti,Fe3+)18O38 a new member of the crichtonite group from the Apuan Alps, Tuscany, Italy	Biagioni, c.; Orlandi, P.; Pasero, M.; Nestola, F.; Bindi, L.	European Journal of Mineralogy (2014) 26, p427-p437	☆ 💾
5364	R 3 m H	Na.73 Ca.01	Tourmaline	Crystal chemistry of the	Bosi, F.; Lucchesi,	European Journal of	☆ 💾

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(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).

					Yuichi		
260949	P n m a	Mn Na (V O4)	Olivine- Mg2SiO4	Synthesis and characterization of the crystal structure and magnetic properties of the ternary manganese vanadate Na Mn V O4	Ben Yahia, H.; Gaudin, E.; Boulahya, K.; Darriet, J.; Son Wonjoon; Whangbo Myunghwan	Inorganic Chemistry (2010) 49, (18) p8578- p8582	☆ 💾

Here is a reasonable picture I built illustrating the columns formed by the edge-shared octahedra of adjacent MnO_6 fragments:
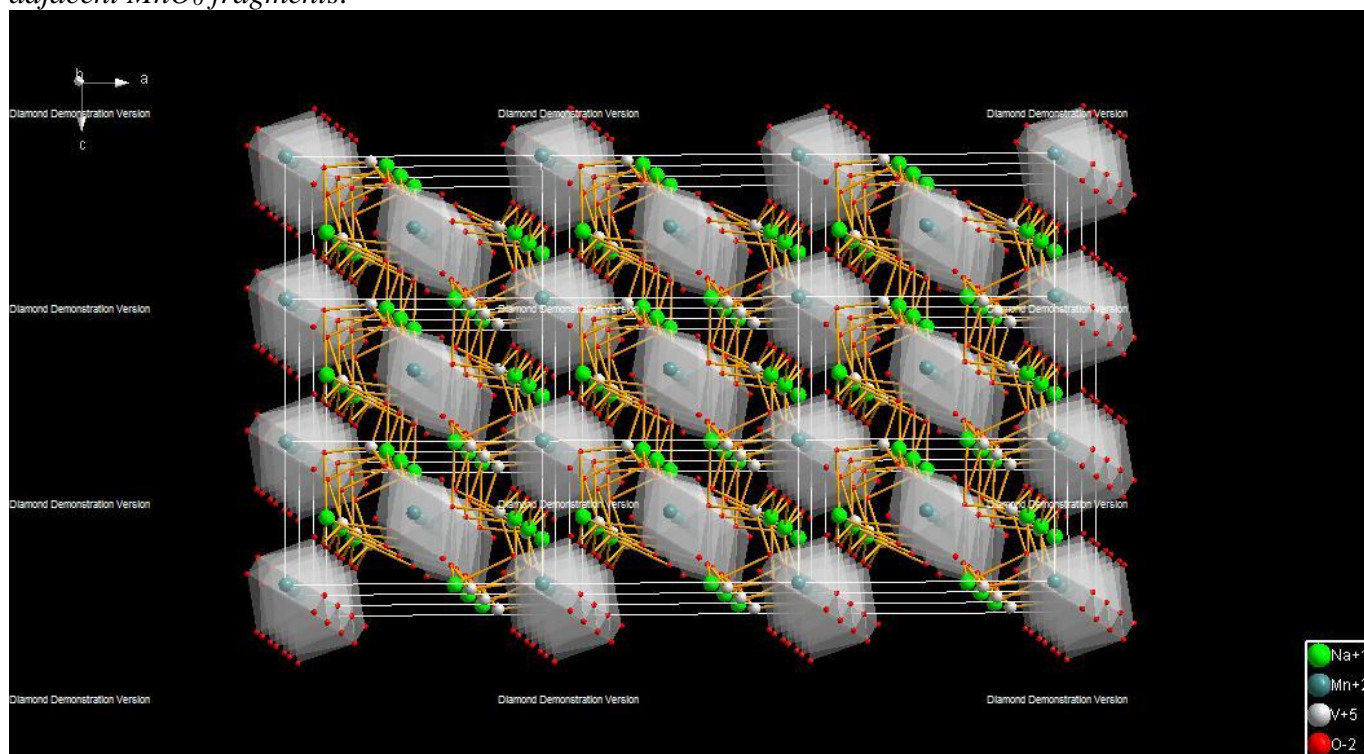
Distances in Å

Mn1	O3	2x	2.0996(10)
	O1	2x	2.1827(9)
	O2	2x	2.3677(11)
Na1	O3	2x	2.2784(12)
	O1	1x	2.4205(18)
	O2	1x	2.4437(18)

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.

(a) Here is a summary of my search parameters and results:

There are 143 hits ranging from AHODOR to ZOMGEP.
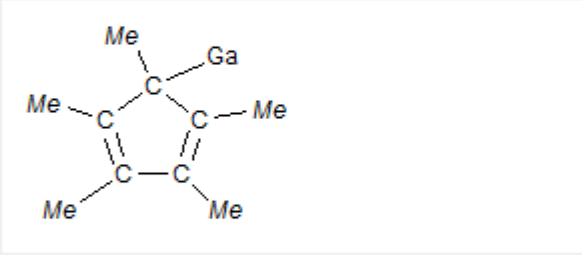
(b) Here is a summary of my search parameters and results:

Search:	search2
Database(s):	CSD version 5.38 updates (Nov 2016)
	CSD version 5.38 (November 2016)
	CSD version 5.38 (November 2016)
Restrict Info:	No refcode restrictions applied
Filter(s):	None
Advanced Options:	None

Single query being used. Search will find structures that:

have

`Query 2`

AZEJOF

Analyse Hitlist

- ✔ **AZEJOF**
- ✔ BIJBEB
- ✔ BIJBIF
- ✔ BIKXAV01
- ✔ BIKXEZ01
- ✔ CIZHEZ
- ✔ CIZHUP
- ✔ CIZJAX
- ✔ CIZJEB
- ✔ DERDOT
- ✔ DERDOT01
- ✔ DERDUZ
- ✔ ENEXEA
- ✔ ENEXIE
- ✔ FAQBEF
- ✔ FEBXAM
- ✔ FEBXOA
- ✔ FEBXUG
- ✔ FEBYAN
- ✔ FEBZAO
- ✔ FEBZIW
- ✔ GEOLOF

<<   >>

40 hits

100%

Stop Search

There are 40 hits ranging from AZEJOF to XIRPOD; only 38 of the hits have 3D data associated with them and the average Ga-C distance is 2.035Å.

(c) Diagrams like these would be nice – you usually would want to add labels too.