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

Assignment 1

Due: Feb. 16, 2017

Question #1

1. Consider an atom at fractional coordinates *x,y,z*. When operated on by the following symmetry elements, what are the fractional coordinates of the symmetry related atoms?

(a) 2 along b (b) -4 along c (c) m perpendicular to b
(d) -1 centered at (000) (e) 4_3 along c (f) b glide plane perpendicular to a
(g) 2_1 along a (h) n glide perpendicular to b.

(a) -x, y, -z
(b) y, -x, -z; -x, -y, z; -y, x, -z
(c) x, -y,z
(d) -x,-y-z
(e) -x, -y, 0.5+z; -y, x, 0.75+z; y, -x, 0.25+z
(f) -x, 0.5+y, z
(g) 0.5+x, -y, -z
(h) 0.5+x, -y, 0.5+z

2. The compound $[Cp^*_3Pb_2][B(C_6F_5)_4]$ (MW = 1499.09) crystallizes in the space group *C2/c* with a = 22.545(5) Å, b = 14.773(5) Å, c = 17.087(5) Å, β = 114.911(5), Z = 4. Calculate the density of this salt and indicate if there are any other conclusions you can draw about the structure.

V = abc·sin(114.911°) = 5161.482 Å^3, thus:

density = (1.6605mol·Å^3·cm^{-3}·4·1499.09 g·mol^{-1})/V = 1.9291 g·cm^{-3}

Also, since the value of Z is 4 and the multiplicity of the general positions in C2/c is 8, it is clear that the asymmetric unit must contain half of each cation and anion so these must be sitting on special positions (symmetry elements), in particular, given the composition and symmetry of the ions, these must be on the 2-axis.

3. The ionic compound $[(C_{11}H_{20}N_2)_2P][Cl]\cdot n(C_7H_8)$ crystallizes in the space group *P-1* with a = 10.134(3), b = 12.243(3), c = 13.037(3) Å, α = 103.358(4), β = 99.906(5), γ = 100.772(4). Given that the measured density is 1.145 g cm^{-3} what conclusions can you draw about the structure.

V = 1506.31 Å^3

$Z = (d \cdot V)/(1.6605\ mol \cdot Å^3 \cdot cm^{-3} \cdot FW)$
$= (1.145\ g \cdot cm^{-3} \cdot 1506.31\ Å^3)/(1.6605\ mol \cdot Å^3 \cdot cm^{-3} \cdot [427.01\ g \cdot mol^{-1} + n \cdot 92.14\ g \cdot mol^{-1}])$

For: n = 1, Z = 2.001; thus n = 1 and Z = 2

Since Z = 2, which is what you would anticipate for P-1, it means that there is one cation, one anion and one molecule of toluene in the asymmetric unit and that none of those objects is sitting on an center of symmetry (i.e. every atomic position is independent).

4. (a) Using diagrams, explain why a *B* centered cell is not a distinct monoclinic cell.
(b) Using diagrams, explain why an *I* centered monoclinic cell is equivalent to a C centered monoclinic cell.

(a) For a putative B centered monoclinic cell, a smaller primitive cell can always be chosen that still clearly displays the monoclinic nature of the lattice, as shown below.

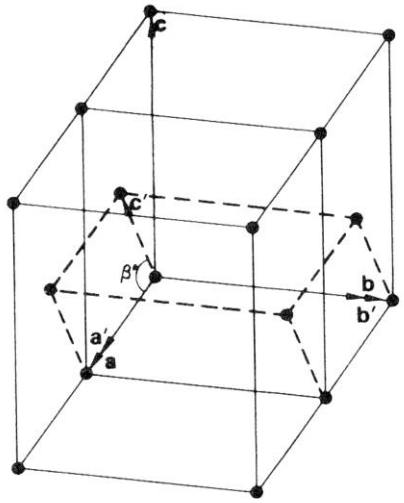


FIGURE 2.7. Monoclinic lattice showing that $B \equiv P$. In Figures 2.7 to 2.10, β is the angle between **c** and **a**, and β' the angle between **c**′ and **a**′.

(b)For a putative I-centered monoclinic cell, an alternate choice of lattice points (illustrated below) can be used obtain a C-centered cell instead. This new cell accurately exhibits the symmetry of the lattice and is chosen by convention.

