

1) For the common space group $P2_1/n$

$$F(h, k, l) = F(-h, -k, -l)$$

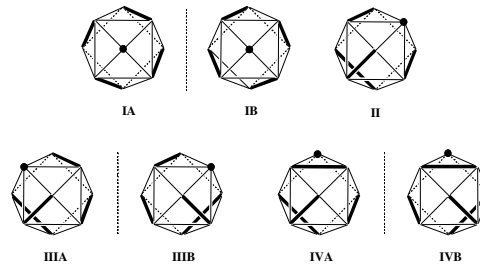
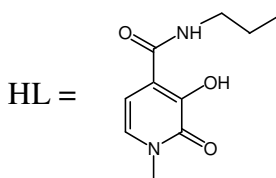
$$F(h, k, l) = (-1)^{h+k+l} F(h, -k, l)$$

For the Hauptman-Karle determinant ($U_{hkl} = F_{hkl}/F_{000}$) shown below

$$\begin{vmatrix} 1 & U_{hkl} & U_{02k0} \\ U_{\overline{hkl}} & 1 & U_{\overline{hk\bar{l}}} \\ U_{02\overline{k}0} & U_{\overline{hkl}} & 1 \end{vmatrix} > 0$$

Evaluate this determinant; what phase information is given?

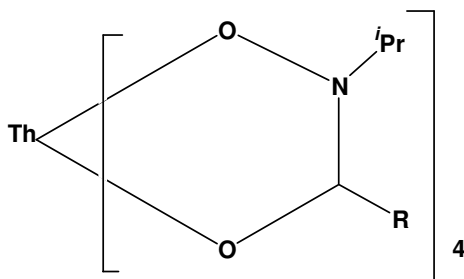
- 2) The compound $\text{Th}(\text{L})_4 \cdot \text{H}_2\text{O}$ [Xu, J.; Whisenhunt, D. W., Jr.; Veeck, A. C.; Uhler, L. C.; Raymond, K. N. *Inorg. Chem.* **2003**, *42*, 2665-2674] crystallizes in $Pna2_1$ (No. 33), $Z = 4$, $a = 17.1250(5) \text{ \AA}$, $b = 12.3036(7) \text{ \AA}$, $c = 23.880(1) \text{ \AA}$. The Th is nine-coordinate (see diagram).



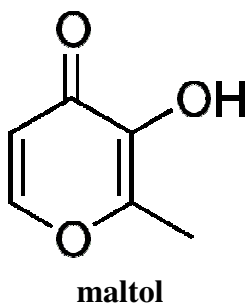
The seven possible coordination geometries of $[\text{M}(\text{bidentate})_4(\text{monodentate})]$ complexes.

- What Wyckoff position would you suggest for the Th atom?
- What is the point group symmetry of this space group?
- Are any coordinates of the Th atom fixed by the structure? Explain.
- Predict the Th-Th vectors in a Patterson function for this compound.
- Which peaks give x, y or z coordinates for the Th atom?
- Will the location of the Th atom enable good phasing of the remainder of the structure? Explain.

- 3) The thorium complex shown below for $R = C(CH_3)_3$ crystallizes in space group $I4_1/a$ with $Z = 4$ so that the Th atom sits on position a).



- What constraints are there on the Th atom positional (x, y, z) and thermal (β) parameters?
 - To which reflections F_{hkl} will the Th atom contribute strongly? To which not at all?
 - On average, what is the relative magnitude of the Th contribution to $|F_{hkl}|$ for low angle reflections?
 - How will this relative contribution change with $\sin\theta/\lambda$? Why?
 - What phase information for reflections of the type $hk0$ can be assigned to begin to generate an electron density synthesis from $|F_{hkl}|_{obs}$ and ϕ_{hkl}^{calc} ? For what fraction of the observed $|F_{hkl}|$'s will you eventually be able to get phase information by this process?
- 4) The plutonium complex of maltol, $Pu(maltol)_4$, crystallizes in space group $I4_1/a$ ($a = 9.2073(4)$, $c = 27.068(3)$, $Z = 4$). The maltol ligands are deprotonated and coordinate in a bidentate fashion.



- What are the choices for positioning the plutonium atoms in the unit cell?
- What symmetry is suggested by your placement in a)?
- Are there any restrictions on the placement of any atoms in the maltol ligands?
- What coordination geometries are possible for this structure? Sketch any possibilities you perceive as reasonable.
- The errors on the Pu coordinates are smaller than other errors in the structure. Why might this be so?

5. The space group $P2_12_12_1$ is orthorhombic with Laue symmetry mmm. Thus:

$$|F_{hkl}| = |F_{\bar{h}\bar{k}l}| = |F_{h\bar{k}\bar{l}}| = |F_{\bar{h}k\bar{l}}|$$

For the actual structure factors, how are they related? (i.e., how are $\varphi_{h,k,l}$, $\varphi_{-\bar{h},k,l}$, $\varphi_{h,-k,l}$, $\varphi_{h,k,-l}$ related?)