Name ________________________________________

**Chemistry 208 X-ray Crystallography**

Midterm Exam #2 March 18, 2009

Total 100 points

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1. (25 points) Explain your answers.

a) What is the point group of $Pna2_1$ (space group #33)? The Laue group? What systematic absences are required?

The point group is C2v (mm2), and the Laue group is mmm. The systematic absences are imposed by the n-glide (0kl, k+l=2n), a-glide (h0l, h=2n), and 2-fold screw axis (00l, l=2n).

b) Add a mirror plane perpendicular to the $2_1$ axis (see the attached space group diagram for $Pna2_1$). Note that, since the origin along the $2_1$ axis is not fixed, you can start with the mirror plane anywhere along z, so for simplicity let the operation be x, y, z → x, y, -z. What other symmetry operations does this generate from those listed for $Pna2_1$?

This additional mirror plane causes this mm2 group to become mmm- and 2-fold axes are now present in each direction. Specifically, the mirror plane adds each of the new xyz-coordinates to the symmetry-related general position:

| Coordinate | (x, y, -z) | (-x, -y, ½-z) | (x+½,½-y, -z) | (½-x, y+½, ½-z) |
|---|---|---|---|---|
| Symm. Operation | mirror | inversion | $2_1$ ‖ to a | $2_1$ ‖ to b |

c) We see that $Pna2_1$becomes Pnam. What is now the point group? The Laue group? What systematic absences are required? Can you distinguish this from $Pna2_1$?

This group now has $D_{2h}$ (mmm) symmetry, and is in Laue group mmm. No additional systematic absences are introduced, as there are no elements of translational symmetry imposed in the new group. The new group will not be distinguishable by systematic absences.

d) When you look in the International Tables you do not find this space group, but you do find Pmna (# 53) and Pnma (# 62). Is either of these equivalent to Pnam?

This group is equivalent to Pnma. If we construct the general positions for Pnma (#62), we get:

(n-glide ‖ a): (-x, y+½, z+½)
(m ‖ b) : (x, -y, z)
(a ‖ c) : (x+½, y, -z)

To identify other elements of symmetry, we need to look at how these elements combine :

n·m = (-x, -y+½, z+½), which is a ($2_1$ ‖ c)
n·a = (-x+½, y+½, -z+½), which is a ($2_1$ ‖ b)
m·a = (x+½, -y, -z), which is a ($2_1$ ‖ a)

This is the same series of operations we had in b). Conversely, the same analysis for Pmna gives instead 2-fold axes ‖ to a and b.

2. (30 points) Comment (not more than 2 sentences) on each of the following. Note any errors you find.

a) The relative intensity (in raw counts) of the two diffraction maxima with Miller indices (4,6,2) and 2,3,1) changes in going from $CuK_\alpha$ to $MoK_\alpha$ radiation.

The dependence of the atomic scattering factors on $\sin(\theta)/\lambda$ mean that the intensities will change with the use of different wavelengths of radaition. This is true.

b) Bigger crystals are always better, because you get more data, faster.

False. Large crystals can require large absorption correction and produce inferior data – smaller crystals which can easily be bathed in a uniform beam are best.

c) Dr. Hollander suggested $P2_13$ for my crystal but it can't be because this is a cubic space group and my molecule is chiral.

False. This space group possesses only proper symmetry elements (axes of rotation, screw axes) and, as a result, can contain only right-handed molecules without also requiring left-handed molecules related by elements of symmetry such as glide planes.

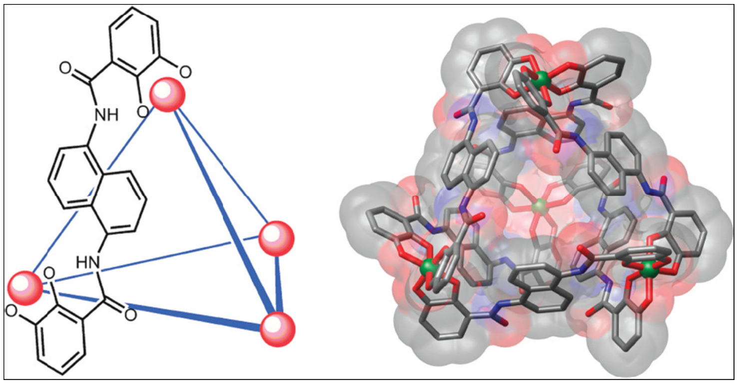
d) How does use of the polarizer on the microscope help you determine if a crystal is twinned?

The crystal will not extinguish uniformly if the crystal is twinned – the 'twins' will extinguish at different angles.

e) What is the Lorentz factor and where does it come from?

