

Assignment 3

Due: Wednesday, Dec 5

1. Derive the Patterson peak locations (and multiplicities) that would be observed for an atom located at a general position in the space group $P2_1/c$. Indicate the positions of any Harker lines and planes.

For $P2_1/c$, the general positions are:

- (1) x, y, z
- (2) $-x, 0.5+y, 0.5-z$
- (3) $-x, -y, -z$
- (4) $x, 0.5-y, 0.5+z$

The vectors connecting these positions are:

Vector	Multiplicity	Comment
$\pm(2x, 2y, 2z)$	1	(the multiplicities refer to each of the peaks)
$\pm(0, 0.5+2y, 0.5)$	2	This is a Harker line
$\pm(2x, 0.5, 0.5+2z)$	2	This is a Harker plane
$\pm(2x, -2y, 2z)$	1	
$(0, 0, 0)$	4	This is the trivial solution that gives rise to the origin peak.

2. A molecule containing two 'heavy' atoms, Co and P, crystallizes with $Z = 4$ in $P2_1/c$. A Patterson synthesis was computed and showed peaks with approximate intensities as follows:

0.000	0.000	0.000	999
0.288	0.500	0.152	380
0.333	0.343	0.193	210
0.045	-0.167	-0.459	210
0.045	0.157	0.041	210
0.333	0.333	-0.0307	210
0.000	0.324	0.500	190
0.000	0.324	-0.500	190
0.288	0.176	-0.348	190
0.378	0.500	0.234	120
0.000	0.010	0.500	60
0.000	0.010	-0.500	60
0.378	0.490	-0.266	60

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

Note: $Z_{Co} = 27$, $Z_P = 15$. Since the peak with intensity 380 appears to be on a Harker section, this suggests that it is a double-weight peak the atoms giving rise to the peaks with 190 intensity, similarly the peak with intensity 120 appears to be a double-weight peak of those with intensity 60. If we assume that the weakest vectors are the P-P interactions, then $(15)^2 \cdot \text{const} = 60$ and the constant used to scale these peaks is: 0.26. Trying $(27)^2 \cdot 0.26 = 189.5 \approx 190$, thus the peak assignments seem to make sense. Thus the peaks assignments are: 380 (double-weight Co-Co), 190 (Co-Co), 120 (double-weight P-P), 60 (P-P). The only other peaks have intensities of 210, which must be a double-weight peak because we've already accounted for the Co-Co vectors, note that $(27)(15)(0.26) = 105.3$, and $(105.3)(2) \approx 210$, so this all makes sense, now we must identify possible positions.

0.000 0.000 0.000 999 Origin peak

To determine possible Co positions, we can use the peak:

0.288 0.500 0.152 380

This corresponds to $\pm(2x, 0.5, 0.5+2z)$ thus $x = 0.144$ and $z = -0.174$ for the positive solution for a Co position. The y coordinate can be obtained using any of these peaks:

0.000 0.324 0.500 190

0.000 0.324 -0.500 190

These correspond to $\pm(0, 0.5+2y, 0.5)$, thus $y = \pm 0.088$ or ± 0.412

0.288 0.176 -0.348 190

This peak corresponds to $x = 0.144$, $y = 0.088$ and $z = -0.174$ and thus suggests a reasonable location for one of the Co atoms – the others can be obtained using the symmetry relationships listed in question #1.

Position	x	y	Z
1	0.144	0.088	-0.174
2	-0.144	0.588	0.674
3	-0.144	-0.088	0.174
4	0.144	0.412	0.326

To determine possible P positions, we can use the peak:

0.378 0.500 0.234 120

This corresponds to $\pm(2x, 0.5, 0.5+2z)$ thus $x = 0.189$ and $z = -0.133$ for the positive solution for a P position. The y coordinate can be obtained using any of these peaks:

0.000 0.010 0.500 60

0.000 0.010 -0.500 60

These correspond to $\pm(0, 0.5+2y, 0.5)$, thus $y = \pm 0.245$ or ± 0.255

0.378 0.490 -0.266 60

This peak corresponds to $x = 0.189$, $y = 0.245$ and $z = -0.133$ and thus suggests a reasonable location for one of the P atoms – the others can be obtained using the symmetry relationships listed in question #1.

