Chemical Crystallography and Structural Chemistry

VO 270063-1

Lecture № 3 — 16th March 2023

Dr. Tim Grüne
Centre for X-ray Structure Analysis
Faculty of Chemistry
University of Vienna

tim.gruene@univie.ac.at

Course Schedule

2rd	March	Lecture № 1	9th	March	Lecture № 2
16th	March	Lecture № 3	23th	March	**Shift?** Exercise № 1
30st	March	Lecture № 4	20th	April	Lecture № 5
27th	April	Exercise № 2	4th	May	Lecture № 6
11th	May	Exercise № 3	25th	May	Lecture № 7
1st	June	**no lecture**	15th	June	Lecture № 8
22nd	June	Exercise № 4	29th	June	Lecture № 9

Previous Lecture

- Diffraction theory
- Laue equations
- Bragg equations
- Ewald sphere
- Symmetry in crystallography

Contents

1 Symmetry in molecules 5

2 Elementary Symmetry Operations 10

3 Combination of symmetry operations 16

4 Point groups and Space groups 25

5 Choosing the Unit Cell 48

6 7 Crystal Systems [4] 59

1 Symmetry in molecules

Symmetry in molecules

1. What is symmetry?
2. elementary symmetry operations: rotation, mirror plan, inversion centre
3. Combination of symmetry operations: point groups

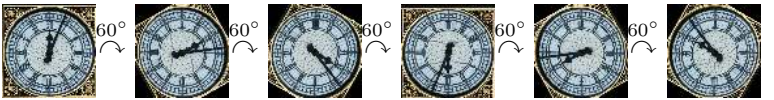
The Term “Symmetry”

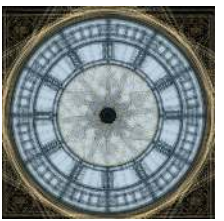
Symmetry is part of our daily lives:

Butterfly with a mirror plane

Flower with 5-fold rotational symmetry

Example: 12-fold Rotational Symmetry

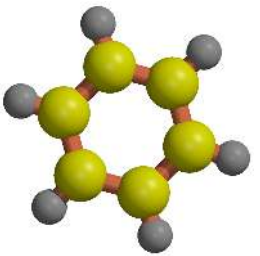




Wikipedia, [1]

Symmetry (in real life) is never ideal.
Ideally, all six images would be identical.
The symmetry of crystals and of individual molecules is much closer to the mathematical meaning of symmetry than macroscopic symmetry.

Symmetric molecules



Benzene: 6-fold rotational symmetry + mirror planes

α-D-Glucose: no proper symmetry

non-symmetric molecules can still crystallise

2 Elementary Symmetry Operations

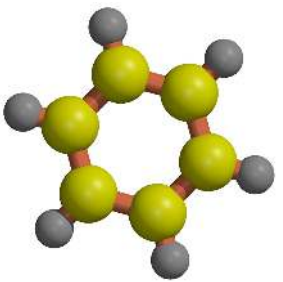
Symmetry Operations

"Definition": A Symmetry operation is a "movement" that does not change what an image looks like.
There are three elementary symmetry operations:

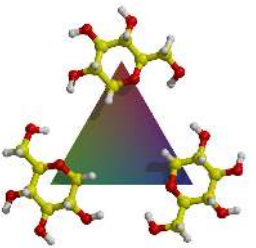
1. (n-fold) **rotation**
2. **mirror plane**
3. **inversion** (=point of reflection)

Symmetry operations: Rotation

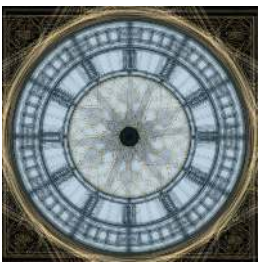
An object with an n-fold axis of rotation can be rotated about this axis by $\frac{360^\circ}{n}$ without changing its apparition.
With n such rotations, the object is back to where it was at the beginning.



Benzene: 6-fold axis of rotation *perpendicularly* to plane of this slide



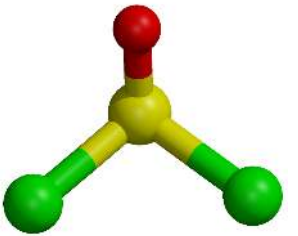
Three glucose molecules with a 3-fold axis of rotation.



