Twinning Workshop

at the Bruker-Nonius Area Detector Users Group Meeting

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Major Classes of Twins

- **Merohedral twins -** The lattices of all twin components coincide perfectly in both direct *and* reciprocal space. 159 of the 230 space groups belong to merohedral point groups.
- **Pseudomerohedral twins -** Common examples are monoclinics with $\beta \sim 90.0°$ or $a \sim c$ with $\beta \sim 120.0°$. These can often be treated properly once the structure is solved. The correct twin law is usually related to the additional symmetry gained.
- **Chameleon twins (Reticular Pseudomerohedral)-** Subclass of non-merohedral twins that emulate higher, centered crystal systems.
- **Non-merohedral twins -** Some axes coincide in reciprocal space, but others do not. Therefore part of the reciprocal lattice is exactly overlapped while other parts are not. The phenomenon of partially overlapping reflections is a serious problem.

Warning Signs for Merohedral and Pseudomerohedral Twins

1) Laue symmetry does not fit for metric symmetry.

2) R_{int} for a higher symmetry Laue class is slightly higher than a lower symmetry Laue class. R_{int} often is lower than that for a normal crystal.

3) The reflection statistic $|E^2-1|$ value is shifted to a lower value: centrosymmetric. ~ 0.8, noncentrosymmetric ~ 0.6.

4) The space group may be in either trigonal or hexagonal: 2 crystal systems with same metrics, 5 Laue classes with 15 point groups.

5) The space group may be tetragonal: 2 Laue classes with 7 point groups.

6) The reflection conditions are not consistent with any known space group.

7) The structure cannot be solved.

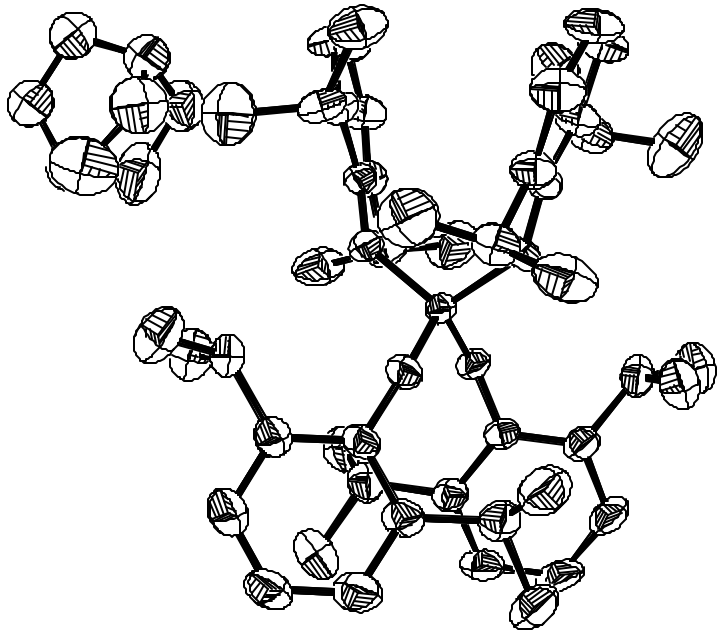
8) The Patterson function is physically impossible.

9) The reciprocal lattice planes have a smooth variation in intensity from low to high resolution instead of a normal statistical variation.

10) K-values are anomalously high.

Source: R. Herbst-Irmer and G Sheldrick, *Acta Cryst*. B**54**, 443 (1998)

Example of Merohedral Twinning in a Trigonal Space Group - $[Al(OC_6H_4(C_3H_7)_2)]^- \cdot [NC_7H_8]^+$



- Laue statistics indicated $P3_121$ or $P3_221$ as the correct space group with R_{int} equal to 0.041 and 0.045 respectively. The solution yielded an R = 0.16 result with an unresolved cation.
- The structure was re-solved in $P3_2$ which provided all atoms including the cation.
- Inclusion of the twin law [0 -10, -10 0, 0 0 1] improved the result to R = 0.043.
- Some bond length restraints were included for the cation.
- Twin ratio was 1:1.

Space Group Determination in the Trigonal Crystal System from the *International Tables for Crystallography*, Vol. A, pg. 798

TRIGONAL, Laue classes $\bar{3}$ and $\bar{3}m$

Reflection conditions				Extinction symbol	Laue class							
					$\bar{3}$		$\bar{3}m1$ ($\bar{3}$ 2/*m* 1) $\bar{3}m$			$\bar{3}1m$ ($\bar{3}$ 1 2/*m*)		
Hexagonal axes					Point group							
hkil	*hh*$\bar{2}$*hl*	*hkil*	0001		3	$\bar{3}$	321 32	3*m*1 3*m*	$\bar{3}$*m*1 $\bar{3}$*m*	312	31*m*	$\bar{3}$1*m*
				P---	*P*3 (143)	*P*$\bar{3}$ (147)	*P*321 (150)	*P*3*m*1 (156)	*P*$\bar{3}$*m*1 (164)	*P*312 (149)	*P*31*m* (157)	*P*$\bar{3}$1*m* (162)
			$l=3n$	*P*3_1--	{*P*3_1 (144) *P*3_2 (145)}		{*P*$3_1$21 (152) *P*$3_2$21 (154)}			{*P*$3_1$12 (151) *P*$3_2$12 (153)}		
		l	l	*P*--*c*							*P*31*c* (159)	*P*$\bar{3}$1*c* (163)
	l		l	*P*-*c*-				*P*3*c*1 (158)	*P*$\bar{3}$*c*1 (165)			
$-h+k+l=3n$	$h+l=3n$	$l=3n$	$l=3n$	*R*(obv)--†	*R*3 (146)	*R*$\bar{3}$ (148)	*R*32 (155)	*R*3*m* (160)	*R*$\bar{3}$*m* (166)			
$-h+k+l=3n$	$h+l=3n;l$	$l=3n$	$l=6n$	*R*(obv)-*c*				*R*3*c* (161)	*R*$\bar{3}$*c* (167)			
$h-k+l=3n$	$-h+l=3n$	$l=3n$	$l=3n$	*R*(rev)--	*R*3 (146)	*R*$\bar{3}$ (148)	*R*32 (155)	*R*3*m* (160)	*R*$\bar{3}$*m* (166)			
$h-k+l=3n$	$-h+l=3n;l$	$l=3n$	$l=6n$	*R*(rev)-*c*				*R*3*c* (161)	*R*$\bar{3}$*c* (167)			
Rhombohedral axes				Extinction symbol	Point group							
hkl		*hhl*	*hhh*		3	$\bar{3}$	32	3*m*	$\bar{3}$*m*			
		l	h	*R*-- *R*-*c*	*R*3 (146)	*R*$\bar{3}$ (148)	*R*32 (155)	*R*3*m* (160) *R*3*c* (161)	*R*$\bar{3}$*m* (166) *R*$\bar{3}$*c* (167)			

† For obverse and reverse settings *cf.* Section 1.2. The obverse setting is standard in these tables.
The transformation reverse → obverse is given by **a**(obv) = − **a**(rev), **b**(obv) = − **b**(rev), **c**(obv) = **c**(rev).

