# Elucidation of Disorder in a Crystal Structure

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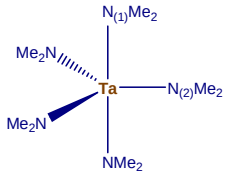
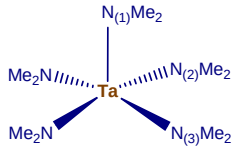
## Outline

- 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
- Acknowledgements

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




$D_{3h}$

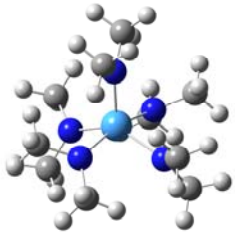



$C_{4v}$

| | |
|---|---|
| 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) |
| $\alpha$/° | |
| $\beta$/° | |
| $\gamma$/° | |
| $U$/Å$^3$ | 1590.8(6) |
| $Z$ | 4 |
| $\mu$(Mo-K$\alpha$)/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.

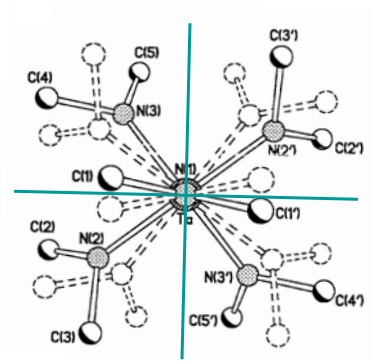
*Selected Coordinates*

| | | | |
|---|---|---|---|
| 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**

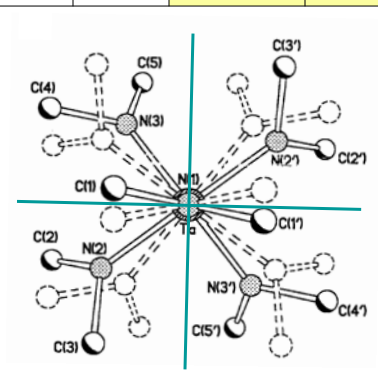
The diffraction pattern of [$Ta(NMe_2)_5$] **2** suggested unequivocally a *C*-centred orthorhombic lattice, and the structure was successfully solved in space group *Cmcm*. The molecule lies across a special position *m2m* (*c*), but only the Ta and N(1) atoms lie on the twofold axis. All other atoms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




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

## 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*** $C_{2v}$

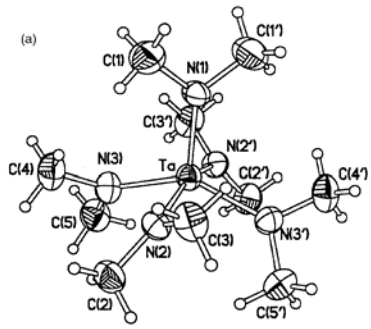
*Selected Coordinates*

| | | | |
|---|---|---|---|
| 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 |

