National School on Neutron and X-ray Scattering
Lecture Date: October 1, 2008

Single Crystal Crystallography

*Example*1 –

Space Group Determination

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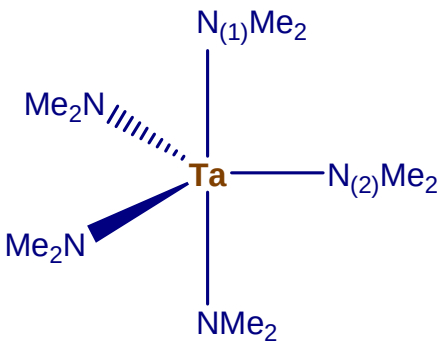
Presented at the ACA Annual Meeting, Salt Lake City, July 23, 2007

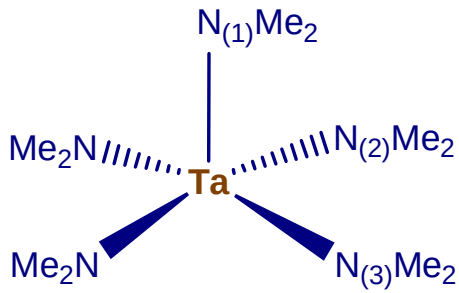
"*Disorder*" of $Ta(NMe_2)_5$ Molecule in the Solid State

- Molecular Structure of $Ta(NMe_2)_5$
- A Symmetry-Imposed Disorder Reported in the Crystal Structure
- Space Group Symmetry and Site Symmetry
- Reflection Conditions and Pseudo Symmetry
- Crystal Structure of $Ta(NMe_2)_5$ without Symmetry-Imposed Disorder
- Summary

$Ta(NMe_2)_5$ – Simple Molecule, Problem Structure



D_{3h}

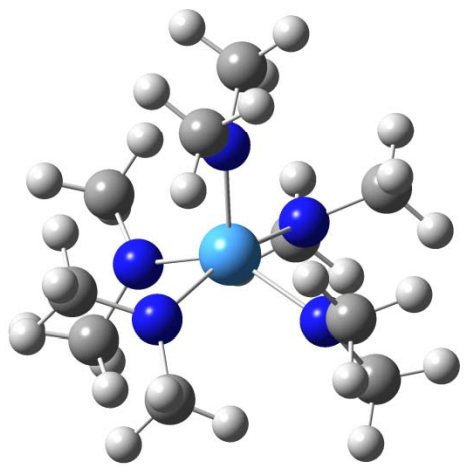


C_{4v}

Ta–N(1)	1.94(3)
Ta–N(2)	2.040(6)
Ta–N(3)	2.040(6)

Electron Diff. - Selected Distances [Å]

C_{2v} *Electron diffraction* [1]



DFT Geometry Optimization - C_2

Ta–N(1)	2.0016
Ta–N(2)	2.0406
Ta–N(3)	2.0636

DFT - Selected Distances [Å]

[1] K. Hagen, C. J. Holwill, D. A. Rice and J. D. Runnacles, *Inorg.Chem.*, 1992, **31**, 4733.

$Ta(NMe_2)_5$ – Reported Crystal Data

J. Chem. Soc., Dalton Trans. **1999**, 3867.

	2
Formula	$C_{10}H_{30}N_5Ta$
M	401.34
Crystal system	Orthorhombic
Space group	*Cmcm* (no. 63)
a/Å	13.845(3)
b/Å	7.900(2)
c/Å	14.544(3)
α/°	
β/°	
γ/°	
U/Å^3	1590.8(6)
Z	4
μ(Mo-Kα)/cm^{-1}	69.0
Reflections measured	5601
Unique reflections	985
R_{int} [a]	0.132, 0.024
Reflections with $I \geq 2\sigma(I)$	979
R [$F^2 \geq 2\sigma(F^2)$]	0.027
$wR(F^2)$, all data	0.066

[a] Before and after the absorption correction.

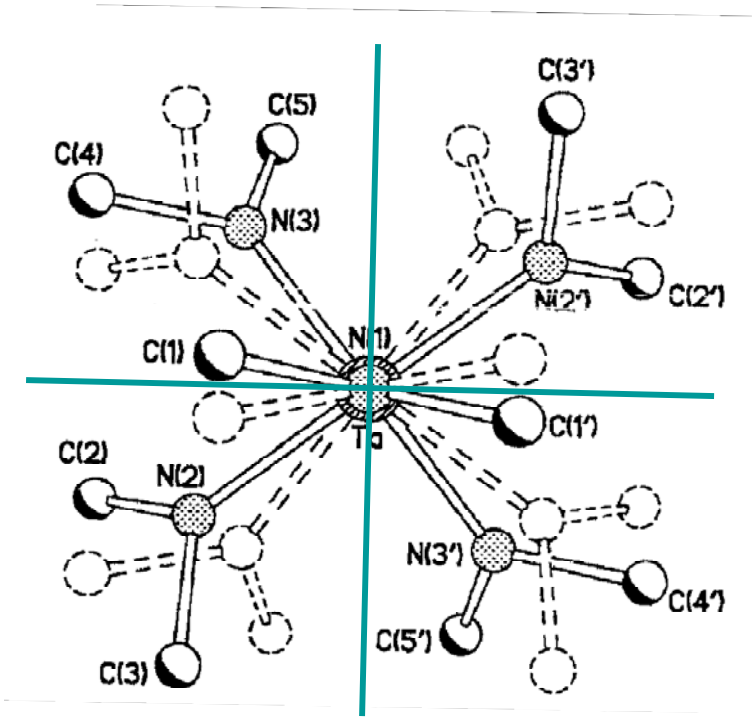
Selected Coordinates

Ta1	0.500000	0.671450	0.250000
N1	0.500000	0.422700	0.250000
N2	0.587300	0.721200	0.140500
N3	0.390800	0.755200	0.169500

$Ta(NMe_2)_5$ – Symmetry-Imposed Disorder?