Logic for the Determination of a Twin Law in the Trigonal Example

1) Noting that two Laue classes, both $\bar{3}$ and $\bar{3}$m1 fit the data equally well *and* no acceptable solution was found in the enantiomeric pair of space groups $P3_121$ and $P3_221$ from higher Laue class, we tested for a merohedral twin in a space group in the lower Laue class.
2) Table 1.3.4.2 from *I.T. for C.*, Vol. C, suggests a possible "simulation" from $P3_121/P3_221$ to $P3_1/P3_2$.
3) The structure must be solved in one of the enantiomeric pair of space groups $P3_1$ or $P3_2$ regardless of the quality.
4) Table 1.3.4.1 suggests inversion, a mirror or a two-fold rotation as possible twinning operations. The twinning is more severe than just a simple inversion.
5) Provide the refinement program with possible applicable twin laws directly from Table 11.3 from *I.T. for C.*, Vol. A.
6) Twin law was determined to be 2 x,x,0. The R improved dramatically.

Possible Space Groups and Merohedral Twin Operations from the *International Tables for Crystallography*, Vol C, pg. 12: Tables 1.3.4.2 and 1.3.4.1

Twinned crystal			Single crystal
Simulated Laue class	Twin extinction symbol	Simulated 'possible space groups'	Possible true space groups
$4/mmm$	P---	$P422$, $P4mm$, $P\bar{4}2m$, $P\bar{4}m2$, $P4/mmm$	$P4$, $P\bar{4}$, $P4/m$
	$P4_2$--	$P4_222$	$P4_2$, $P4_2/m$
	$P4_1$--	$P4_122$, $P4_322$	$P4_1$, $P4_3$
	Pn--	$P4/nmm$	$P4/n$
	$P4_2/n$--	-	$P4_2/n$
	I---	$I422$, $I4mm$, $I\bar{4}2m$, $I\bar{4}m2$, $I4/mmm$	$I4$, $I\bar{4}$, $I4/m$
	$I4_1$--	$I4_122$	$I4_1$
	$I4_1/a$--	-	$I4_1/a$
$\bar{3}m1$	P---	$P321$, $P3m1$, $P\bar{3}m1$	$P3$, $P\bar{3}$
	$P3_1$--	$P3_121$, $P3_221$	$P3_1$, $P3_2$
$\bar{3}1m$	P---	$P312$, $P31m$, $P\bar{3}1m$	$P3$, $P\bar{3}$
	$P3_1$--	$P3_112$, $P3_212$	$P3_1$, $P3_2$
$\bar{3}m$	R--	$R32$, $R3m$, $R\bar{3}m$	$R3$, $R\bar{3}$
$6/m$	P---	$P6$, $P\bar{6}$, $P6/m$	$P3$, $P\bar{3}$
	$P6_2$--	$P6_2$, $P6_4$	$P3_1$, $P3_2$
$6/mmm$	P---	$P622$, $P6mm$, $P\bar{6}m2$, $P\bar{6}2m$, $P6/mmm$	$P3$, $P\bar{3}$, $P321$, $P312$, $P3m1$, $P31m$, $P\bar{3}m1$, $P\bar{3}1m$, $P6$, $P\bar{6}$, $P6/m$
	$P6_3$--	$P6_322$	$P6_3$, $P6_3/m$
	$P6_2$--	$P6_222$, $P6_422$	$P3_1$, $P3_2$, $P3_121$, $P3_221$, $P3_112$, $P3_212$
	$P6_1$--	$P6_122$, $P6_522$	$P6_1$, $P6_5$
	P--c	$P6_3mc$, $P\bar{6}2c$, $P6_3/mmc$	$P31c$, $P\bar{3}1c$
	P-c-	$P6_3cm$, $P\bar{6}c2$, $P6_3/mcm$	$P3c1$, $P\bar{3}c1$
$m\bar{3}m$	P---	$P432$, $P\bar{4}3m$, $Pm\bar{3}m$	$P23$, $Pm\bar{3}$
	$P4_2$--	$P4_232$	$P2_13$
	Pn--	$Pn\bar{3}m$	$Pn\bar{3}$
	I---	$I432$, $I\bar{4}3m$, $Im\bar{3}m$	$I23$, $I2_13$, $Im\bar{3}$
	Ia--	-	$Ia\bar{3}$
	F---	$F432$, $F\bar{4}3m$, $Fm\bar{3}m$	$F23$, $Fm\bar{3}$
	Fd--	$Fd\bar{3}m$	$Fd\bar{3}$
	$P2_1/a$, b--	-	$Pa\bar{3}$

Step 1:

Simulated space group of $P3_221$ can be twinned $P3_2$.

Step 2:

Point group 3 can have inversion, mirror or two-fold operators.

Step 3:

Find the twin law and test it.

Holohedry	Bravais lattice	Point group	m	Possible twin operations
1	aP	1	2	$\bar{1}$
$2/m$	mP, mS	2	2	$\bar{1}$
		m	2	$\bar{1}$
mmm	oP, oS, oI, oF	222	2	$\bar{1}$
		$mm2$	2	$\bar{1}$
$4/mmm$	tP, tI	*4	4	$\bar{1}$, $.m.$, $.2.$
		*$\bar{4}$	4	$\bar{1}$, $.m.$, $.2.$
		*4/m	2	$.m.$
		422	2	$\bar{1}$
		$4mm$	2	$\bar{1}$
		$\bar{4}2m$/$\bar{4}m2$	2	$\bar{1}$
$\bar{3}m$	hR	*3	4	$\bar{1}$, $.m$, $.2$
		*$\bar{3}$	2	$.m$
		32	2	$\bar{1}$
		$3m$	2	$\bar{1}$
$6/mmm$	hP	*3	8	$\bar{1}$, $.m.$, $.2.$, $m..$, $..m$, $2..$, $..2$
		*$\bar{3}$	4	$.m.$, $m..$, $..m$
		*321/312	4	$\bar{1}$, $m..$, $..2/.2.$
		*$3m1/31m$	4	$\bar{1}$, $m..$, $..m/.m.$
		*$\bar{3}m1/\bar{3}1m$	2	$m..$
		*6	4	$\bar{1}$, $.m.$, $.2.$
		*$\bar{6}$	4	$\bar{1}$, $.m.$, $..m$
		*6/m	2	$.m.$
		622	2	$\bar{1}$
		$6mm$	2	$\bar{1}$
		$\bar{6}2m$/$\bar{6}m2$	2	$\bar{1}$
$m\bar{3}m$	cP, cI, cF	*23	4	$\bar{1}$, $..m$, $..2$
		*$m\bar{3}$	2	$..m$
		432	2	$\bar{1}$
		$\bar{4}3m$	2	$\bar{1}$