Position	x	y	Z
5	0.189	0.245	-0.133
6	-0.189	0.745	0.633
7	-0.189	-0.245	0.133
8	0.189	0.255	0.367

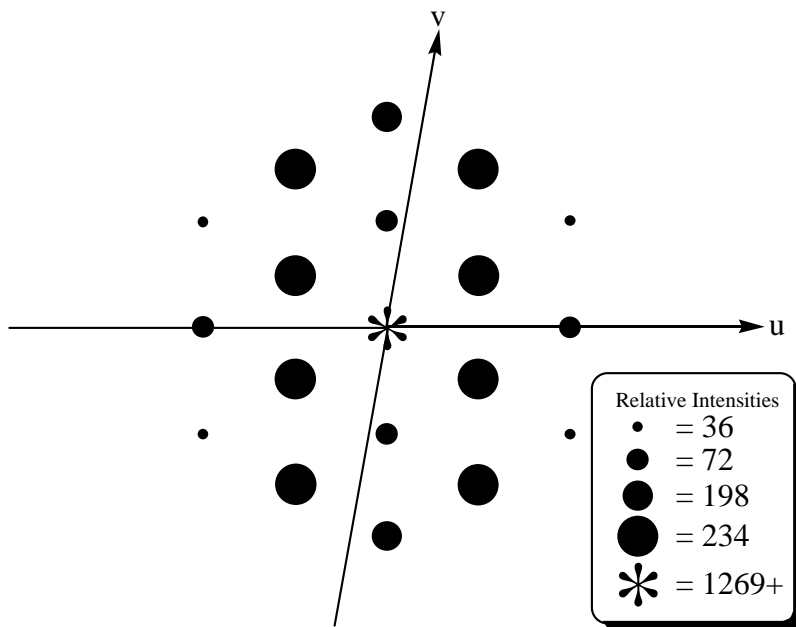
The positions of the Co-P peaks can be obtained from the positions listed above:

0.333 0.343 0.193 210 "P8-Co3"
 0.045 -0.167 -0.459 210 "P5-Co4"
 0.045 0.157 0.041 210 "P5-Co1"
 0.333 0.333 -0.0307 210 "P7-Co1"

Thus all of the peaks are accounted for by the atomic positions that we have determined.

3. Draw a reasonable Patterson map for the molecule AsC_5H_5 (arsabenzene, 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 $a = 10 \text{ \AA}$, $b = 8 \text{ \AA}$ and $\gamma = 80^\circ$. 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.

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	Ideal TBP
	2.446	3	2.450	0.005657	no requirement
	2.454	3			

Eq	Value	ESD	Avg	SD	Ideal TBP
	2.509	5	2.520	0.011533	no requirement
	2.519	4			
	2.532	5			

Ax	Value	ESD	Avg	SD	Ideal TBP
1,3	90.4	3	89.9	0.477493	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	Value	ESD	Avg	SD	Ideal TBP
3,4	119.7	3	120.0	0.264575	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.

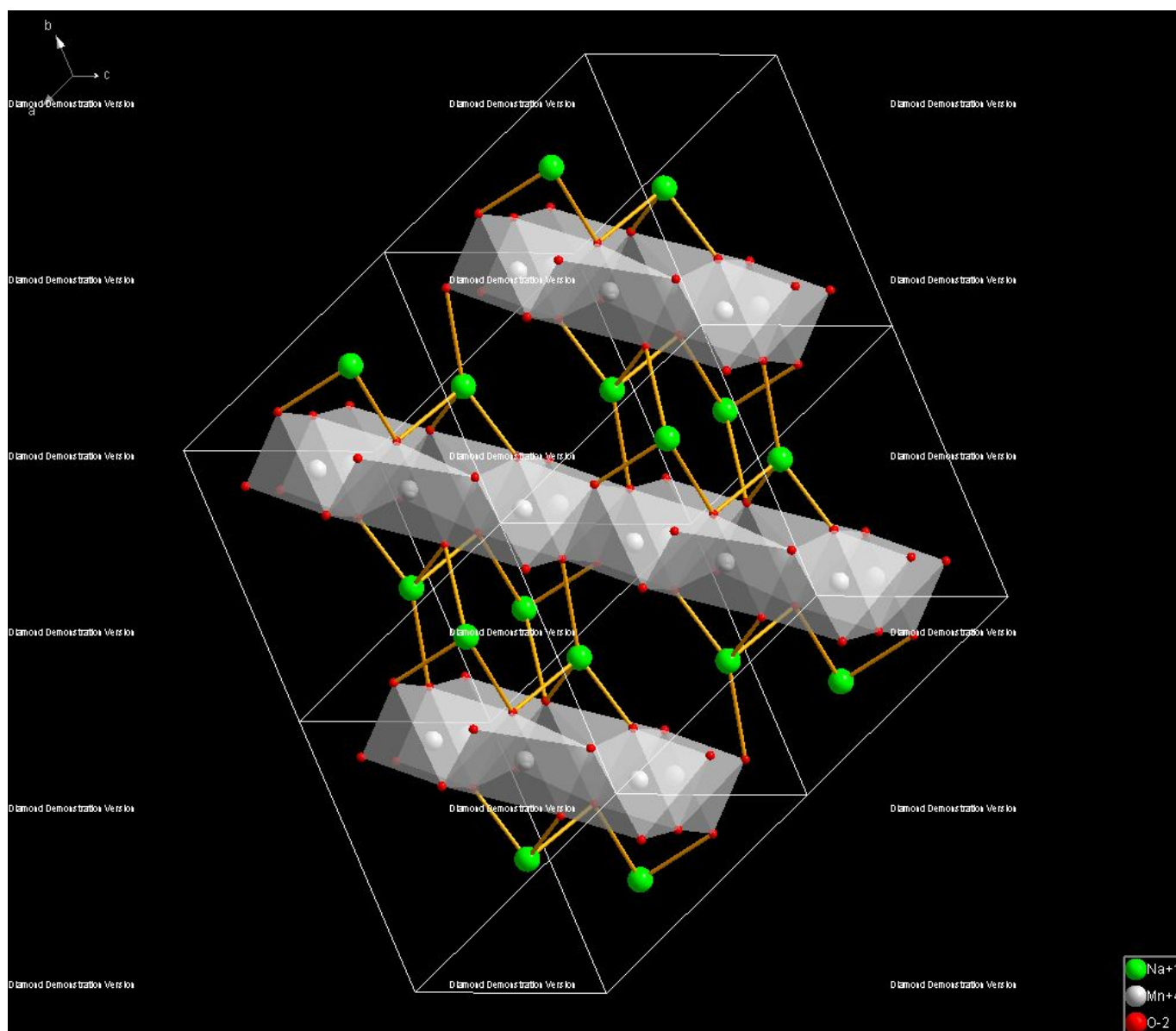
5.