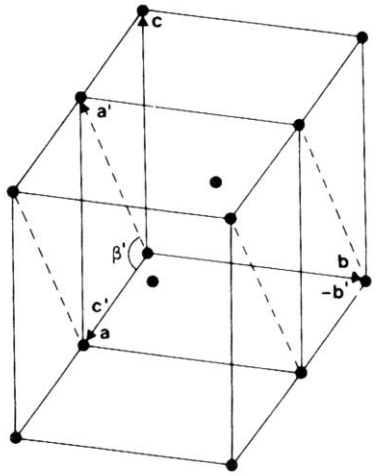
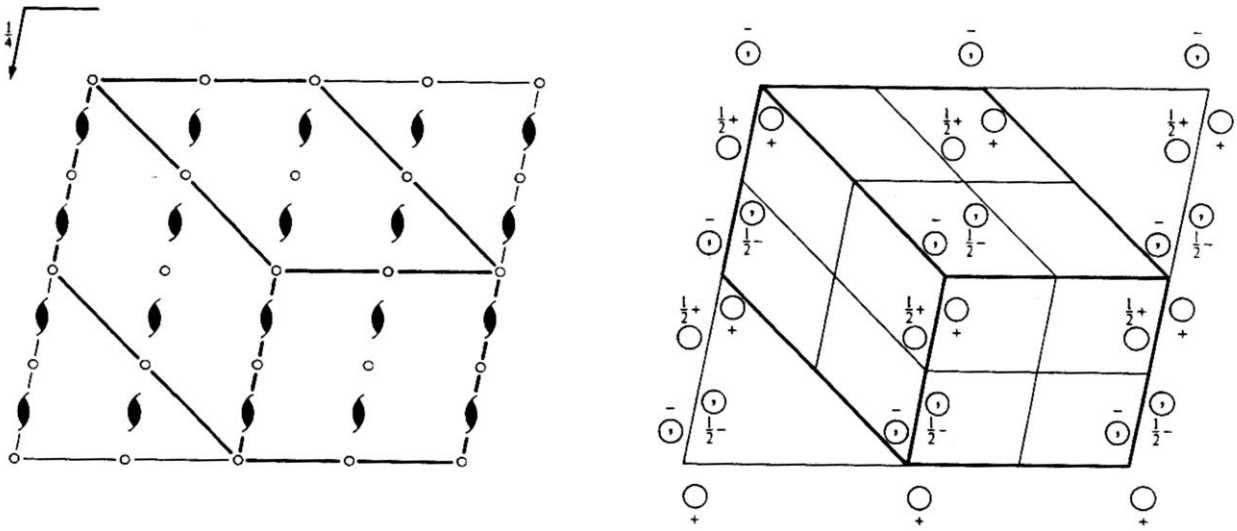


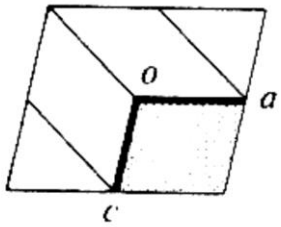
FIGURE 2.8. Monoclinic lattice showing that $I \equiv C$.

5. Use diagrams to show and explain the relationship between $P2_1/n$ and $P2_1/c$.

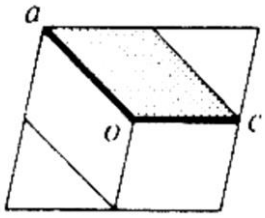
Below is a diagram from the International Tables of the symmetry elements and general positions of a monoclinic lattice for space group #14 that can be labeled either as $P2_1/c$, $P2_1/n$ or $P2_1/a$. The most important thing to realize is that these three space group symbols refer to the exact same lattice and that they differ only in the choice of the axes used to define the unit cell.



For $P2_1/c$ (which is the standard setting), one chooses the cell parameters consistent with the cell drawn at the bottom right-hand corner of the diagrams shown above and highlighted below. With this choice, the glide plane perpendicular to the b axis is chosen to be along the direction of the c axis.



For $P2_1/n$, one chooses the cell parameters consistent with the cell drawn at the top of the diagrams shown above and highlighted below. With this choice, the glide plane perpendicular to the b axis (which is obviously still in the same direction with regard to the lattice) is now located half-way between the new a and c axes and is thus described with an n instead.