Symmetry Operations in the Hexagonal Coordinate System from the *International Tables for Crystallography*, Vol. A, pg. 798

Table 11.3. *Matrices for point-group symmetry operations and orientation of corresponding symmetry elements, referred to a hexagonal coordinate system* (*cf. Table* 2.1.1)

Symbol of symmetry operation and orientation of symmetry element	Transformed coordinates $\tilde{x},\tilde{y},\tilde{z}$	Matrix W	Symbol of symmetry operation and orientation of symmetry element	Transformed coordinates $\tilde{x},\tilde{y},\tilde{z}$	Matrix W	Symbol of symmetry operation and orientation of symmetry element	Transformed coordinates $\tilde{x},\tilde{y},\tilde{z}$	Matrix W
1	x,y,z	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$	3^+ 0,0,z [001]	$\bar{y},x-y,z$	$\begin{pmatrix}0&\bar{1}&0\\1&\bar{1}&0\\0&0&1\end{pmatrix}$	3^- 0,0,z [001]	$y-x,\bar{x},z$	$\begin{pmatrix}\bar{1}&1&0\\\bar{1}&0&0\\0&0&1\end{pmatrix}$
2 0,0,z [001]	$\bar{x},\bar{y},z$	$\begin{pmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{pmatrix}$	6^+ 0,0,z [001]	$x-y,x,z$	$\begin{pmatrix}1&\bar{1}&0\\1&0&0\\0&0&1\end{pmatrix}$	6^- 0,0,z [001]	$y,y-x,z$	$\begin{pmatrix}0&1&0\\\bar{1}&1&0\\0&0&1\end{pmatrix}$
2 $x,x,0$ [110]	$y,x,\bar{z}$	$\begin{pmatrix}0&1&0\\1&0&0\\0&0&\bar{1}\end{pmatrix}$	2 $x,0,0$ [100]	$x-y,\bar{y},\bar{z}$	$\begin{pmatrix}1&\bar{1}&0\\0&\bar{1}&0\\0&0&\bar{1}\end{pmatrix}$	2 0,y,0 [010]	$\bar{x},y-x,\bar{z}$	$\begin{pmatrix}\bar{1}&0&0\\\bar{1}&1&0\\0&0&\bar{1}\end{pmatrix}$
2 $x,\bar{x},0$ [1$\bar{1}$0]	$\bar{y},\bar{x},\bar{z}$	$\begin{pmatrix}0&\bar{1}&0\\\bar{1}&0&0\\0&0&\bar{1}\end{pmatrix}$	2 $x,2x,0$ [120]	$y-x,y,\bar{z}$	$\begin{pmatrix}\bar{1}&1&0\\0&1&0\\0&0&\bar{1}\end{pmatrix}$	2 $2x,x,0$ [210]	$x,x-y,\bar{z}$	$\begin{pmatrix}1&0&0\\1&\bar{1}&0\\0&0&\bar{1}\end{pmatrix}$
$\bar{1}$ 0,0,0	$\bar{x},\bar{y},\bar{z}$	$\begin{pmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&\bar{1}\end{pmatrix}$	$\bar{3}^+$ 0,0,z [001]	$y,y-x,\bar{z}$	$\begin{pmatrix}0&1&0\\\bar{1}&1&0\\0&0&\bar{1}\end{pmatrix}$	$\bar{3}^-$ 0,0,z [001]	$x-y,x,\bar{z}$	$\begin{pmatrix}1&\bar{1}&0\\1&0&0\\0&0&\bar{1}\end{pmatrix}$
m $x,y,0$ [001]	$x,y,\bar{z}$	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&\bar{1}\end{pmatrix}$	$\bar{6}^+$ 0,0,z [001]	$y-x,\bar{x},\bar{z}$	$\begin{pmatrix}\bar{1}&1&0\\\bar{1}&0&0\\0&0&\bar{1}\end{pmatrix}$	$\bar{6}^-$ 0,0,z [001]	$\bar{y},x-y,\bar{z}$	$\begin{pmatrix}0&\bar{1}&0\\1&\bar{1}&0\\0&0&\bar{1}\end{pmatrix}$
m $x,\bar{x},z$ [110]	$\bar{y},\bar{x},z$	$\begin{pmatrix}0&\bar{1}&0\\\bar{1}&0&0\\0&0&1\end{pmatrix}$	m $x,2x,z$ [100]	$y-x,y,z$	$\begin{pmatrix}\bar{1}&1&0\\0&1&0\\0&0&1\end{pmatrix}$	m $2x,x,z$ [010]	$x,x-y,z$	$\begin{pmatrix}1&0&0\\1&\bar{1}&0\\0&0&1\end{pmatrix}$
m x,x,z [1$\bar{1}$0]	y,x,z	$\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$	m $x,0,z$ [120]	$x-y,\bar{y},z$	$\begin{pmatrix}1&\bar{1}&0\\0&\bar{1}&0\\0&0&1\end{pmatrix}$	m 0,y,z [210]	$\bar{x},y-x,z$	$\begin{pmatrix}\bar{1}&0&0\\\bar{1}&1&0\\0&0&1\end{pmatrix}$

Comparative Determination of the Twin Law

- These are the listings of general positions for $P3_2$ (top) and $P3_221$ (bottom).
- Since a poorly-refining, simulated result is obtained in $P3_221$, we can obtain the twin law directly from its set of general positions.
- The twin law can be any general position in the simulated cell not appearing in the correct space group.
- Either the *-y,-x,z* (mirror) or *y,x,-z* (two-fold rotation) are both possible operations.
- But, inversion twinning is also possible!!