Crystal and molecular structures

The diffraction pattern of $[Ta(NMe_2)_5]$ **2** suggested unequivocally a *C*-centred orthorhombic lattice, and the structure was successfully solved in space group *Cmcm*. The molecule lies across a special position *m2m* (*c*), but only the Ta and N(1) atoms lie on the twofold axis. All other atoms are disordered over two positions, symmetrically related *via* mirror planes



J. Chem. Soc., Dalton Trans. **1999**, 3867.

CONTINUED

No. 63 $Cmcm$

Hermann-Mauguin notation

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},0)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
			$(0,0,0)+$	$(\frac{1}{2},\frac{1}{2},0)+$			General:
16	h	1	(1) x,y,z	(2) $\bar{x},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y,\bar{z}+\frac{1}{2}$		
			(5) $\bar{x},\bar{y},\bar{z}$	(6) $x,y,\bar{z}+\frac{1}{2}$	(7) $x,\bar{y},z+\frac{1}{2}$		
8	g	$..m$	$x,y,\frac{1}{4}$	$\bar{x},\bar{y},\frac{3}{4}$	$\bar{x},y,\frac{1}{4}$	$x,\bar{y},\frac{3}{4}$	no extra conditions
8	f	$m..$	$0,y,z$	$0,\bar{y},z+\frac{1}{2}$	$0,y,\bar{z}+\frac{1}{2}$	$0,\bar{y},\bar{z}$	no extra conditions
8	e	$2..$	$x,0,0$	$\bar{x},0,\frac{1}{2}$	$\bar{x},0,0$	$x,0,\frac{1}{2}$	hkl : $l=2n$
8	d	$\bar{1}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{3}{4},\frac{1}{2}$	$\frac{3}{4},\frac{1}{4},\frac{1}{2}$	$\frac{1}{4},\frac{3}{4},0$	hkl : $k,l=2n$
4	c	$m2m$	$0,y,\frac{1}{4}$	$0,\bar{y},\frac{3}{4}$			no extra conditions
4	b	$2/m..$	$0,\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $l=2n$
4	a	$2/m..$	$0,0,0$	$0,0,\frac{1}{2}$			hkl : $l=2n$

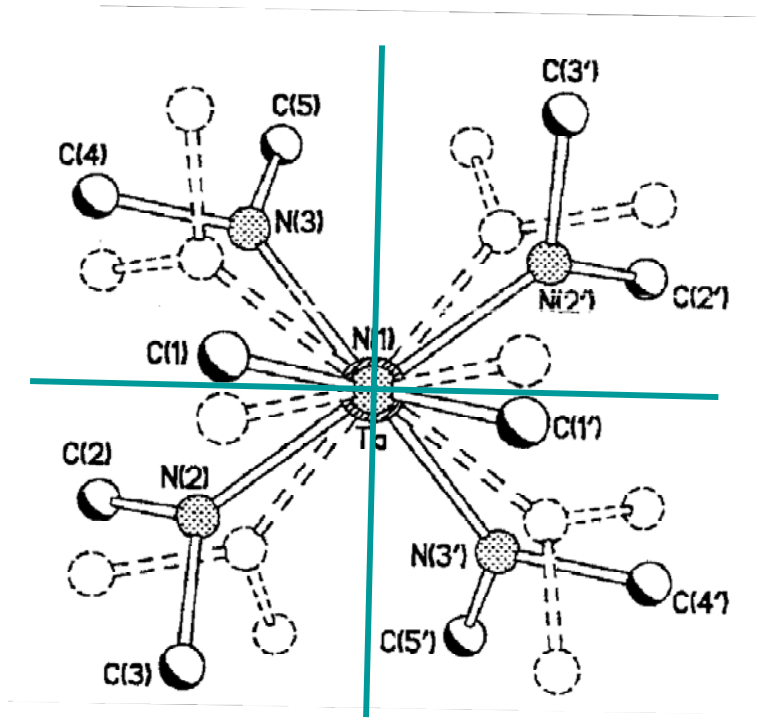
Selected Coordinates

Ta1	0.500000	0.671450	0.250000
N1	0.500000	0.422700	0.250000
N2	0.587300	0.721200	0.140500
N3	0.390800	0.755200	0.169500

ITA *p301*

Symmetry-Imposed Disorder in Space Group *Cmcm*?

Space Group Cmcm				
Multiplicity	**Wyckoff letter**	**Site symmetry**	**Coordinates**	
			(0, 0, 0)+	(1/2, 1/2, 0)+
16	h	1	x, y, z	…
4	c	*m2m*	0, *y*, 1/4	0, -*y*, 3/4



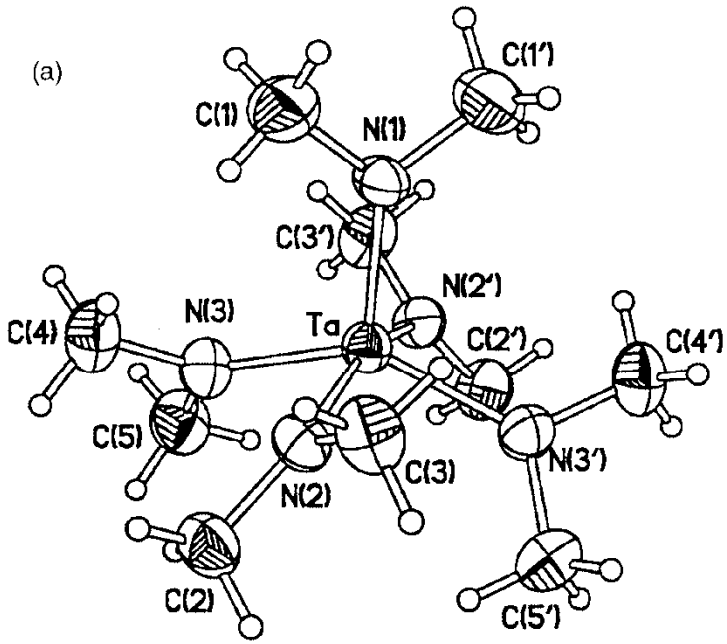
Point Group Symmetry C_{2v}

Selected Coordinates

Ta1	0.500000	0.671450	0.250000
N1	0.500000	0.422700	0.250000
N2	0.587300	0.721200	0.140500
N3	0.390800	0.755200	0.169500

$Ta(NMe_2)_5$ – Molecular Structure in Space Group *Cmcm*

Select only a subset of atoms with C_2 point group symmetry.



Selected Distances [Å]

Ta–N(1)	1.965(5)
Ta–N(2)	2.023(9)
Ta–N(3)	2.038(8)

J. Chem. Soc., Dalton Trans. **1999**, 3867.

Site Symmetry & Molecular Point Group Symmetry

Subgroups of *Cmcm*

Number	HM symbol
…	…
60	*Pbcn*
62	*Pnma*
63	*Cmcm*

Space Group Pbcn

Multiplicity	Wyckoff letter	Site symmetry	Coordinates	
8	d	1	x, y, z	…
4	c	*.2.*	0, *y*, 1/4	0, -*y*, 3/4

Point Group Symmetry C_2

$Ta(NMe_2)_5$??