Clock face with 12-fold axis of rotation

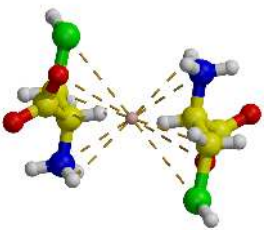
Symmetry operations: Mirror plane

Butterfly with mirror plane

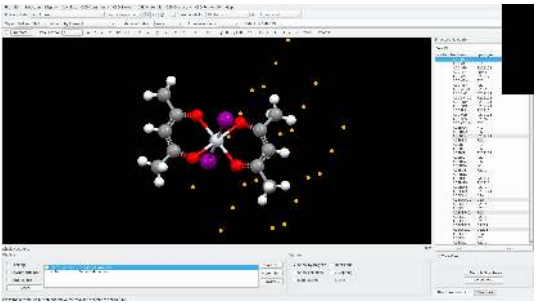


Thionyl chloride ($SOCl_2$) with mirror plane.

Symmetry operations: Inversion



L- and D-Cysteine

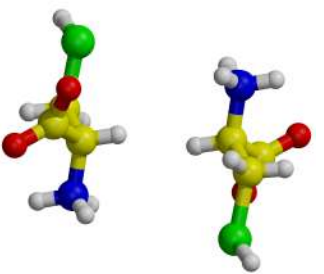


$C_{10}H_{14}I_2O_4Pt$, CSD entry № ACDIPT displayed with MERCURY

All connections of corresponding atoms run through one single point, the *inversion centre* of the object.

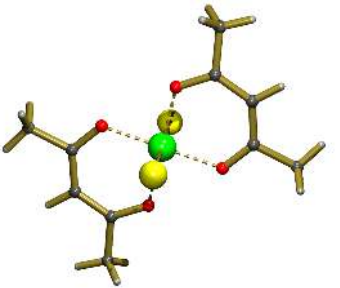
Chiral Molecule

A molecule without *centre of inversion* and without *mirror plane* is called *chiral*.
Inversions or mirroring the molecule creates a *different* molecule.
The two forms are called right handed (R(ectus)) and left handed (S(inister)).



Important example: amino acids (and therefore all proteins), and nucleic acids (and therefore DNA and RNA)

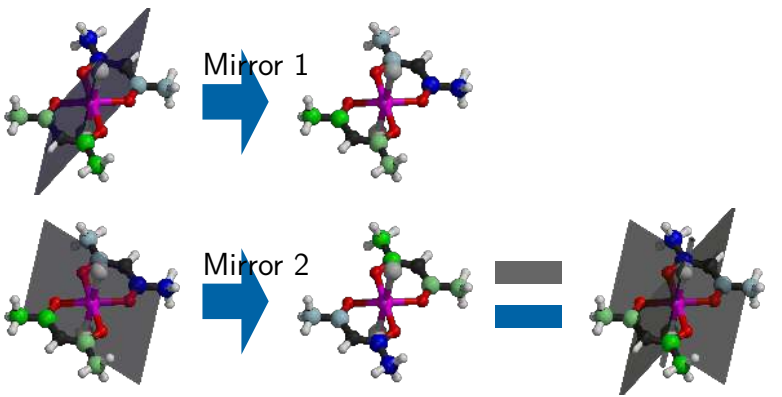
3 Combination of symmetry operations



CCDC ID ACDIPT [2]
trans-bis(Acetylacetonato)-di-iodo-platinum(iv)

Combination of symmetry operations

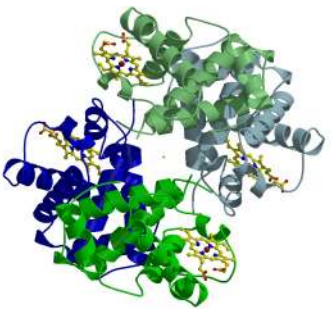
Symmetry operations can be combined arbitrarily: any object with two different symmetry operators is also symmetry with respect to the third symmetry operators, the combination of the two.



two perpendicular mirrors = 180° rotation axis

"De-"combination of Symmetry operations

N. B.: The inverse statement is not necessarily correct: not every molecule with a 2-fold rotation axis contains two mirror planes:



natural proteins are composed of S-amino acids and are always chiral. They never contain a centre of inversion, or a mirror plane.