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		
3	*a*	1	(1) x,y,z	(2) $\bar{y},x-y,z+\frac{2}{3}$	(3) $\bar{x}+y,\bar{x},z+\frac{1}{3}$

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		
6	*c*	1	(1) x,y,z	(2) $\bar{y},x-y,z+\frac{2}{3}$	(3) $\bar{x}+y,\bar{x},z+\frac{1}{3}$
			(4) $y,x,\bar{z}$	(5) $x-y,\bar{y},\bar{z}+\frac{1}{3}$	(6) $\bar{x},\bar{x}+y,\bar{z}+\frac{2}{3}$
3	*b*	.2.	$x,0,\frac{1}{6}$	$0,x,\frac{5}{6}$	$\bar{x},\bar{x},\frac{1}{2}$
3	*a*	.2.	$x,0,\frac{2}{3}$	$0,x,\frac{1}{3}$	$\bar{x},\bar{x},0$

Now, is that Twin Law Correct?

In enantiomorphic space groups one needs to determine which of the two possible space groups is correct, because inversion twinning is also possible. Flack parameter may indicate conversion to enantiomorph.

Expansion of the twin law to:

BASF 0.1 0.1 0.1

TWIN 0 1 0 1 0 0 0 0 -1 –4

Will test all four possibilities:

Two-fold	[0 1 0 1 0 0 0 0 –1]	
Two-fold +inversion	[0 –1 0 –1 0 0 0 0 1]	* correct one
Mirror	[0 1 0 1 0 0 0 0 1]	
Mirror + inversion	[0 –1 0 –1 0 0 0 0 –1]	

Common Pseudo-Merohedral Twins

1) A pseudo-merohedral twin can occur *if* the cell constants from a specimen imitate a higher crystal system.

2) Common examples are:

   a) triclinic with two of the three angles near 90° which could imitate monoclinic (Laue class 2/m).

   b) monoclinic with β near 90° which could imitate orthorhombic (Laue class mmm).

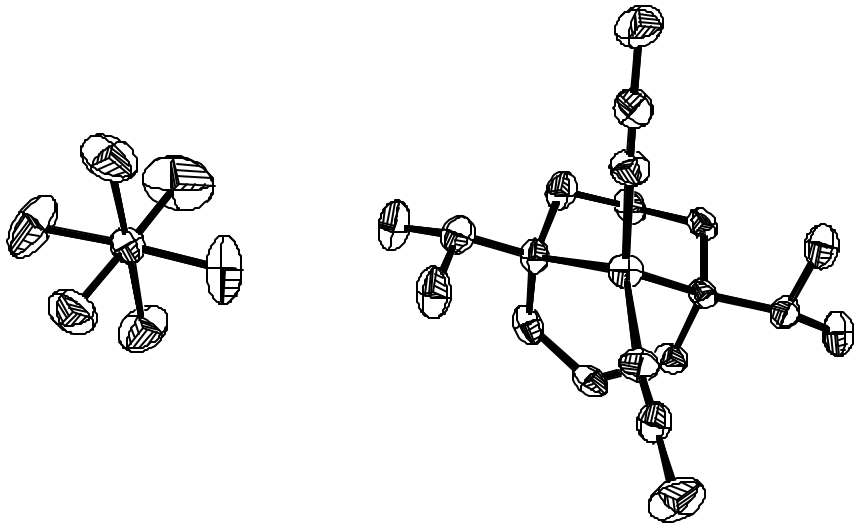
   c) monoclinic with *a* and *c* near equal length and β near 120° which could imitate trigonal or hexagonal (several possible Laue classes).

   d) monoclinic with *a* and *c* near equal length and β near 90° which could imitate tetragonal (4/m Laue class).

3) The reduction in symmetry between the "simulated" Laue class and true Laue class leads to a possible twin law.

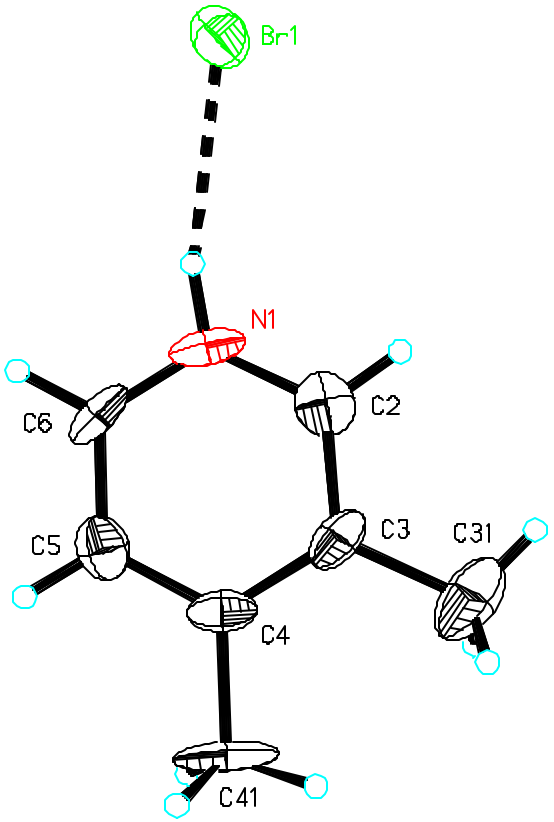
4) If the twin components are not equal, then the "simulated" Laue class will be apparent when viewing the reciprocal lattice.

Example of Pseudo-Merohedral Twinning in a Monoclinic Space Group



- The cell constants are metrically orthorhombic.
- No solution could be determined in any orthorhombic space group.
- Contents and unit cell volume suggested Z = 4.
- $P\bar{1}$solution was generated: A glide plane suggested $P2_1/c$ was true space group.
- R = 0.28 before twin was modeled.
- R = 0.036 after [-10 0, 0 -1 0, 0 0 1] twin law: ratio of twins was 1:1.

Pseudomerohedral Twinning in a Triclinic Organic: "The Twinned Crystal Structure of 3,4-Dimethylpyridine Hydrobromide at 157 K," M. Bolte and M. Kettner, *Acta Cryst.*, **C54**, 963-964 (1998).



- The triclinic cell was a = 7.336Å, b = 7.798Å, c = 8.396Å, $\alpha = 69.99°$, $\beta = 64.15,°$ $\gamma = 90.06°$.
- Data reduction indicated the cell could be transformed to C-centered monoclinic with a =15.112Å, b = 7.337Å, c = 7.797Å, and β = 112.35°.
- $|E^2-1|$ was suspiciously low at 0.488.
- R_{int} for triclinic =0.046 *vs.* monoclinic = 0.146.
- Structure was solved in $P\bar{1}$ with difficulty.
- Twin law [-1 0 0, 0 1 0, -1 0 1] was derived and applied.
- R1 = 0.062 and wR2 = 0.132 for 87 parameters and 1386 reflections.

Derivation of the Twin Law: "The Twinned Crystal Structure of 3,4-Dimethylpyridine Hydrobromide at 157 K," M. Bolte and M. Kettner, *Acta Cryst.*, **C54**, 963-964 (1998).