(a) Use the ICSD to search for compounds containing Na, Mn and O. Print out a list of the “hits” you obtained.

You should have obtained 21 hits (ranging from Postt in 2002 to Mumme in 1968).

(b) For the compound $\text{Na}_2(\text{Mn}_3\text{O}_7)$, export the structural data into Diamond and use it to make a picture of structure that highlights the “layered” nature of the crystal structure. In addition, determine the Na-O and Mn-O distances for the 6 oxygen atoms closest to each metal.

Any nice picture will do, here is the one I made:



I could have emphasized the layer structure in a different manner etc. The bond lengths in Å (courtesy of Diamond 3) are:

Na1	O4	x, y, z	2.0698(114)
	O1	1-x, 1-y, 1-z	2.1794(113)
	O7	x, y, z	2.2097(145)
	O6	x, 1+y, z	2.4339(130)
	O4	-x, 1-y, 1-z	2.7012(132)
Na2	O2	1-x, 1-y, 1-z	2.9612(127)
	O2	x, 1+y, z	2.2248(191)
	O3	-x, 1-y, -z	2.2924(215)
	O5	1-x, 1-y, -z	2.4202(208)
	O1	x, 1+y, z	2.4793(191)
Mn1	O7	x, y, z	2.5974(247)
	O2	1-x, 1-y, -z	2.7510(253)
	O4	x, y, z	1.8403(192)
	O3	x, y, z	1.8580(264)
	O6	x, y, z	1.8667(250)
Mn2	O2	-1+x, y, z	1.8817(189)
	O1	x, y, z	2.0450(205)
	O3	-x, -y, -z	2.0949(200)
	O3	x, y, z	1.6621(181)
	O7	x, y, z	1.8457(176)
Mn3	O5	1-x, 1-y, -z	1.8690(261)
	O1	x, y, z	2.0223(249)
	O5	x, y, z	2.0852(185)
	O2	1-x, -y, -z	2.2073(198)
	O5	1-x, 1-y, 1-z	1.7772(195)
	O6	-x, -y, 1-z	1.7842(198)
	O4	x, y, z	1.9182(269)
	O6	x, y, z	1.9362(205)
	O2	1-x, -y, 1-z	2.0347(266)
	O7	1-x, 1-y, 1-z	2.0714(209)

6.

(a) Use the CSD (ConQuest) to search for structures containing any type of bond between a pentamethylcyclopentadienyl (C₅Me₅, Cp*) group and a gallium atom. Provide me with a printout of your search parameters and results. Note: Use the “Write PDF to view/print results” selection under the File menu and select the “list” option – just print out the summary page and the first couple of pages of results (i.e. don't waste too much paper).

This search should have been done with the following model and would provide 75 hits.