Space Group Cmcm

Multiplicity	Wyckoff letter	Site symmetry	Coordinates	
			(0, 0, 0)+	(1/2, 1/2, 0)+
16	h	1	x, y, z	…
4	c	*m2m*	0, *y*, 1/4	0, -*y*, 3/4

Point Group Symmetry C_{2v}

Bilbao Crystallographic Server http://www.cryst.ehu.es

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

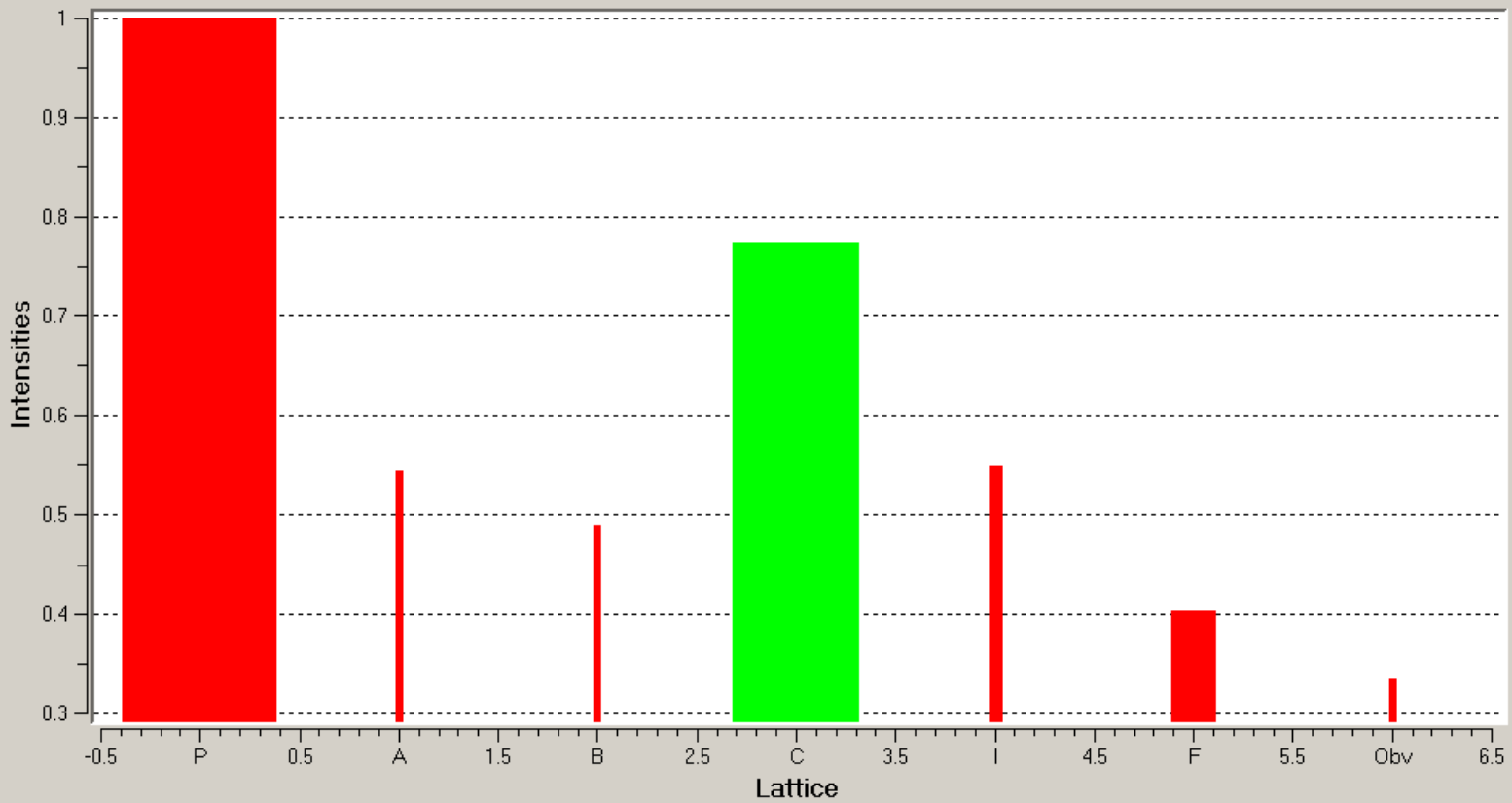
Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	d	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},z+\frac{1}{2}$	(3) $\bar{x},y,\bar{z}+\frac{1}{2}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	$0kl$: $k=2n$
			(5) $\bar{x},\bar{y},\bar{z}$	(6) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(7) $x,\bar{y},z+\frac{1}{2}$	(8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z$	$h0l$: $l=2n$
							$hk0$: $h+k=2n$
							$h00$: $h=2n$
							$0k0$: $k=2n$
							$00l$: $l=2n$
							Special: as above, plus
4	c	. 2 .	$0,y,\frac{1}{4}$	$\frac{1}{2},\bar{y}+\frac{1}{2},\frac{3}{4}$	$0,\bar{y},\frac{3}{4}$	$\frac{1}{2},y+\frac{1}{2},\frac{1}{4}$	hkl : $h+k=2n$
4	b	$\bar{1}$	$0,\frac{1}{2},0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$	hkl : $h+k,l=2n$
4	a	$\bar{1}$	$0,0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	hkl : $h+k,l=2n$

Diffraction Data at 100 K – A *Primitive* or *C*-centered Cell?

Setup | Lattice Exceptions | Space Group Determination | Statistics | Unit Cell Contents | Set Up Files | Cell Information | Diagnostics

	P	A	B	C	I	F	Obv	Rev	All
N (total)	0.0	5547.0	5565.0	5602.0	5548.0	8357.0	7430.0	7434.0	11138.0
N (int>3sigma)	0.0	2946.0	3297.0	1471.0	2910.0	3857.0	4302.0	4306.0	6455.0
Mean intensity	0.0	548.2	547.0	12.5	545.9	368.3	562.3	565.9	561.1
Mean int/sigma	0.0	16.1	16.4	3.0	15.1	11.8	16.7	16.7	16.7



Select Lattice Type P

Use Lattice Type: C Next

APEX2

Space Group Determined with Bruker APEX2 Program

Systematic absence exceptions

	c--	n--	-c-	-n-	--a	--b	--21
N	281	281	95	95	118	118	15
N I>3s	9	9	74	74	118	118	0
<I>	2.2	2.2	1630.7	1630.7	1510.5	1510.5	1.4
<I/s>	0.8	0.8	29.3	29.3	35.1	35.1	0.6

E-value statistics

Non-centrosymmetric: 0.736 Mean |E*E-1| 0.616 Centrosymmetric: 0.968

Identical indices and Friedel opposites combined before calculating R(sym)

Space Group	No.	Type	Axes	CSD	R(sym)	N(eq)	Syst. Abs.	CFOM
Space Groups								
Ama2	# 40	non-cen	5	21	0.014	2170	0.8 / 16.7	6.62
Cmc2(1)	# 36	non-cen	2	102	0.014	2170	0.8 / 16.7	3.05
Cmcm	# 63	centro	2	100	0.014	2170	0.8 / 16.7	14.03