- A distinct symmetry element of the higher symmetry, or emulated cell, may be tested for the twin law.
- The mirror plane perpendicular to the *b* axis of the emulated C-centered monoclinic cell was chosen as the twin operation.
- The transformation matrix is [1 0 -2, -1 0 0 , 0 1 0].
- The possible mirror operation is [1 0 0, 0 -1 0, 0 0 1].
- [1 0 0, 0 -1 0, 0 0 1] X [1 0 -2, -1 0 0 , 0 1 0] = [1 0 -2, 1 0 0 , 0 1 0] leads to the second twin component relative to the triclinic cell.
- The putative twin law is calculated by :
  $[1\ 0\ -2, -1\ 0\ 0, 0\ 1\ 0]^{-1}$ X [1 0 -2, 1 0 0 , 0 1 0] = [-1 0 0, 0 1 0, $-1\ 0\ 1$].
- A rotation parallel to *b* could also work since the space group is P1.

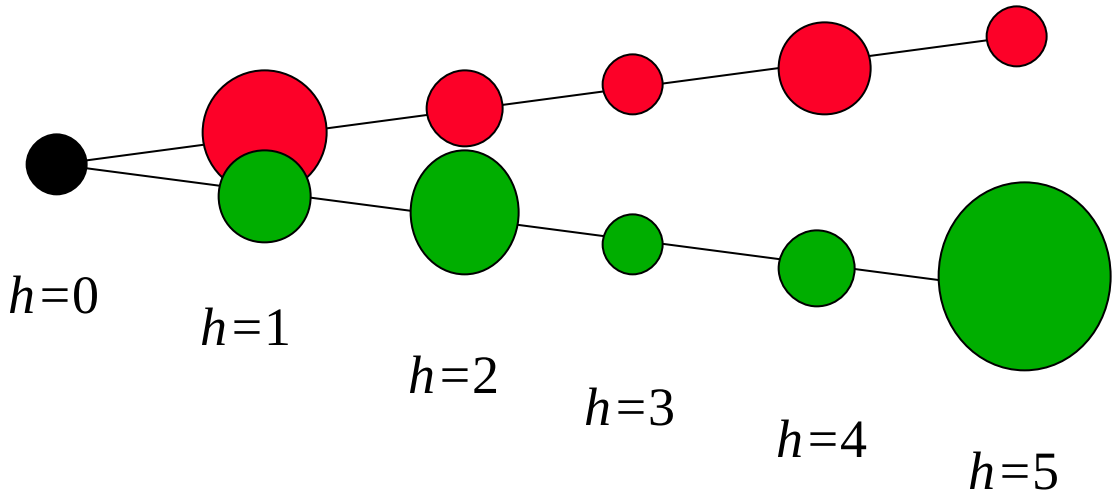
Warning Signs of a Chameleon Twin

1) The specimen usually diffracts well. There is no indication of split reflections.
2) The specimen will index, but based on chemical knowledge it appears to have a unit cell with an unexpectedly large volume. Expected Z is too big. Often one cell constant is questionably long.
3) The space group choices are for unexpectedly low symmetry.
4) Lattice centering is present, but there are additional voids in the reciprocal lattice unaccounted by this reflection condition.
5) Visual inspection of reciprocal lattice indicates possible reflection conditions not found in the initial data reduction.
6) The reflection statistic $|E^2-1|$ value is an unreliable indicator of centrosymmetricity: False centering often raises this above 1.0.
7) Structure solution success varies: Usually, correct structural features related by the twin operation are observed in the model.
8) The twins in the correct, lower-symmetry crystal system must be determined with alternate indexing tools like GEMINI.

Warning Signs of a Non-Merohedral Twin

1. The specimen will not index with the standard software. If it does index, then many reflections do not fit the cell. The reflections that do not index may have 1 or 2 non-integer *h*, *k*, *l* indices.
2. The specimen may index, but based on chemical knowledge it appears to have a unit cell with an unexpectedly large volume. The expected Z is likely too large based on the maximum number for the crystal system.
3. The unit cell has a sensible volume, but Laue symmetry is not confirmed in the initial analysis; twinning can make the Rint much greater than the final R1.
4. The reflection statistic $|E^2-1|$ value is shifted to a lower value when twins have frequent overlap: centrosymmetric ~ 0.8 and non-centrosymmetric ~0.6.
5. Reflections with $Fo^2 >> Fc^2$ in the"50 Worst" list may have a systematic trend in some or combined indices of *h*, *k*, and/or *l*.

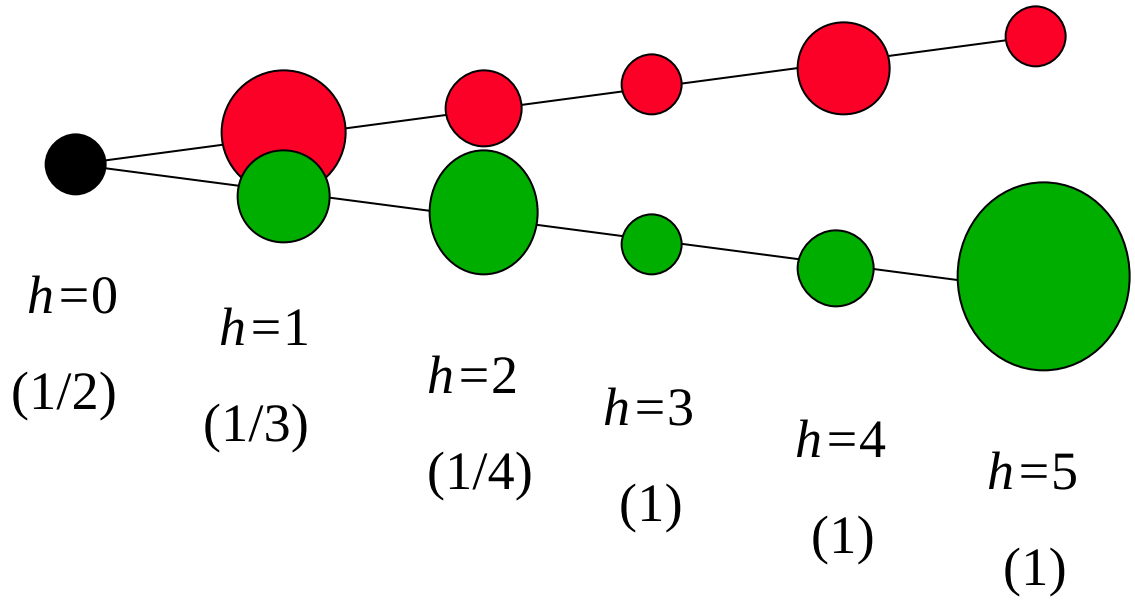
The Problem of Partially Overlapped Reflections



Regular and increasing separation

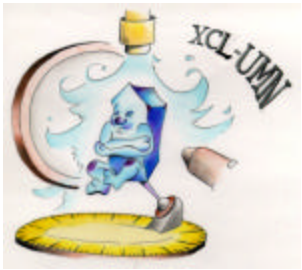
- The reflection at h=0 is the sum of red and green twin comps.
- Both h=1,2 are severely overlapped. The integration program has problems yielding accurate intensities for these.
- There is no problem with the integration of h=3,4,5.
- Should the partially overlapped reflections be omitted or treated specially?