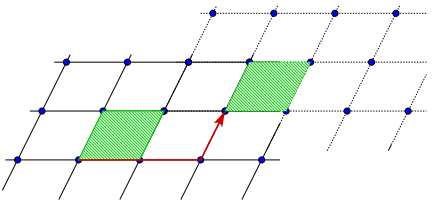
Symmetry of crystals

1. Additional symmetry operations due to translational symmetry
2. Restrictions for the total number of symmetry groups (space groups)

Symmetry of crystals: Translation

ideal crystal: infinitely large

Therefore: Additional symmetry due to translation by integer shifts of the unit cell.

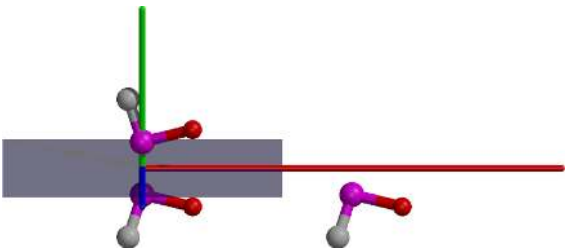


Additional symmetry operations:

1. **glide plane**
2. **screw axis**

Glide Plane

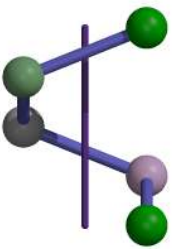
1. mirror plane
2. translation along one unit cell axis by 1/2 of its length



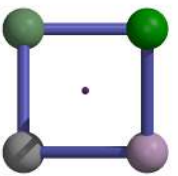
racemates (*i.e.* equimolar mixtures of R- and S-form) often crystallise with glide mirror planes: efficient packing.

Screw Axis

A combination of an n-fold rotation axis by $\frac{360^\circ}{n}$ with a shift along one of the unit cell axes by $1/n$ of its length is called a *scree axis*. Screw axis always run parallel to one it the unit cell axes.



Side view

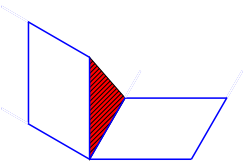


top view

Example for a 4_1 screw axis:
Rotation about $1/4 \cdot 360^\circ = 90^\circ$ plus shift by $1/4$ along the rotation axis

Symmetry of crystals: Limitations

The lattice of crystals creates additional symmetry operations in comparison with single molecules (glide mirror plancs and scew axes). However, since every symmetry operation must map the lattice into itself, the number of combinations is finite.

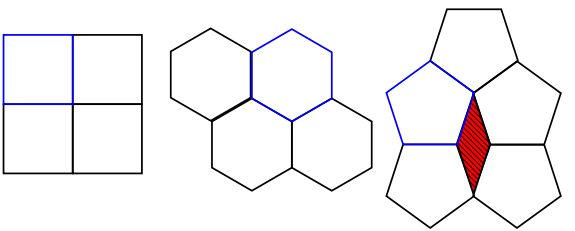


This cell as angles $\neq 90°$. This prohibits a 4-fold rotation: a rotation by $90°$ creates gaps in the crystal lattice.

We cannot combine any symmetry operation with any cell.

Symmetry of crystals: Limitations

- A mirror plane, or a centre of inversions, or a rotation axis imposes restrictions onto the crystal lattice.
- Therefore, not every combination of lattice and symmetry operation is possible.
- Only 2-fold, 3-fold, 4-fold, or 6-fold rotations are possible



(gap-free tiling of the plane with regular squares or hexagons. Impossible with regular pentagons.)

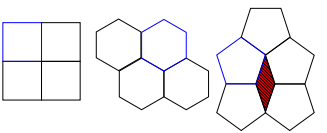
4 Point groups and Space groups

Point Groups and Space Groups

1. Classification and nomenclature
2. Symbols for symmetry elements

Point Groups

- Point groups consider symmetry without translation
- Symmetry operations:
  1. mirror plane
  2. inversion centre
  3. n-fold rotation
- In crystallography: only 2-fold, 3-fold, 4-fold,6-fold rotations



Point Groups

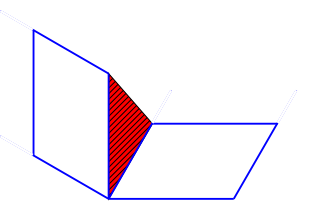
The combination of all symmetry operations that are compatible with unit cells leads to 32 different groups, the

32 crystallographic point groups

N.B. There are many more point groups for molecules, only 32 are compatible with the "translational symmetry" of the crystal [3].