Choose a different space group: P1

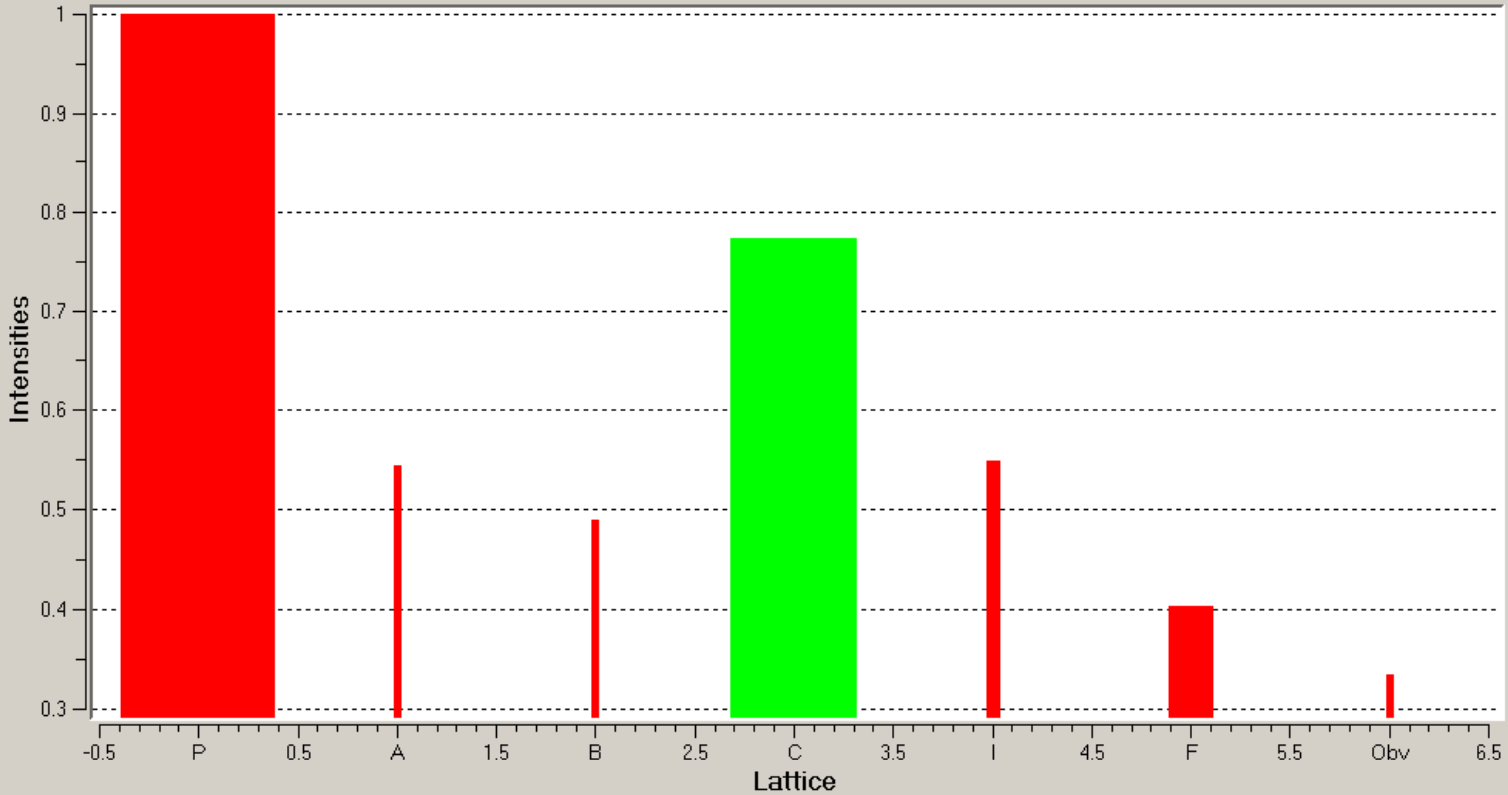
Repeat

Next

Manual Selection of a *P* Lattice

Setup | Lattice Exceptions | Space Group Determination | Statistics | Unit Cell Contents | Set Up Files | Cell Information | Diagnostics

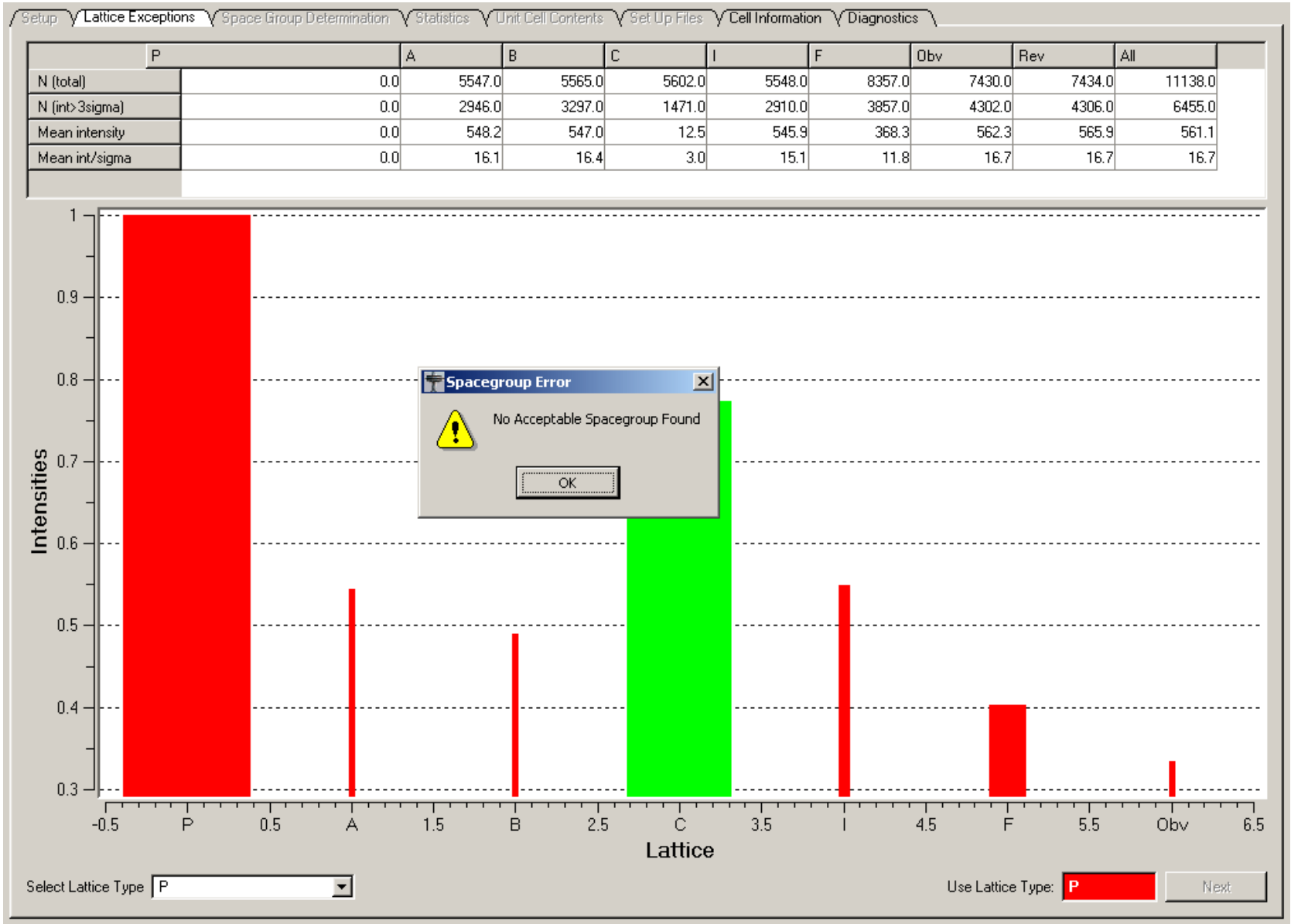
	P	A	B	C	I	F	Obv	Rev	All
N (total)	0.0	5547.0	5565.0	5602.0	5548.0	8357.0	7430.0	7434.0	11138.0
N (int>3sigma)	0.0	2946.0	3297.0	1471.0	2910.0	3857.0	4302.0	4306.0	6455.0
Mean intensity	0.0	548.2	547.0	12.5	545.9	368.3	562.3	565.9	561.1
Mean int/sigma	0.0	16.1	16.4	3.0	15.1	11.8	16.7	16.7	16.7