A Solution for the Use of Partially Overlapped Reflections



Green component is refined with overall scale factor. Reflections with red contribution are refined in ascending batches in HKLF 5 format based on the separation of reflections in reciprocal space.

- The answer to problem of the use of partially overlapped reflections in L-S refinement is not clear.
- Both the removal of and scaling of these will affect the results.
- The exact overlap at h=0 is BASF 2 in HKLF 5 format.
- The regular pattern of partial overlaps suggests the same use for h=1 & 2 with BASF 3 & 4, resp.



Indexing a Twin – Step 1

Threshold a large, random distribution of reflections from the suspected twin. The example below contains 179 reflections. The initial solution fit 138 of the 179 reflections to a reasonable monoclinic unit cell:

***** Solution number: 4

Number of reflections that fit: 138 Total reflections: 179

The average derivation from integer value: 0.001447

Unit cell constants, volume and the corresponding standard deviations:

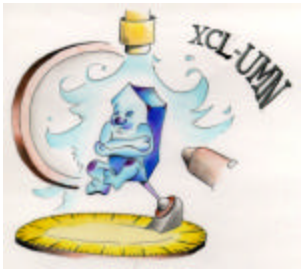
8.261	20.243	21.424	89.860	89.793	87.193	3578.09
0.004	0.007	0.006	0.026	0.032	0.034	2.36

Orientation matrix:

0.05776	-0.03445	0.02634
-0.04641	0.02161	0.03845
-0.09592	-0.02815	-0.00254

Center of the reciprocal space:

0.00225	-0.00136	0.00114



Indexing a Twin – Step 2

The flags on the reflections are reversed to determine whether a twin component is present. This leaves 41 reflections while ignoring the initial solution. 39 reflections fit the second.

***** Solution number: 14

Number of reflections that fit: 39 Total reflections: 41

The average derivation from integer value: 0.001236

Unit cell constants, volume and the corresponding standard deviations:

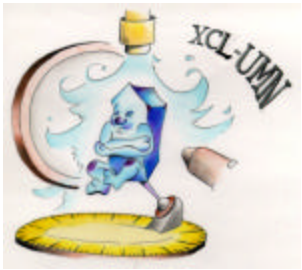
8.281	20.240	21.414	90.160	90.201	93.372	3582.84
0.007	0.019	0.014	0.066	0.060	0.071	5.03

Orientation matrix:

-0.04914	0.03439	0.02630
0.04051	-0.02154	0.03851
0.10284	0.02834	-0.00240

Center of the reciprocal space:

0.00145	-0.00237	-0.00007



Indexing a Twin – Step 3

The flags on the reflections are reversed once again to determine the best cell constants for the initial solution. Any reflections that index with integer values of *h*,*k*, and *l* are also flagged off.

***** Solution number: 9

Number of reflections that fit: 73 Total reflections: 73

The average derivation from integer value: 0.001369

Unit cell constants, volume and the corresponding standard deviations:

8.275	20.254	21.406	89.829	89.896	87.112	3583.11
0.005	0.008	0.007	0.029	0.038	0.040	2.78

Orientation matrix:

0.05795	-0.03444	0.02636
-0.04616	0.02159	0.03848
-0.09567	-0.02813	-0.00250

Center of the reciprocal space:

0.00163	-0.00250	0.00028

Comparing Reflection Indexing – Step 4

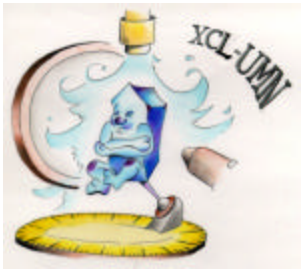
0.00145	138	179		0.00124	39	41	
unit cells =							
8.261	20.243	21.424		8.281	20.240	21.414	
0.004	0.007	0.006		0.007	0.019	0.014	
89.860	89.793	87.193	3578.09	90.160	90.201	93.372	3582.84
0.026	0.032	0.034	2.36	0.066	0.060	0.071	5.03

orientation matrices =

0.057756454	-0.034452826	0.026344327	-0.049144149	0.034387946	0.026301797
-0.046414889	0.021613805	0.038448948	0.040514667	-0.021536386	0.038514126
-0.095915824	-0.028145475	-0.002535729	0.102839552	0.028342815	-0.002401760

Refl#	H	K	L	Flags	H	K	L
1	5.991	-5.018	-13.002	1 + 0 -	-5.992	6.551	-13.024
8	2.016	8.514	5.978	0 + 1 +	-2.005	-7.986	5.987

0+0+	0+0-	0+1+	0+1-	0-0+	0-0-	0-1+	0-1-	1+0+	1+0-	1+1+	1+1-	1-0+	1-0-	1-1+	1-1-
2	0	39	0	0	0	0	15	0	73	0	65	0	18	0	12



Orientation Matrix Cleanup – Step 5

In this step the Bravais lattice is selected and monoclinic constraints are added while optimizing the number of fit reflections. Notice that the 2nd and 3rd columns of the UB matrices are identical while the 1st is similar except for the sign of the vectors.

