

1.)

$$\begin{vmatrix} 1 & U_{hkl} & U_{02k0} \\ U_{\bar{h}\bar{k}\bar{l}} & 1 & U_{\bar{h}\bar{k}\bar{l}} \\ U_{0\bar{2}\bar{k}\bar{0}} & U_{\bar{h}\bar{k}\bar{l}} & 1 \end{vmatrix} = -U_{\bar{h}\bar{k}\bar{l}}U_{\bar{h}\bar{k}\bar{l}} - U_{hkl}(U_{\bar{h}\bar{k}\bar{l}} - U_{\bar{h}\bar{k}\bar{l}}U_{0\bar{2}\bar{k}\bar{0}}) + U_{0\bar{2}\bar{k}\bar{0}}(U_{\bar{h}\bar{k}\bar{l}}U_{\bar{h}\bar{k}\bar{l}} - U_{0\bar{2}\bar{k}\bar{0}})$$

$$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}} \Rightarrow U_{hkl} = U_{\bar{h}\bar{k}\bar{l}} \Rightarrow U_{\bar{h}\bar{k}\bar{l}} = U_{\bar{h}\bar{k}\bar{l}} \Rightarrow U_{02k0} = U_{0\bar{2}\bar{k}\bar{0}}$$

$$\therefore -U_{\bar{h}\bar{k}\bar{l}}^2 - U_{hkl}^2 - U_{02k0}^2 + 2U_{hkl}U_{\bar{h}\bar{k}\bar{l}}U_{02k0} > 0$$

$$F_{hkl} = (-1)^{k+\ell} F_{\bar{h}\bar{k}\bar{l}}$$

$$\Rightarrow 1 - U_{\bar{h}\bar{k}\bar{l}}^2 - U_{hkl}^2 - U_{02k0}^2 + 2(-1)^{h+k+\ell} U_{\bar{h}\bar{k}\bar{l}}^2 U_{02k0} > 0$$

This phases U_{02k0}

2.) The compound $\text{Th}(\text{L})_4 \cdot \text{H}_2\text{O}$ [Xu, J.; Whisenhunt, D. W., Jr.; Veeck, A. C.; Uhlir, L. C.; Raymond, K. N. *Inorg. Chem.* **2003**, *42*, 2665-2674] crystallizes in $\text{Pna}2_1$ (No. 33), $Z = 4$, $a = 17.1250(5)$ Å, $b = 12.3036(7)$ Å, $c = 23.880(1)$ Å.

- What Wyckoff position would you suggest for the Th atom?
A Th atom at each of the four Wyckoff positions (x, y, z) , $(-x, -y, z + 1/2)$, $(x + 1/2, -y + 1/2, z)$, $(-x + 1/2, y + 1/2, z + 1/2)$
- What is the point group symmetry of this space group? C_{2v}
- Are any coordinates of the Th atom fixed by the structure? Explain. *The Th atoms are at general positions, so there are not specific constraints on the coordinates*
- Predict the Th-Th vectors in a Patterson function for this compound.

	Th	C	H	N	O
#atoms	1	40	54	8	13
#electrons	90	6	1	7	8
scaled for atoms	90	240	54	56	104
% electrons	16.54	44.12	9.93	10.29	19.12
#electrons*atoms	8100	1440	54	392	832
% in Patterson	74.88	13.31	0.50	3.62	7.69

n	atoms	Z	Z ²	nZ ²
4	Th	90	8100	32400
52	O	8	64	3328
32	N	7	49	1568
160	C	6	36	5760
216	H	1	1	216
		Sum		43272
		f=		0.023087

The peak heights in the Patterson map are scaled by the relationship: fZ_1Z_2

Peak Height	
Th-Th	187.0008
Th-O	16.6223
Th-N	14.54451
Th-C	12.46672

- e) Which peaks give x, y or z coordinates for the Th atom?

The combination of the Th-Th peaks give information about the x, y, and z coordinates for the Th atom.

From two of the peaks, the third coordinate can be calculated using the Harker-peaks

	x, y, z	$-x, -y, z + 1/2$	$x + 1/2, -y + 1/2, z$	$-x + 1/2, y + 1/2, z + 1/2$
x, y, z	-	$-2x, -2y, 1/2$	$1/2, -2y + 1/2, z$	$-2x + 1/2, 1/2, 1/2$
$-x, -y, z + 1/2$	$2x, 2y, 1/2$	-	$2x + 1/2, 1/2, 1/2$	$1/2, 2y + 1/2, 0$
$x + 1/2, -y + 1/2, z$	$1/2, 2y, 0$	$-2x + 1/2, 1/2, 1/2$	-	$-2x, 2y, 1/2$
$-x + 1/2, y + 1/2, z + 1/2$	$2x + 1/2, 1/2, 1/2$	$1/2, -2y + 1/2, 0$	$2x, -2y, 1/2$	-

- f) Will the location of the Th atom enable good phasing of the remainder of the structure? Explain.