The Lorentz factor compensates for the 'smearing out' of spots which move more quickly through the Ewald Sphere, possessing a larger intensity because they spend more time in contact with the sphere (and thus producing diffraction).

3. (25 points) The compound $K_8(Cp^*_2Co)_3[Cp^*_2Co \subset Ga_4L_6]$ (here the ⊂ sign indicates host/guest encapsulation) [M. Pluth et al. *Inorg. Chem.* **2009**, *48,* 111-12*0*] crystallizes in the space group *Fd*3*c* with Z =16, a = 50.004 Å. The ligand L (with a -4 charge) is defined in the upper left of the diagram. It spans the edges of the $Ga_4L_6$ cluster shown. The organometallic cation $Cp^*_2Co^+$ is a cobalt sandwich complex (Cp* = $\eta^5$-pentamethylcyclopentadienyl).




Schematic representation of the $M_4L_6$ assembly with only one ligand shown for clarity. (Right) A space-filling model of the assembly looking toward the aperture coincident with the 3-fold axis.

a) What Wycoff position would you suggest for the cluster?

Position *a* is the only appropriate choice for Z = 16.

b) What is the point group symmetry of the cluster in this space group?

This imposes 23 (T) symmetry upon the assembly.

c) Is it chiral?

The assembly is certainly chiral (due to the helical chirality at the Ga centers). There are no mirror planes which pass through the assembly.

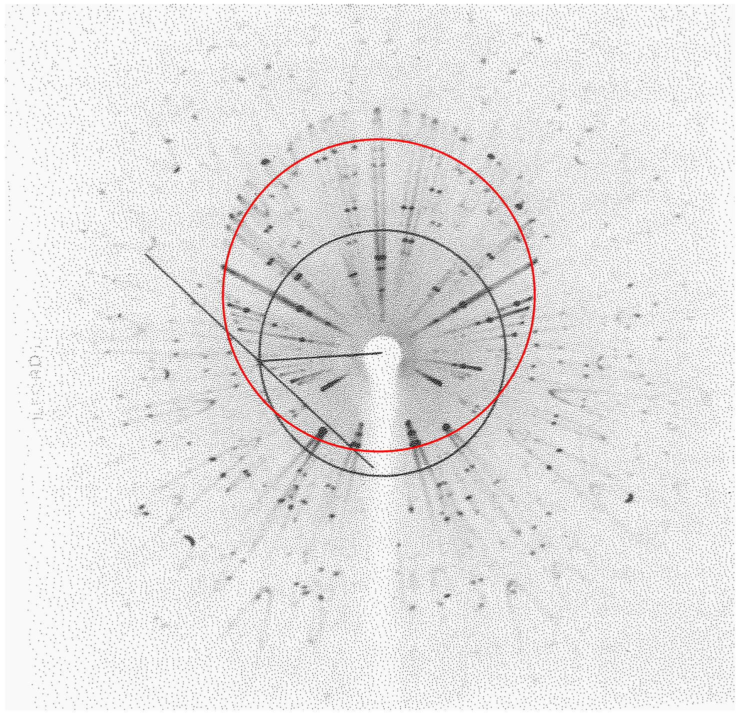
d) Is the space group chiral?

This space group does contain improper symmetry elements (the c glide) which will take a right-handed molecule to its left-handed counterpart. The space group is not chiral, and each of these chiral molecules will each be accompanied by its enantiomer in the unit cell.

e) Are any coordinates of the Ga atoms fixed by the structure? Explain.

The 64 Ga atoms will be at Wycoff position *e*, and so their coordinates are not fixed (only needing to be at x,x,x – one parameter instead of 3).

4. (20 points) The alignment photograph at right was taken with Mo X-rays, unfiltered, with μ (precession angle) = 10%. [It is the actual size you would see for your Polaroid, although different in details not important for this problem.] Because the precession film faces the fluorescent screen (and behind that the X-ray beam) you may view this as if the X-rays were coming from behind you as you view the film. The spindle axis (S) is from left to right and the upper arc(UA) axis is from up to down. The lower arc (LA) axis is in and out of the plane of view.



Three members of another lab group show you this as their photo and ask you to adjudicate a disagreement they are having.

Here is what they say:

Student 1. Adjust the LA 5° and the UA – 17°

Student 2. Adjust the LA + 17°.

Student 3. Adjust S by 9°.

Who is correct? Explain.

The circle drawn must be brought into alignment such that it is centered on the drawn circle, requiring that the up/down axis (UA) be adjusted heavily (17 degrees), and that the in-and-out plane also be adjusted (LA) somewhat less (5 degrees).