Major twin component

CELL	8.2628	21.4294	20.1866	90.0000	93.0202	90.0000	3569.394
CELLSD	0.0063	0.0147	0.0135	0.0256	0.0176	0.0198	7.259
ORT1	-0.05831674	0.02631052	-0.03450959				
ORT2	0.04623795	0.03845609	0.02173899				
ORT3	0.09565027	-0.00254873	-0.02823719				

Minor twin component

CELL	8.2574	21.4237	20.1702	90.0000	92.9392	90.0000	3563.519
CELLSD	0.0075	0.0185	0.0172	0.0393	0.0191	0.0226	8.949
ORT1	0.05002582	-0.02623359	-0.03449220				
ORT2	-0.04014004	-0.03854041	0.02180544				
ORT3	-0.10291160	0.00228018	-0.02827137				

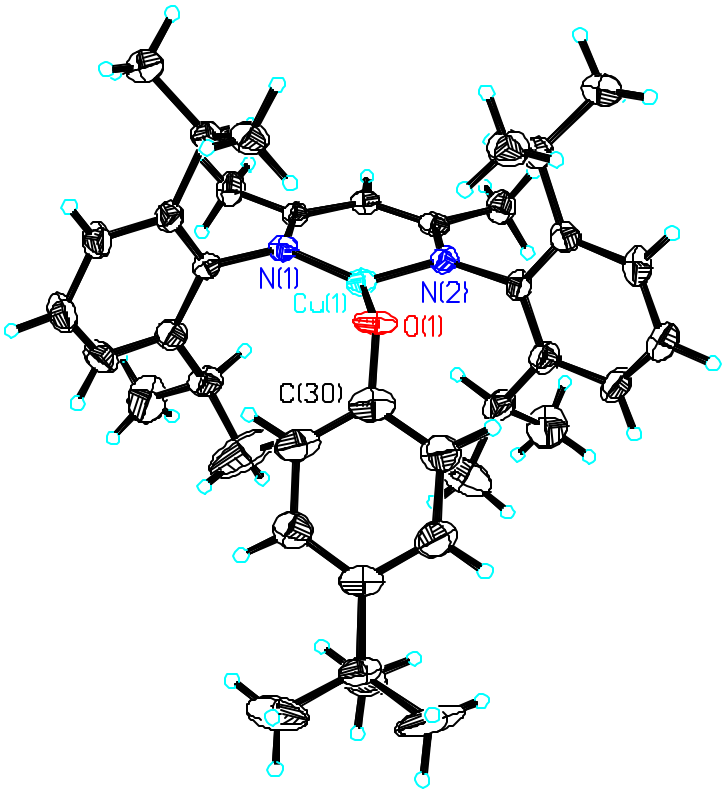
Twin Law Calculation – Step 6

The TWINROT program of GEMINI will permute the second UB matrix through many possible settings to give the user a number of choices for a twin law. The most sensible one for this example is provided below. A rotation axis bisecting the a^* axes is the easiest to understand – a 180° rotation of (100) accomplishes this.

A1 [Orientation matrix] =
-0.05832 0.02631 -0.03451
0.04624 0.03846 0.02174
0.09565 -0.00255 -0.02824
unit cell parameters =
8.2628 21.4294 20.1866 90.000 93.020 90.000
A2 [Orientation matrix] =
-0.05003 -0.02623 0.03449
0.04014 -0.03854 -0.02181
0.10291 0.00228 0.02827
unit cell parameters =
8.2574 21.4237 20.1702 90.000 92.939 90.000

A2(inverse) * A1 [transforms h1 to h2] =
0.99935 -0.00235 0.00010
-0.01564 -0.99972 0.00142
-0.25321 -0.00096 -0.99928
rotation axis in reciprocal space=
-1.00000 0.00791 0.12756
angle of rotation around -1.00 0.01 0.13 =
-179.92325
rotation axis in direct space=
-1.00000 0.00118 -0.00020
angle of rotation around -1.00 0.00 0.00 =
-179.92325

Trial Structure Solution with Twinned Data – Step 7



The intensity data are determined using the UB matrix from the presumed larger mass twin component. The twinning should not hamper the structure solution or crude refinement. The space group was determined to be $P2_1/n$ with the mean $|E^2-1| = 0.883$, and Rint = 0.0787. The copper complex looks OK, but R1 = 0.091, nearly every reflection in the Fo^2/Fc^2 "50 Worst List" has indices *hkl*: *h*=4n, and a number of difference peaks in the 1–2 $e^-Å^{-3}$ range. It sort of *looks* like a bad structure.

Preparation of HKLF 5 Data– Step 8

h	k	l	Fo^2	s (Fo^2)	BN
-4	-3	0	4.22	0.18	-2
-4	3	1	4.22	0.18	1
-3	3	1	39.29	0.41	1
-2	3	1	3.56	0.12	1
-1	3	1	43.98	0.49	1
0	-3	-1	0.15	0.04	-2
0	3	1	0.15	0.04	1
1	3	1	30.45	0.33	1
2	3	1	10.22	0.17	1
3	3	1	32.50	0.47	1
4	-3	-2	43.79	0.70	-2
4	3	1	43.79	0.70	1

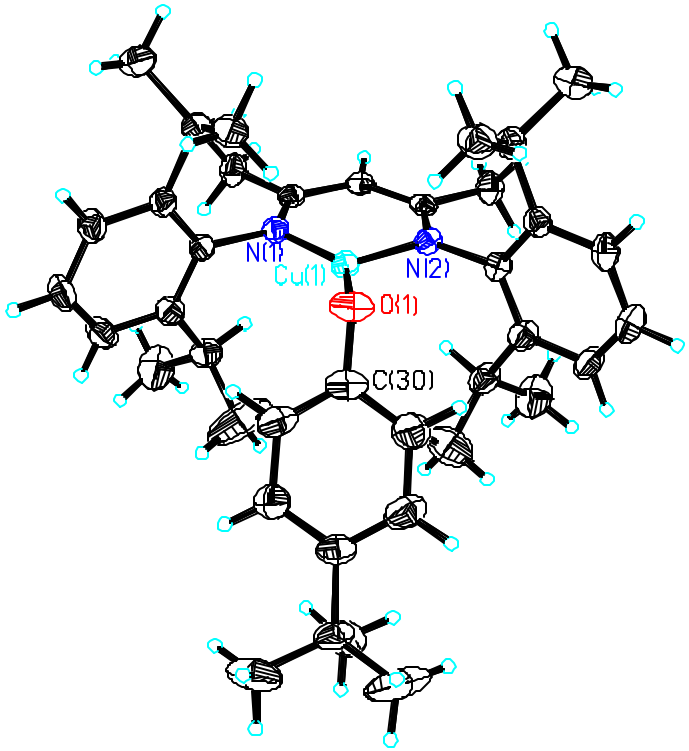
The data in the HKLF 4 format must be transformed into HKLF 5 format in order to correct the *hkl*: *h* =4n reflections that exactly overlap with the reciprocal lattice of the twin component. The transformation equation is:

$[h_1 k_1 l_1] \times [UB]^T = [h_2 k_2 l_2]$

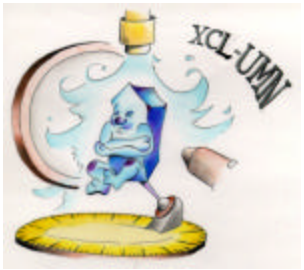
Exactly overlapped reflections are paired together with BN 1 & -2. The "-" sign means that the calculated Fc^2 must be split by the ratio of the refined batch scalefactors.