Yes, the Th atom has the largest contribution to the Patterson function and the Th-Th, and Th-X vectors are enough to phase the structure.

3. The Thorium sits on Wyckoff position (a) $(0, 0, 0)$, $(1/2, 1/2, 1/2)$, $(0, 1/2, 1/4)$, $(1/2, 0, 3/4)$ with site symmetry $\bar{4}$.

(a) The x, y, z coordinates are fixed to the coordinates of the Wyckoff position, so in order to find the constraints for the thermal parameters, we need to determine how $\bar{4}$ axis transforms x, y, z.

$$\bar{4}: x, y, z \rightarrow y, -x, -z$$

Now we look at the β 's:

$$\begin{array}{l}
\beta_{11}: x^2 \xrightarrow{\frac{\bar{4}}{4}} y^2 \\
\beta_{22}: y^2 \xrightarrow{\frac{\bar{4}}{4}} x^2 \\
\beta_{33}: z^2 \xrightarrow{\frac{\bar{4}}{4}} z^2
\end{array} \left. \vphantom{\begin{array}{l} \beta_{11} \\ \beta_{22} \\ \beta_{33} \end{array}} \right\} \beta_{11} = \beta_{22} \text{ No Constraints}$$

$$\beta_{12}: xy \xrightarrow{\frac{\bar{4}}{4}} -xy \left. \vphantom{\beta_{12}} \right\} \beta_{12} = -\beta_{12} = 0$$

$$\begin{array}{l}
\beta_{13}: xz \xrightarrow{\frac{\bar{4}}{4}} -yz \\
\beta_{23}: yz \xrightarrow{\frac{\bar{4}}{4}} xz
\end{array} \left. \vphantom{\begin{array}{l} \beta_{13} \\ \beta_{23} \end{array}} \right\} \beta_{13} = -\beta_{23} \text{ and } \beta_{13} = -\beta_{23} \Rightarrow \beta_{13} = \beta_{23} = 0$$

(b) The Thorium atom sits on Wyckoff position (a) and will contribute strongly to these reflections (i.e F_{hkl} for $l = 2n + 1$ or $2h + l = 4n$). No Thorium contributions are observed for reflections not satisfying these conditions and there is no contribution to any $h k l$ indices which do not satisfy the general reflection conditions

$$\begin{array}{l}
h k l: h + k + l = 2n \\
h k 0: h, k = 2n \\
0 k l: k + l = 2n \\
h h l: l = 2n \\
0 0 l: l = 4n \\
h 0 0: h = 2n \\
h -h 0: h = 2n
\end{array}$$

(c) The overall molecular formula is $C_{32}H_{64}N_4O_8Th$ which has 438 total electrons. Thorium has 90 electrons. For reflections to which Thorium contributes, 20.5% (90/438) of the reflection comes from Thorium scattering. But, if we consider the reflection conditions necessary (listed above), it implies that the Thorium only contributes to about 75% of the total number of reflections observed. So, on average, the Thorium contribution is 15% overall.

(d) As $\sin \theta/\lambda$ increases, the relative Thorium contribution increases due to the large amount of electron density in orbitals closer to the nucleus for Thorium. This makes f_{Th} fall off much more slowly with $\sin \theta/\lambda$ in comparison to the scattering factor for lighter elements such as C, H, N, O, etc.

(e) From the International Tables:

$$F_{hkl} = \sum f_j 8 \cos 2\pi \left(\frac{h+k+l}{4} \right) \left[\cos 2\pi \left(\frac{h+k+l}{4} \right) \cos 2\pi (hx + ky - k/4) \cos 2\pi (\ell z + k/4) \right. \\
\left. + \cos 2\pi (hy - kx - h/4) \cos 2\pi (\ell z + h/4) \right] \text{ For } h \\
k 0: h, k = 2n \text{ for all spots}$$

Since $2h + l = 2(2n) + 0 = 4n$ for all $h k 0$ observed (Th contribution for all $h k 0$ reflections).

The Thorium atom at 0, 0, 0 contributes to F_{hk0} as follows:

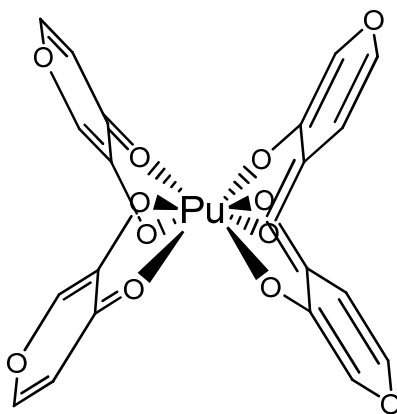
$$f_j 8 \cos \left(\frac{h+k}{2} \right) \left[\cos \pi \left(\frac{h+k}{2} \right) \cos \pi \left(\frac{-k}{2} \right) \cos \pi \left(\frac{-k}{2} \right) + \cos \pi \left(\frac{-h}{2} \right) \cos \pi \left(\frac{h}{2} \right) \right]$$

We know that both h and k are even, so the expression is positive which means that F_{hk0} for all h k 0 observed is positive (i.e. the phase angle is always 0). This means that one can get the phase information for all reflections to which Thorium contributes (or about 75% of all F_{hkl} phases can be guessed ahead of time).