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

## $Ta(NMe_2)_5$ – 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*** $C_2$

**$Ta(NMe_2)_5$ ??**

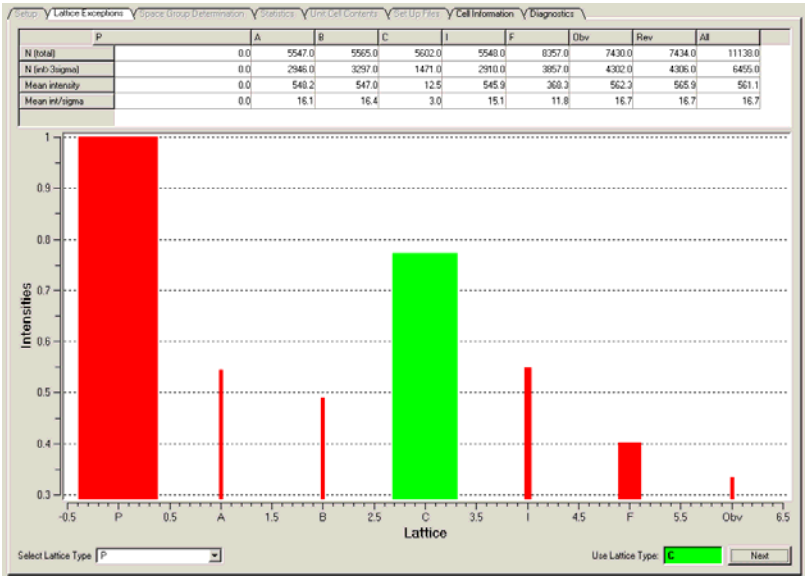
***Space Group Cmcm***

| 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

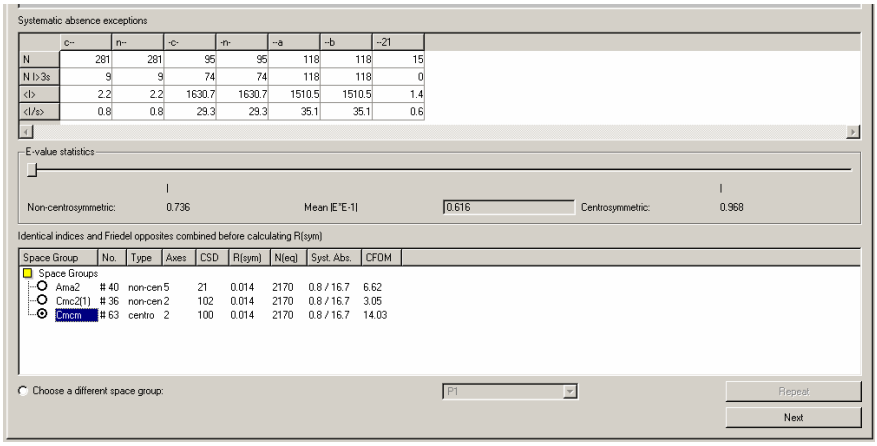
## Diffraction Data at 100 K – A *Primitive* or *C*-centered Cell?




| | 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 | 369.3 | 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 |

APEX2

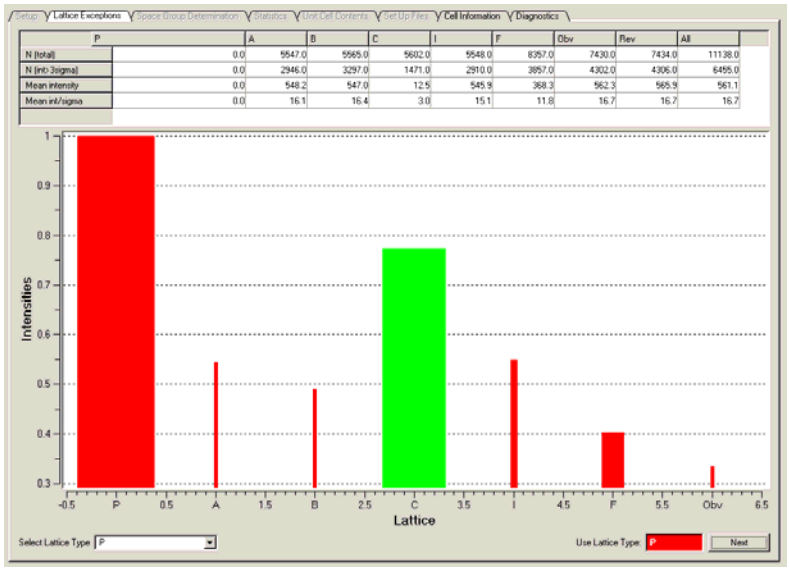
## Space Group Determined with Bruker APEX2 Program




| | 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 |

| 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 |

## Manual Selection of a *P* Lattice




| | 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 (inb 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 |

## 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 (inb 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 |

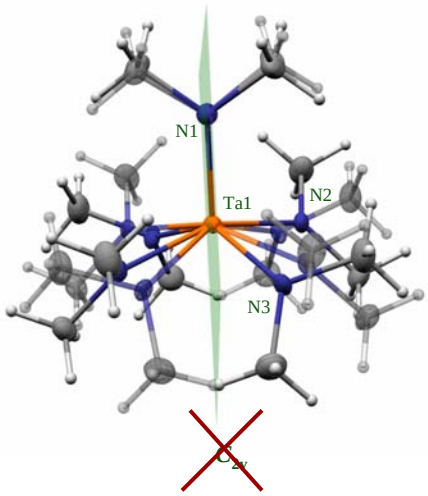
## Bravais Lattice and Space Group Selection – XPREP

*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?

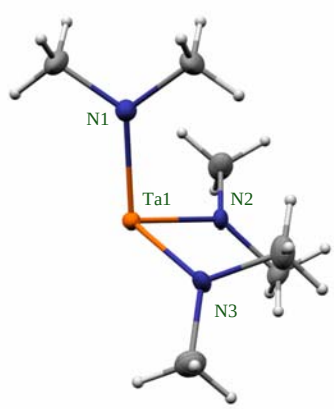
## Space Group Selection – Change Tolerance

```
[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
```