The $P2_1/a$ setting, one chooses the cell parameters consistent with the cell drawn at the left-hand side of the diagrams shown above. With this choice, the glide plane perpendicular to the b axis is set along the direction of the a axis. In any event, the most important thing to realize is that the lattice and symmetry elements are identical, it is just the choice of how the unit cell box is drawn ***with respect to the lattice*** *that determines the space group symbol employed.*

6. For a primitive unit cell from each of the 7 crystal systems:

(a) identify the point group of the unit cell

triclinic: -1 (C_i)
monoclinic: 2/m (C_{2h})
orthorhombic: mmm (D_{2h})
tetragonal: 4/mmm (D_{4h})
trigonal (rhombohedral): -3m (D_{3d})
hexagonal: 6/mmm (D_{6h})
cubic: m3m (aka m-3m) (O_h)

(b) use a drawing to show the location of the symmetry elements of the cell

Any reasonable pictures would do that indicate the position of each of the independent symmetry elements for the box. Go to the website: http://neon.mems.cmu.edu/degraef/pg/pg_gif.html for some nice animated pictures of symmetry elements; you can also use Mercury to see how the symmetry elements are situated when the unit cell extended to an infinite lattice.

7. What systematic absences are expected if the following symmetry elements are present?

(a) *I* centered lattice *For (hkl), $h+k+l = 2n+1$*

(b) c glide perpendicular to a — *For (0kl), l = 2n+1*
(c) mirror perpendicular to b — *No systematic absences*
(d) 2_1 along c — *For (00l), l = 2n+1*

8. Explain in detail, the information implied by the space group symbol *Fd-3m*.

The symbol indicates that the space group consists of a face-centered (F) cubic (m-3m) lattice combined with the m-3m point group. Note that the d-3m indicates the presence of a diamond glide perpendicular to the z axis, a -3 operation in the [111] direction, and an m perpendicular to the [110] direction (the positions do not correspond to x,y,z as they do in many other point groups) There are many other details implied such as that the space group (#227) is centro-symmetric, the location of the special positions, symmetry elements etc. but I really just wanted to indicate the most important ones.

9. Identify the possible space groups implied by the following information. Also indicate if the space group is uniquely determined (see section 3.1 of the *International Tables for Crystallography Volume A*).

(a) primitive monoclinic lattice, for *h0l, h00 ,00l* present only for *l* = 2n.
(b) primitive orthorhombic lattice, for *00l*, present only for *l* = 2n.
(c) C centered orthorhombic lattice, no other absences observed.
(d) F centered orthorhombic lattice, no other absences observed.
(e) centrosymmetric C centered monoclinic lattice, no other absences observed.

I should have made it clear that the systematic absences listed are the only ones observed (other than those caused by centering, where applicable). The possible space groups are:

(a) Pc, P2/c – not uniquely determined
(b) $P222_1$ – uniquely determined
(c) C222, Cmm2, Cm2m, C2mm, Cmmm – not uniquely determined
(d) F222, Fmm2, Fm2m, F2mm, Fmmm – not uniquely determined
(e) C2/m, C2/c, C2/n are centrosymmetric but since no other absences, it must be C2/m - uniquely determined

10. At low temperatures, methane crystallizes in a cubic cell with a = 5.89 Å. Assuming that the density of the solid methane is similar to that of liquid methane (d = 0.466 g cm^{-3}), determine whether methane adopts a primitive, body-centered or face-centered structure.