Also, the Thorium dominates the phase contributions, and since $\phi = 0$ or π (centrosymmetric structure), we can assume the phase angle of $F_{hk0} = \phi_{hkl}(\text{Th})$ which gives us the sign the Thorium contribution.

4. The plutonium complex of maltol, $\text{Pu}(\text{maltol})_4$, crystallizes in space group $I4_1/a$ ($a = 9.2073(4)$, $c = 27.068(3)$, $Z = 4$)

- (a) Since $Z = 4$, the Pu atoms must be at a special position with the appropriate multiplicity. Special positions a or b will fulfill this requirement.
- (b) These special positions have $\bar{4}$ symmetry. This is a requirement at either of the appropriate special positions.
- (c) The maltol ligands have no similar requirements – since there are sixteen of these ligands within the unit cell, they are able to lie on general positions (which have a multiplicity of 16).
- (d) Remarkably, this information gives us one extremely likely configuration for the complex – alternating maltol ligands must be ‘flipped’ to create the $\bar{4}$ axis. While somewhat complicated to draw in 3-dimensions, it looks something like:



- (e) The Pu atoms have their coordinates fixed by the description of the unit cell, and so have errors of the order of the unit cell determination. The other atoms, which are placed during the more complete structural determination, have somewhat larger errors as a result.

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

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

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

For $P2_12_12_1$, we have the following symmetry-equivalent positions:

$$(x,y,z) \quad (-x + 1/2, -y, z + 1/2) \quad (-x, y + 1/2, -z + 1/2) \quad (x + 1/2, -y + 1/2, -z)$$

So, if we write an expansion of the structure factors associated with these positions, we obtain :

$$\sum_{j=1}^{N/4} f_j [e^{2\pi i(hx+ky+lz)} + e^{2\pi i(-hx-ky+lz+(h+l)/2)} + e^{2\pi i(-hx+ky-lz+(k+l)/2)} + e^{2\pi i(hx-ky-lz+(h+k)/2)}] \quad [\text{Eq. 1}]$$

But, were I to write the equivalent expression for the equal $F(h,-k,-l)$ [which is itself equal to $F(-h,k,l)$] according to Friedel's Law, and thus defined in the problem as also being equal]:

$$\sum_{j=1}^{N/4} f_j [e^{2\pi i(hx-ky-lz)} + e^{2\pi i(-hx+ky-lz+(h+l)/2)} + e^{2\pi i(-hx-ky+lz+(k+l)/2)} + e^{2\pi i(hx+ky+lz+(h+k)/2)}]$$

It should be clear that these two expressions are related. (The careful reader will note that I have not changed the signs of the $(k+)_/2$ terms – note that $-k/2 = +k/2$ by modulo k arithmetic). Each term is equal to a term in the above expression with a shift of $(h+k)/2$. This allows us to factor as follows:

$$e^{2\pi i \frac{(h+k)}{2}} \sum_{j=1}^{N/4} f_j [e^{2\pi i(hx+ky+lz)} + e^{2\pi i(-hx-ky+lz+(h+l)/2)} + e^{2\pi i(-hx+ky-lz+(k+l)/2)} + e^{2\pi i(hx-ky-lz+(h+k)/2)}]$$

Which, of course, is simply:

$$(-1)^{\frac{(h+k)}{2}} \sum_{j=1}^{N/4} f_j [e^{2\pi i(hx+ky+lz)} + e^{2\pi i(-hx-ky+lz+(h+l)/2)} + e^{2\pi i(-hx+ky-lz+(k+l)/2)} + e^{2\pi i(hx-ky-lz+(h+k)/2)}]$$

So, the phases of $F(h,-k,-l)$ and $F(-h,k,l)$ are equal to $\pm F(h,k,l)$, depending on whether $(h+k)$ is even or odd.

Similarly, we can obtain expressions for the other reflections, $F(-h,k,-l)=F(h,-k,l)$

$$\sum_{j=1}^{N/4} f_j [e^{2\pi i(-hx+ky-lz)} + e^{2\pi i(hx-ky-lz+(h+l)/2)} + e^{2\pi i(hx+ky+lz+(k+l)/2)} + e^{2\pi i(-hx-ky+lz+(h+k)/2)}]$$

Which is a $(k+1)/2$ phase shift, with the last expression for $F(-h,-k,l)=F(h,k,-l)$ giving the phase shift of $(h+1)/2$.