Select Lattice Type P

Use Lattice Type: P Next

Ambiguity in Space Group Selection



	P	A	B	C	I	F	Obv	Rev	All
N (total)	0.0	5547.0	5565.0	5602.0	5548.0	8357.0	7430.0	7434.0	11138.0
N (int>3sigma)	0.0	2946.0	3297.0	1471.0	2910.0	3857.0	4302.0	4306.0	6455.0
Mean intensity	0.0	548.2	547.0	12.5	545.9	368.3	562.3	565.9	561.1
Mean int/sigma	0.0	16.1	16.4	3.0	15.1	11.8	16.7	16.7	16.7

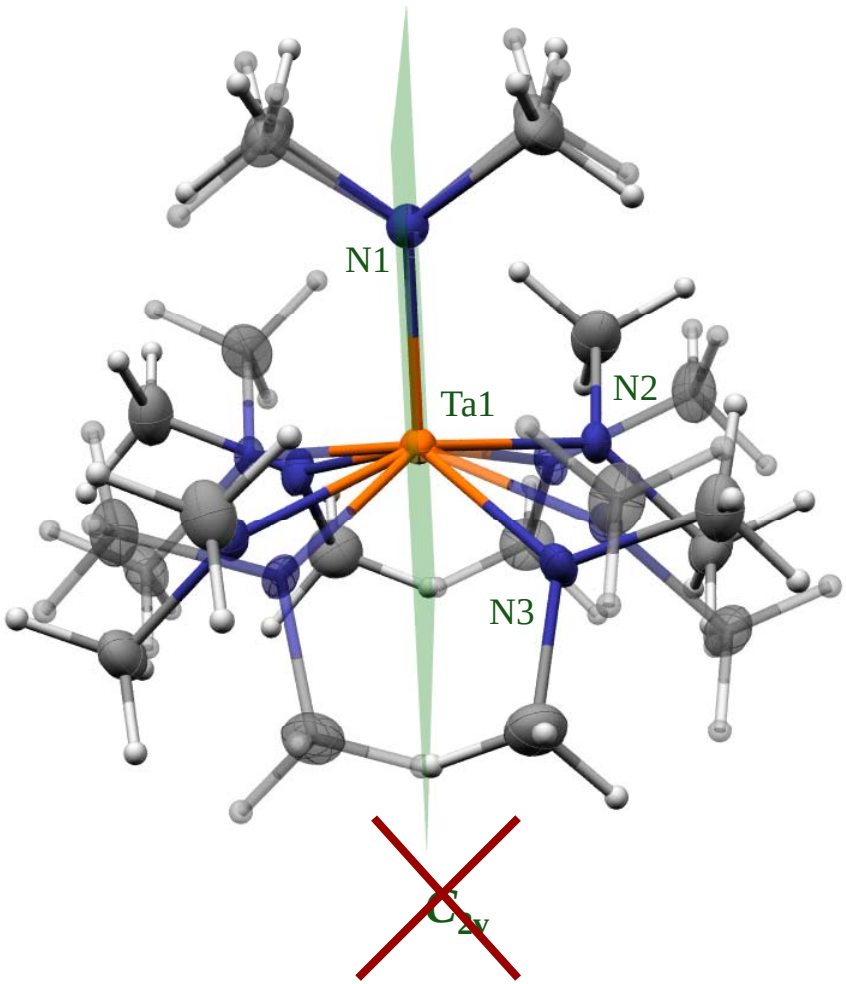
Bravais Lattice and Space Group Selection – XPREP

Using XPREP

```
Lattice exceptions: P      A      B      C      I      F     Obv    Rev    All

N (total) =          0   5549   5567   5602   5550   8359   7432   7436  11140
N (int>3sigma) =     0   2766   2996   1034   2628   3398   3961   3960   5929
Mean intensity =   0.0  235.1  234.6    5.5  233.7  158.0  240.9  242.4  240.4
Mean int/sigma =   0.0   21.6   21.7    2.2   20.6   15.2   21.8   21.9   21.8

Lattice type [P, A, B, C, I, F, O(obv.), R(rev. rhomb. on hex. axes)]

Select option [C]:
```

```
Mean |E*E-1| = 0.616 [expected .968 centrosym and .736 non-centrosym]


Systematic absence exceptions:

        c--   n--   -c-   -n-   --a   --b  --21

N       283   283    95    95   118   118    15
N I>3s   18    18    75    75   118   118     2
<I>     1.3   1.3 692.3 692.3 649.8 649.8   1.4
<I/s>   0.9   0.9  60.2  60.2  58.1  58.1   1.7


Identical indices and Friedel opposites combined before calculating R(sym)

Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM

[A] Cmc2(1)        # 36  non-cen  2   102  0.030   2170  1.7 / 21.8   2.90
[B] Cmcm           # 63  centro   2   100  0.030   2170  1.7 / 21.8  13.89
[C] Ama2           # 40  non-cen  5    21  0.030   2170  1.7 / 21.8   6.47

Select option [A]: B
```