Search Overview

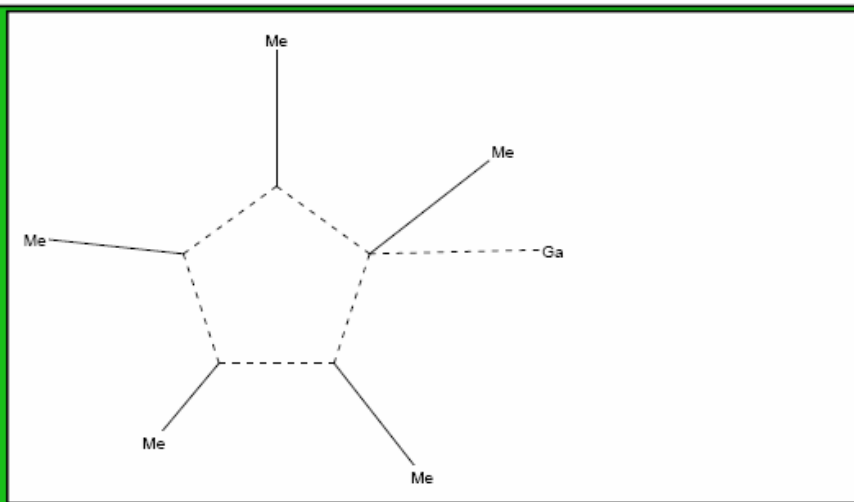
Search: search2
Date/Time done: Thu Nov 29 14:05:10 2007
Database(s): CSD version 5.28 (November 2006)
CSD version 5.28 updates (Jan 2007)
CSD version 5.28 updates (May 2007)
CSD version 5.28 updates (Aug 2007)
Restriction Info: No refcode restrictions applied
Filters: None
Percentage Completed: 100%
Number of Hits: 75

Single query used. Search found structures that:

match

Query 2

Query 2



(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 – again, just print out the summary page and the first couple of pages of results.

This search should have been done with the following model and would provide 24 hits, if you used a more general model, you would get more hits but the bonding between the Cp and the Ga might not be correct – this would require closer examination and may skew the results of your average value.*

Search Overview

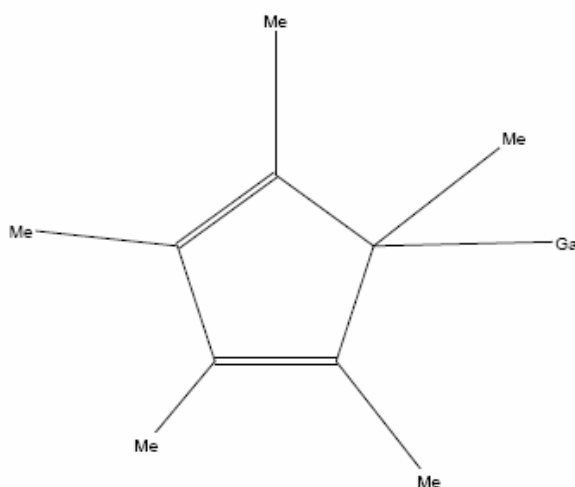
Search:	search4
Date/Time done:	Thu Nov 29 19:06:57 2007
Database(s):	CSD version 5.28 (November 2006) CSD version 5.28 updates (Jan 2007) CSD version 5.28 updates (May 2007) CSD version 5.28 updates (Aug 2007)
Restriction Info:	No refcode restrictions applied
Filters:	None
Percentage Completed:	100%
Number of Hits:	24

Single query used. Search found structures that:

match

Query 1

Query 1



Note, the average value of the bond length obtained from this search is:

Note that there are more distances than hits because several of the structures contain more than one bond that fits the search parameter.

Parameter Values for Query: 4

Refcode	DIST1 (D)
BIJBEB	1.981
BIJBIF	2.02
DERDOT	2.031
DERDOT	1.978
DERDOT	1.971
DERDOT	1.974
DERDOT	2.041
DERDOT	1.963
DERDUZ	1.965
ENEXEA	2.054
ENEXIE	2.038
FAQBEF	2.042
FEBXAM	2.086
FEBXOA	2.027
FEBXOA	2.028
FEBXOA	2.049
FEBXUG	2.094
FEBYAN	2.106
FEBYAN	2.105
FEBYAN	2.06
FEBYAN	2.06
FEBZAO	2.078
FEBZIW	2.034
IFUWOV	2.102
IFUWOV	2.118
LENZOT	2.04
LENZOT	2.032
LENZOT	2.041
MIKPOL	1.972
MOJCAP	2.077
MOJCAP	2.046
MUKHAB	2.001
PONGII	2.039
PONGII	2.04
PONGII	2.05
RARHIB	1.997
RARHIB	2.013
XIRPIX	2.072
XIRPOD	2.08
GEQLOE	2.057
GEQLOE	2.048
GEQLOE	2.068
GEQLOE	2.06
GEQLOE	2.059

GEQLOE	2.031
GEQLOE	2.072
REVNEM	2.034
Average	2.041149

(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. *Something like these would be nice – you usually would want to add labels too.*