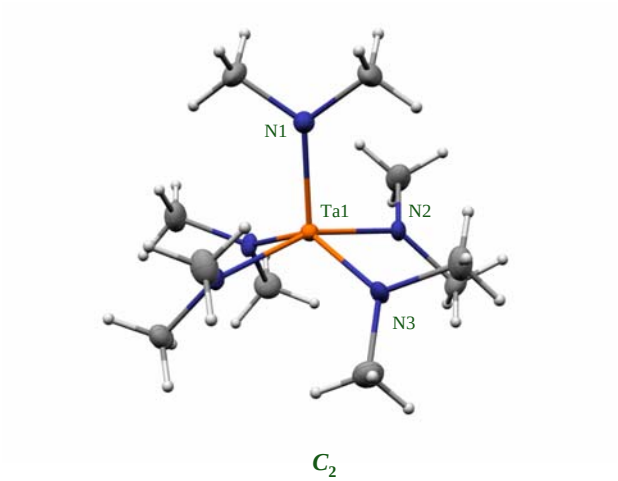
## Space Group Selection - Continue

```
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*



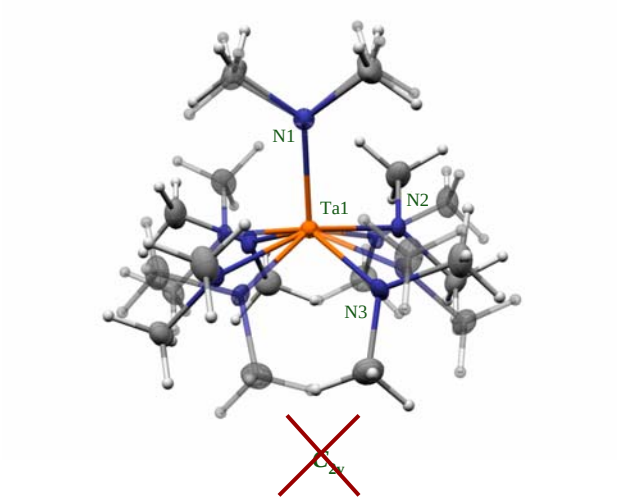
## Structure of $Ta(NMe_2)_5$ at 100 K – Space Group *Pbcn*




$C_2$

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<br>h0l: l=2n<br>hk0: h+k=2n<br>h00: h=2n<br>0k0: k=2n<br>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**<br>0kl: k=2n<br>h0l: h,l=2n<br>hk0: h+k=2n<br>h00: h=2n<br>0k0: k=2n<br>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 |

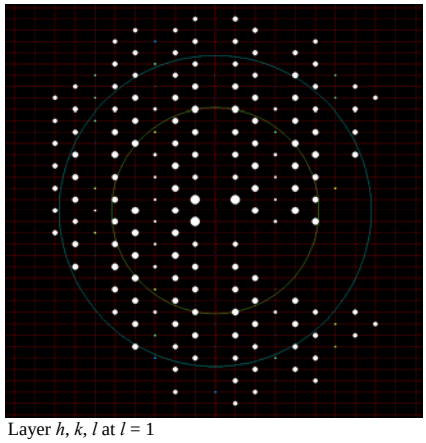
Ta accounts for 37% of the electrons in $Ta(NMe_2)_5$

## Intensity Plot for a *C*-centered Lattice

| Reflection conditions |
|---|
| hkl: h+k=2n<br>0kl: k=2n<br>h0l: h,l=2n<br>hk0: h+k=2n<br>h00: h=2n<br>0k0: k=2n<br>00l: l=2n |

……

*Centered*



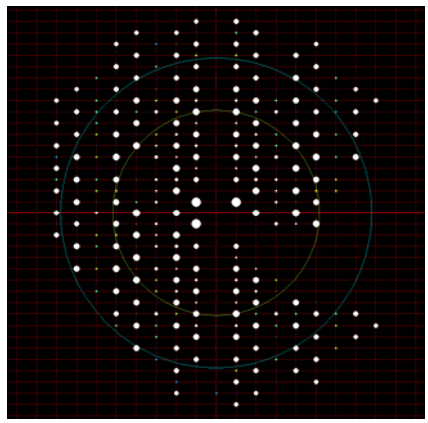
Layer *h*, *k*, *l* at *l* = 1

## Intensity Plot for a *Primitive* Lattice

| Reflection conditions |
|---|
| 0kl: k=2n<br>h0l: l=2n<br>hk0: h+k=2n<br>h00: h=2n<br>0k0: k=2n<br>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.

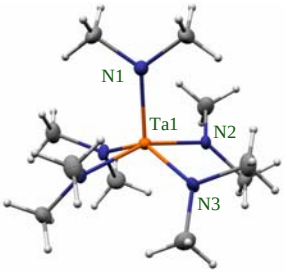
## $Ta(NMe_2)_5$ – Summary of Crystal Data

| | | |
|---|---|---|
| *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 θ = 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.**

## Acknowledgements

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