Structure of $Ta(NMe_2)_5$ at 100 K – Space Group *Cmcm*



Symmetry-Imposed Disorder

Or …

Manual Selection of Space Group

```
Lattice exceptions: P      A      B      C      I      F    Obv    Rev    All

N (total) =          0   5549   5567   5602   5550   8359   7432   7436  11140
N (int>3sigma) =     0   2766   2996   1034   2628   3398   3961   3960   5929
Mean intensity =   0.0  235.1  234.6    5.5  233.7  158.0  240.9  242.4  240.4
Mean int/sigma =   0.0   21.6   21.7    2.2   20.6   15.2   21.8   21.9   21.8

Lattice type [P, A, B, C, I, F, O(obv.), R(rev. rhomb. on hex. axes)]

Select option [C]: P
```

```
Mean |E*E-1| = 1.154 [expected .968 centrosym and .736 non-centrosym]


Systematic absence exceptions:

        b--   c--   n--  21--   -c-   -a-   -n-  -21-   --a   --b   --n  --21

N       559   562   563     7   195   199   194    27   238   236   238    15
N I>3s  112    24   124     1    75     1    76     3   119   121     4     2
<I>     6.8   1.0   7.1   0.7 337.5   0.5 339.3   0.8 322.4 325.2   0.6   1.4
<I/s>   2.5   0.7   2.7   1.6  29.5   0.4  29.7   1.3  29.0  29.3   0.5   1.7


Identical indices and Friedel opposites combined before calculating R(sym)

Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM

No acceptable space group -  change tolerances or unset chiral flag
or possibly change input lattice type, then recheck cell using H-option

Select option [?]:
```

What to do Next?

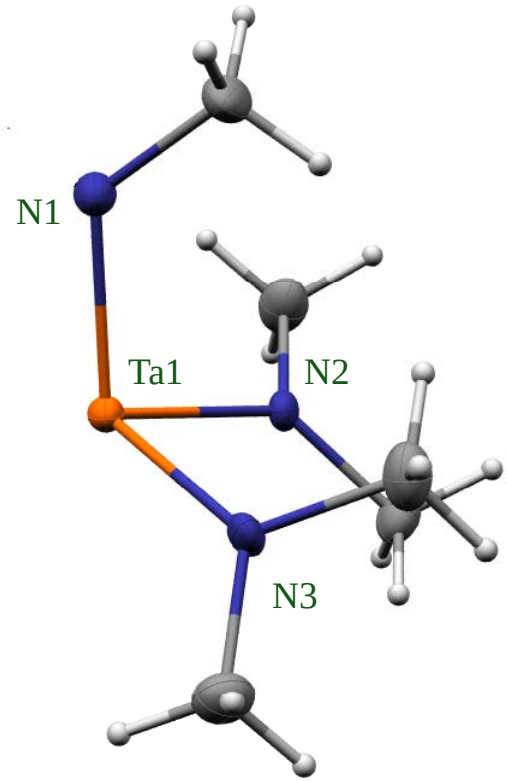
Space Group Selection – Change Tolerance

```
[D] Maximum DEVIATION in degrees in higher symmetry cell search [ 1.00 ]
[T] THRESHOLD in degrees for terminating cell search [ 0.05 ]
[R] R(int) maximum for terminating cell search [  0.12 ]
[S] Maximum R(int) gap for SPACE group determination [ 0.300 ]
[N] Minimum NUMBER of data in group for systematic absence test [  5 ]
[A] Maximum mean I/sigma(I) for systematic ABSENCES [ 3.67 ]
[G] Minimum I/sigma GAP between absences and others [ 4.35 ]
[E] EXIT to main menu  or  [Q] QUIT program

Select option [E]: G

Enter new minimum I/sigma gap: 0.1
```

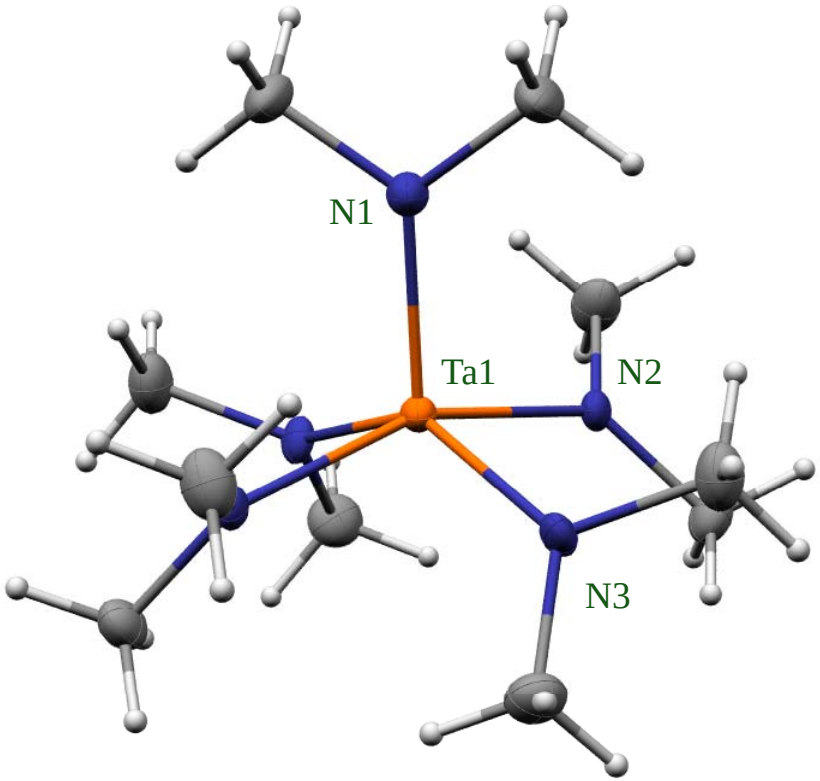
Space Group Selection - Continue

```
Lattice exceptions: P      A      B      C      I      F    Obv    Rev    All

N (total) =          0   5567   5549   5602   5550   8359   7436   7432  11140
N (int>3sigma) =     0   2996   2766   1034   2628   3398   3960   3961   5929
Mean intensity =   0.0  234.6  235.1    5.5  233.7  158.0  242.4  240.9  240.4
Mean int/sigma =   0.0   21.7   21.6    2.2   20.6   15.2   21.9   21.8   21.8

Lattice type [P, A, B, C, I, F, O(obv.), R(rev. rhomb. on hex. axes)]

Select option [C]: P


Mean |E*E-1| = 1.154 [expected .968 centrosym and .736 non-centrosym]


Systematic absence exceptions:

        b--   c--   n--  21--   -c-   -a-   -n-  -21-   --a   --b   --n  --21

N       559   562   563     7   195   199   194    27   238   236   238    15
N I>3s  112    24   124     1    75     1    76     3   119   121     4     2
<I>     6.8   1.0   7.1   0.7 337.5   0.5 339.3   0.8 322.4 325.2   0.6   1.4
<I/s>   2.5   0.7   2.7   1.6  29.5   0.4  29.7   1.3  29.0  29.3   0.5   1.7


Identical indices and Friedel opposites combined before calculating R(sym)

Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM

[A] P222           # 16  chiral   1    14  0.031   4369  0.0 /  0.4  44.13
[B] Pmm2           # 25  non-cen  1     9  0.031   4369  0.0 /  0.4  47.46
[C] Pmm2           # 25  non-cen  5     9  0.031   4369  0.0 /  0.4  47.46
[D] Pmm2           # 25  non-cen  3     9  0.031   4369  0.0 /  0.4  47.46
[E] Pmmm           # 47  centro   1     7  0.031   4369  0.0 /  0.4  35.96
[F] Pbcn           # 60  centro   2   571  0.031   4369  1.7 /  2.5   9.13

Select option [F]:
```