Both GEMINI and UNTWIN will prepare a corrected HKLF 5 reflection file.

Final Structure Refinement with HKLF 5 Data – Step 9



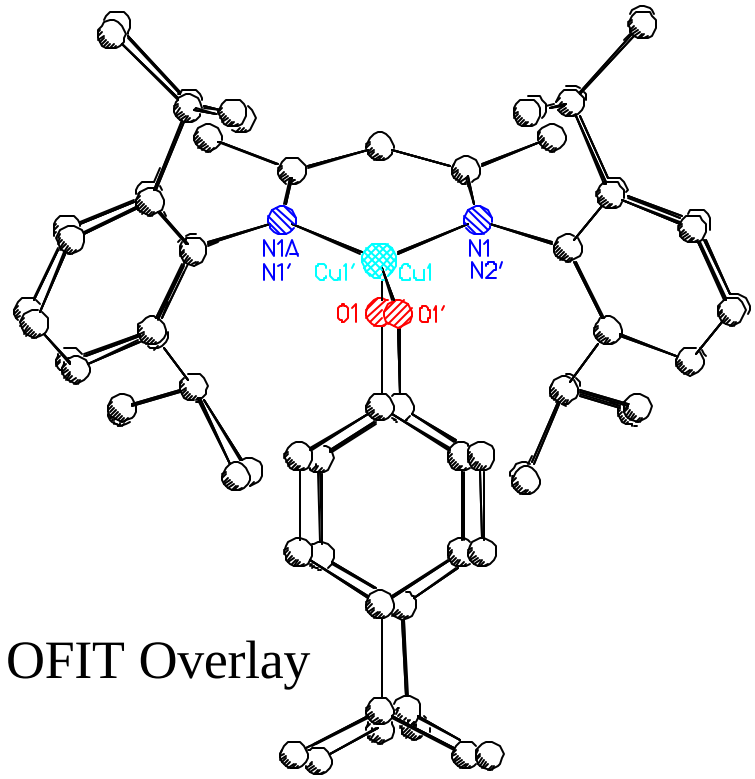
After the HKLF 5 correction, R1 improves from 0.091 to 0.051. This is no systematic trend in the "50 Worst List". The largest difference Fourier peak is now 0.6 instead of 2 $e^{-}Å^{-3}$. This result is not much worse than if there was no twinning in the first place. The final R1 is nearly 3% better than Rint.



Non-Destructive, Reversible Phase Transitions Accompanied by Non-Merohedral Twinning

- All samples have a sharp phase transition. Some of these were monitored by magnetic susceptibility and resistivity measurements.
- The higher temperature phase in all samples is found to have a higher symmetry crystal system and space group.
- The lower temperature phase always forms a non-merohedral twin in the relatively lower symmetry crystal system.
- It is *truly remarkable* that in all of these examples are reversible without damage to any of the samples.
- All of the samples presented here are small molecule specimens, but it is conceivable this phenomena could occur during the flash-freezing of protein crystals. The specimen might otherwise be mistaken to be cracked and therefore discarded.

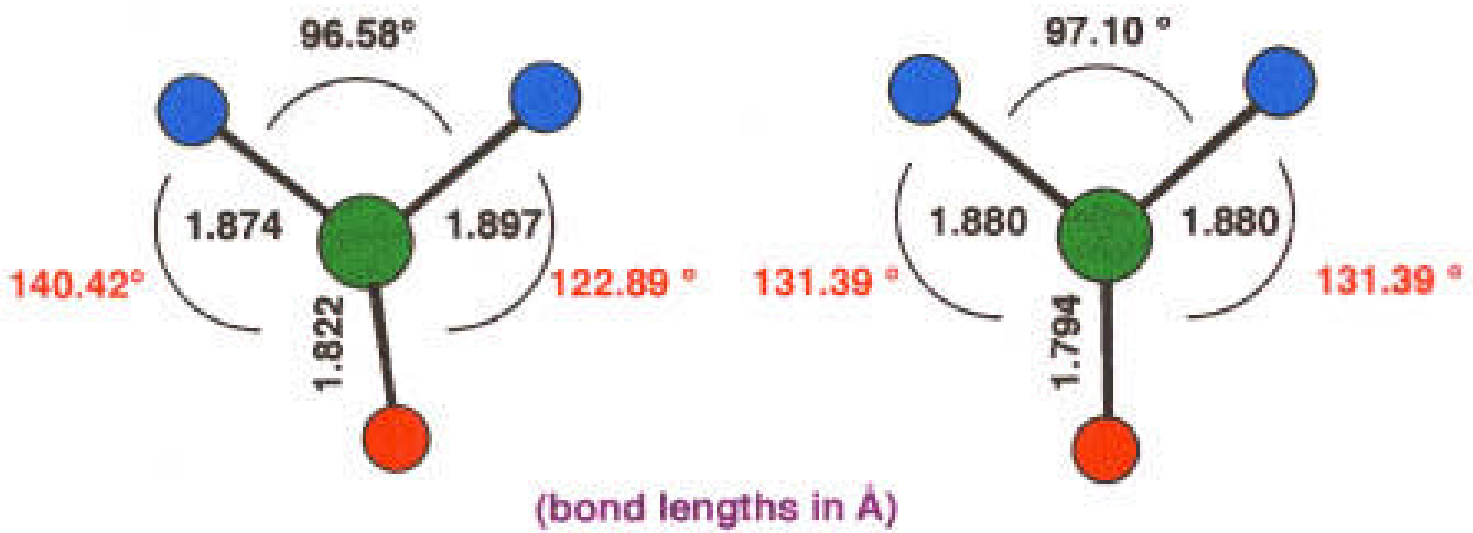
Phase Transition for L^{iPr}Cu(OPhtBu)



OFIT Overlay

298 K	173 K
Pnma	$P2_1/n$ (TWIN)
a=21.620(2) Å	*a*= 8.263(6) Å
b=20.252(2) Å	*b*= 21.429(1) Å
c=8.3555(6) Å	*c*= 20.187(1) Å
	β= 93.02(2)º
V= 3658.4(5) Å^3	V= 3569(4) Å^3

Coordination Sphere Changes for $L^{iPr}Cu(OPhtBu)$



$L^{iPr}Cu(OPhtBu)$ (-100 °C)

$L^{iPr}Cu(OPhtBu)$ (25 °C)

a^* Zone Image for $L^{iPr}Cu(OPhtBu)$ – Pnma orientation