$V = 204.336\ Å^3$

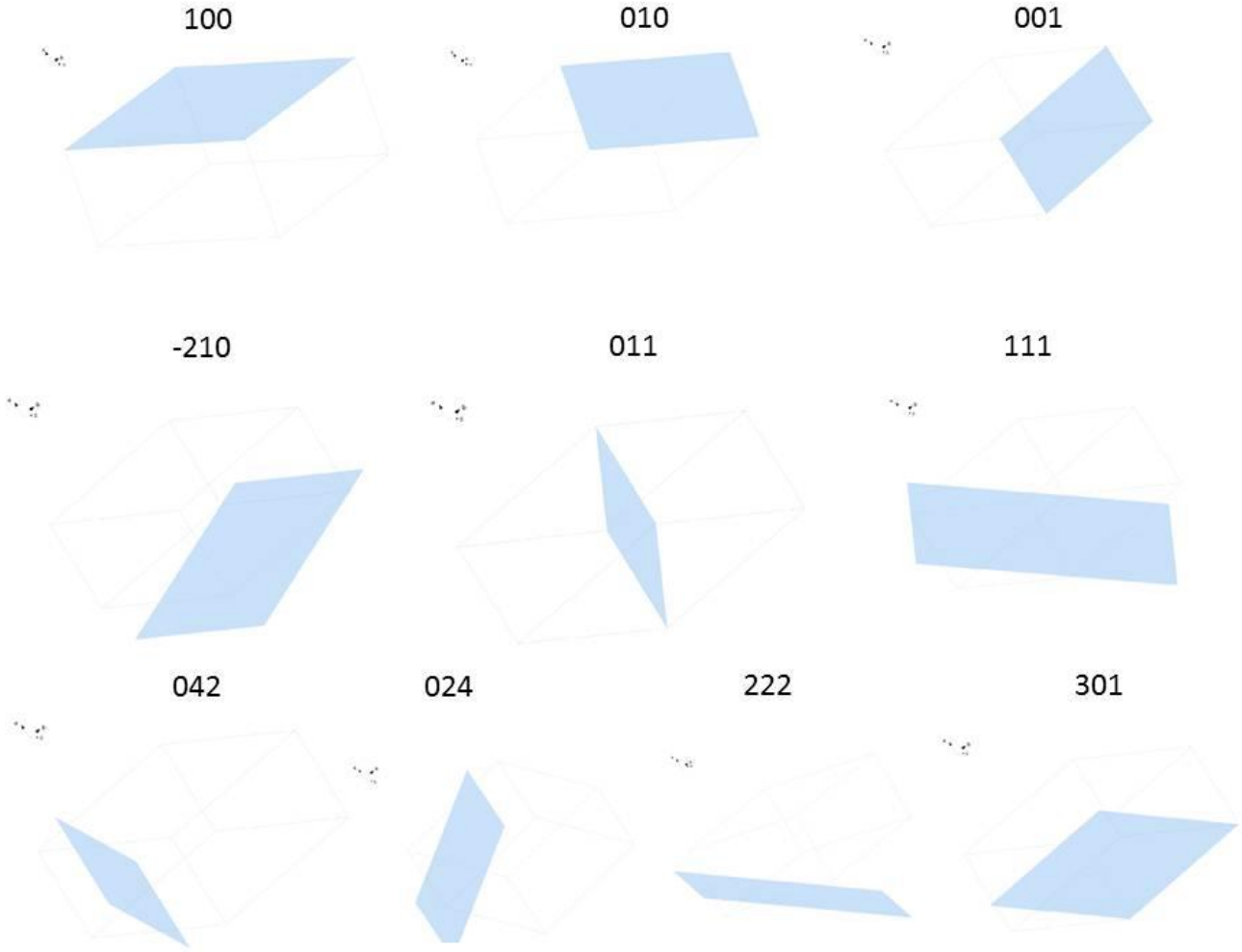
$Z = (d \cdot V)/(1.6605 mol \cdot Å^3 \cdot cm^{-3} \cdot FW)$
$= (0.446\ g \cdot cm^{-3} \cdot 204.336\ Å^3)/(1.6605 mol \cdot Å^3 \cdot cm^{-3} \cdot 16.04 g \cdot mol^{-1})$
$= 3.574 \approx 4$

A primitive lattice would contain 1 molecule per unit cell, a body-centered lattice would contain 2 molecules and a face-centered lattice should contain 4, thus methane must crystallize with a ***face-centered*** *lattice. The reason that the number of formula units in our calculation does not equal 4 exactly is that the density in the solid state is actually greater than the density of the liquid for methane.*

11. What are the Miller indices for planes with the following unit cell intercepts:

(a) ∞ a, 1/3 b, c	*(0 3 1)*
(b) a, b, c	*(1 1 1)*
(c) -1/4 a, 1/2 b, 3 c	*(-12 6 1)*
(d) 1/6 a, 1/3 b, 3/4 c	*(18 9 4)*
(e) 2/3 a, ∞ b, 1/6 c	*(3 0 12), while this can be reduced to (1 0 4) they are not the same!*

12. Draw orthorhombic unit cells with dimensions of a = 4 Å, b = 7 Å and c = 9 Å. Draw the following planes (make sure to label them): (100), (010), (001), (-210), (011), (111), (042), (222), (301), (024)



13. Determine the d-spacing for each family of planes in question 12.

14. Using MoKα X-rays, what would be diffraction angle for each family of planes in question 12.

Answers for 13 and 14

a	4	lamda	0.71073
b	7		
c	9		

h	**k**	**l**	**d**	**theta**
1	0	0	4	5.096949
0	1	0	7	2.909953
0	0	1	9	2.262912
-2	1	0	1.923048	10.64904
0	1	1	5.525466	3.687468
1	1	1	3.240102	6.296701
0	4	2	1.631008	12.58458
2	2	2	1.620051	12.6711
3	0	1	1.318938	15.63051
0	2	4	1.892652	10.82211