Structure of $Ta(NMe_2)_5$ at 100 K – Space Group *Pbcn*



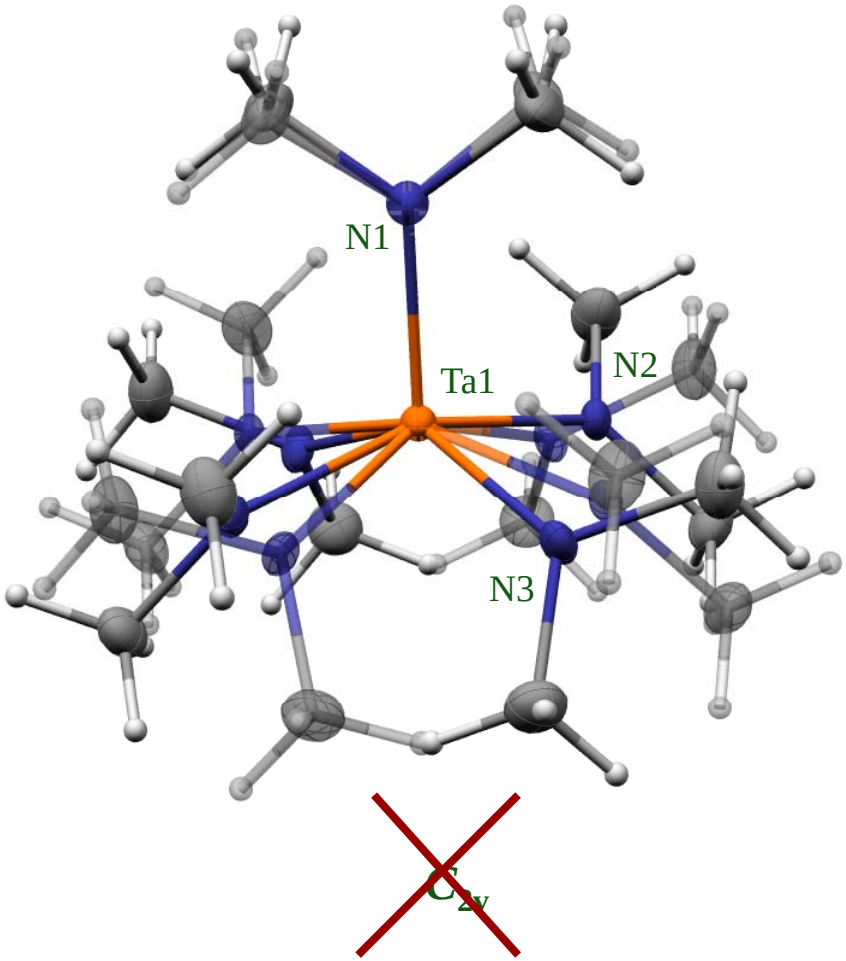
Structure of $Ta(NMe_2)_5$ at 100 K – Space Group *Pbcn*



C_2

No Symmetry-Imposed Disorder

Structure of $Ta(NMe_2)_5$ at 100 K – Space Group *Cmcm*



Reflection Conditions and Pseudo Symmetry

Space group *Pbcn* —**Ta1 at 4*c*** simulates→ **Space Group *Cmcm***

Mult.	Letter	Site Sym.	WP Representative	Reflection conditions
				General:
8	d	1	(x,y,z)	0kl: k=2n h0l: l=2n hk0: h+k=2n h00: h=2n 0k0: k=2n 00l: l=2n
				Special: as above, plus
4	c	.2.	(0,y,1/4)	hkl: h+k=2n
4	b	-1	(0,1/2,0)	hkl: h+k,l=2n
4	a	-1	(0,0,0)	hkl: h+k,l=2n

Mult.	Letter	Site Sym.	WP Representative	Reflection conditions
				General:
16	h	1	(x,y,z)	hkl: h+k=2n 0kl: k=2n h0l: h,l=2n hk0: h+k=2n h00: h=2n 0k0: k=2n 00l: l=2n
				Special: as above, plus
8	g	..m	(x,y,1/4)	no extra conditions
8	f	m..	(0,y,z)	no extra conditions
8	e	2..	(x,0,0)	hkl: l=2n
8	d	-1	(1/4,1/4,0)	hkl: k,l=2n
4	c	m2m	(0,y,1/4)	no extra conditions
4	b	2/m..	(0,1/2,0)	hkl: l=2n
4	a	2/m..	(0,0,0)	hkl: l=2n

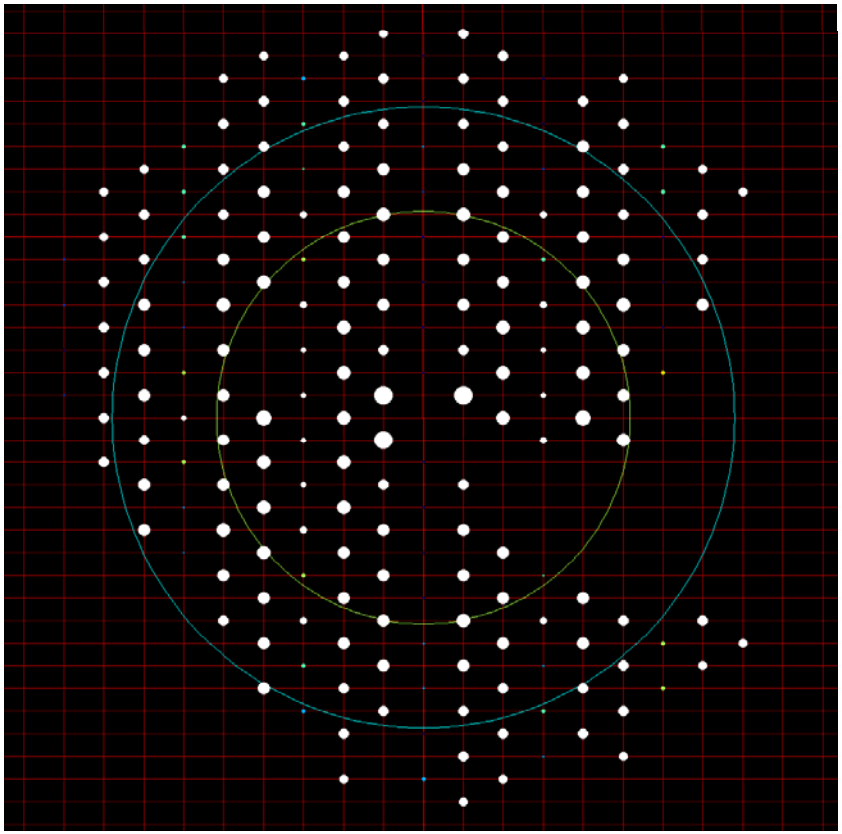
Ta accounts for 37% of the electrons in $Ta(NMe_2)_5$

Intensity Plot for a *C*-centered Lattice

Reflection conditions
hkl: h+k=2n 0kl: k=2n h0l: h,l=2n hk0: h+k=2n h00: h=2n 0k0: k=2n 00l: l=2n

……

Centered



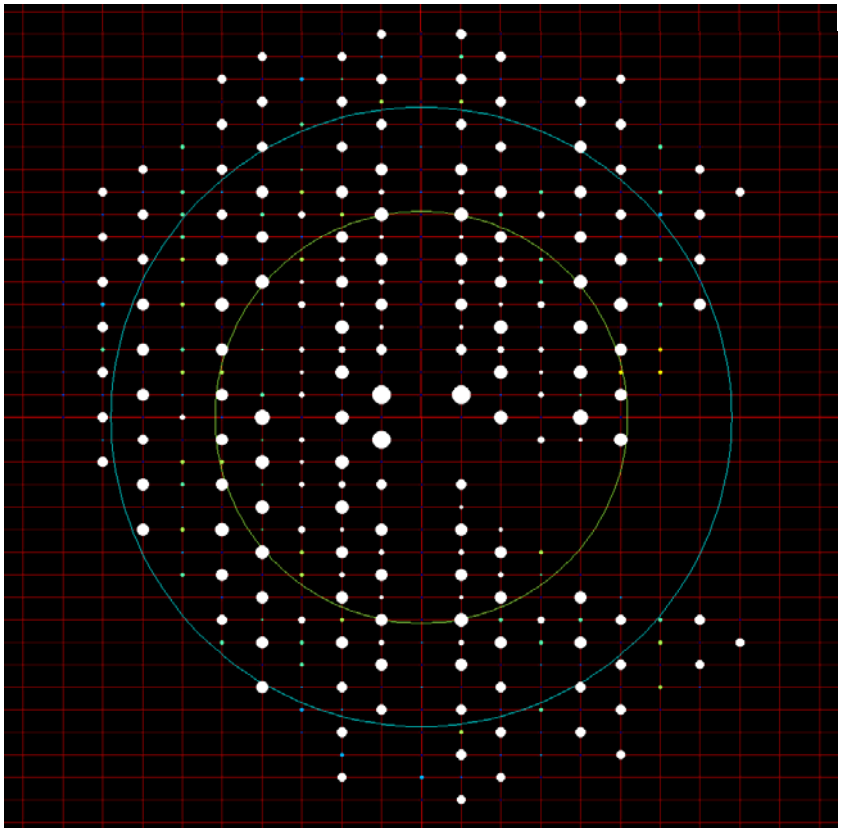
Layer *h*, *k*, *l* at *l* = 1

Intensity Plot for a *Primitive* Lattice

Reflection conditions
0kl: k=2n h0l: l=2n hk0: h+k=2n h00: h=2n 0k0: k=2n 00l: l=2n

Special: as above, *plus*	
0, y, 1/4	**hkl: h+k=2n**
0, ½, 0	hkl: h+k,l=2n
0, 0, 0	hkl: h+k,l=2n

Primitive



Layer *h*, *k*, *l* at *l* = 1

Weak intensities for *hkl*: $h+k = 2n+1$
because of Ta atom lies on a special position.

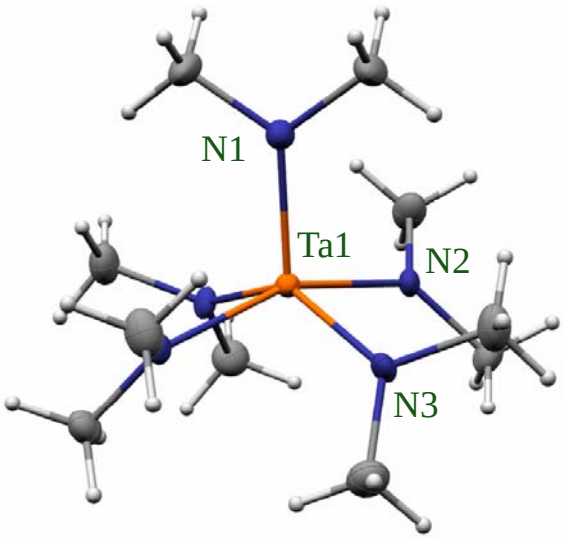
$Ta(NMe_2)_5$ – Summary of Crystal Data

Crystal system	Orthorhombic	
Space group	***P b c n***	***C m c m***
Unit cell dimensions	a = 13.7892(12) Å; b = 7.8111(7) Å; c = 14.4961(13) Å	
Volume	1561.4(2) Å3	
Z	4	
Index ranges	-17<=h<=17, -8<=k<=9, -17<=l<=18	
Reflections collected	**10148**	**5255**
Independent reflections	1680 [R(int) = 0.0201]	908 [R(int) = 0.0185]
Completeness to $\theta = 26.85°$	100.0 %	100.0 %
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	**1680** / 0 / 79	**908** / 0 / 77
Goodness-of-fit on F^2	1.075	1.187
Final R indices [I>2σ(I)]	R1 = 0.0146, wR2 = 0.0375	R1 = 0.0124, wR2 = 0.0316
R indices (all data)	R1 = 0.0227, wR2 = 0.0435	R1 = 0.0127, wR2 = 0.0318
Largest diff. peak and hole	0.908 and -1.244 e.$Å^{-3}$	0.878 and -1.212 e.$Å^{-3}$

$Ta(NMe_2)_5$ – Summary of Crystal Data

Selected Distances (Å) and Angles (deg).

Space Group	*Pbcn*	*Cmcm**
Ta1–N1	1.981(4)	1.981(4)
Ta1–N2	2.025(2)	2.019(5)
Ta1–N3	2.029(2)	2.032(5)
N1–Ta1–N2	101.35(7)	101.37(14)
N1–Ta1–N3	108.82(7)	108.93(15)
N2–Ta1–N3	87.25(9)	86.9(2)
N2–Ta1–N2	157.31(13)	157.3(3)
N3–Ta1–N3	142.36(13)	142.1(3)



C_2

*** Assuming a *C*-centered lattice has resulted a disordered structure.**