Space Groups

- Point groups combined with translation of the infinite lattice
- Symmetry operations:
  1. mirror plane
  2. inversion centre
  3. n-fold rotation
  4. glide plane
  5. screw axis
- Not every unit cell type is compatible with every symmetry operation



Space Groups

The combination of 32 point groups with translation of the infinite crystal lattice creates

230 space groups

- Every crystal belongs to one out of 230 different space groups.
- Chiral compounds belong to a subset, 65 different Sohncke groups [1]. The Sohncke groups do not violate the chirality of the compound.
- All point groups and space groups are listed in the in *"International Tables of Crystallography"*, Volume A (International Union of Crystallography, IUCr)

[1] Leonhard Sohncke, 1842–1897, German mathematician and physicist

Nomenclature

There are mainly two different types of nomenclatures for point groups and for space groups:

- Hermann-Mauguin System (primarily used in crystallography)
- Schönflies System (primarily used for symmetry of molecules, spectroscopy)

Nomenclature: Hermann-Mauguin System [4, Ch. 6]

- Space groups have names like $P2_1/c$ or $I\bar{4}3m$.
- subscripts can be replaced with brackets: $P2(1)/c$
- bars can be replaced with a minus sign: I-43m
- first,capital letter: lattice type (see below)
- next: three positions for a, b, c axes
- by conventions, axes with '1' are dropped: $P2_1/c = P\ 1\ 2_1/c\ 1$

Nomenclature: Hermann-Mauguin System [4, Ch. 6]

- n-fold rotation axis: n
- centre of inversion: $\bar{1}$ or $\bar{N}$
- mirror plane: m
- glide mirror plane: a, b, c, n, d, g

Nomenclature: Hermann-Mauguin System [4, Ch. 6] ct'd.

- glide mirror plane:
  - **a** translation along $\vec{a}$, i.e. $1a1$ or $11a$
  - **b** translation along $\vec{b}$, *i.e.* $b11$ or $11b$
  - **c** translation along $\vec{c}$, *i.e.* $c11$ or $1c1$
  - **n, d** translation along diagonal
  - **g** translation along arbitrary direction, needs to be followed by direction and position of mirror plane (not a standard setting).

Example: $Pnma$: n-glide plane along $\vec{b} + \vec{c}$, mirror plane perpendicular to $\vec{b}$-axis, glide mirror plane perpendicular to $\vec{c}$-axis

List of 32 crystallographic point groups

Schönflies	Hermann-Mauguin	Schönflies	Hermann-Mauguin	Schönflies	Hermann-Mauguin
C_1	1	C_4	4	$C_{3i} = S_6$	$\bar{3}$
C_i	$\bar{1}$	S_4	$\bar{4}$	D_3	32
C_2	2	D_4	422	C_{3v}	$3m$
$C_s = C_{1v}$	m	C_{4v}	$4mm$	D_{3d}	$\bar{3}m$
C_{2h}	$2/m$	C_{4h}	$4/m$	C_6	6
C_{2v}	$mm2$	D_{2d}	$\bar{4}2m$	C_{3h}	$\bar{6}$
D_2	222	D_{4h}	$4/mmm$	D_6	622
D_{2h}	mmm	C_3	3	D_{3h}	$\bar{6}m2$
C_{6h}	$6/m$	C_{6v}	$6mm$	D_{6h}	$6/mmm$
T	23	T_h	$m\bar{3}$	T_d	$\bar{4}3m$
O	432	O_h	$m\bar{3}m$		

Representation of Symmetry operators — Matrices

Each symmetry operator of the **point groups** can be expressed by a matrix:

4-fold rotation axis about $\vec{a}$ $\quad R_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$

4-fold rotation axis about $\vec{b}$ $\quad R_2 = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$

centre of inversion (at origin) $\quad R_3 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

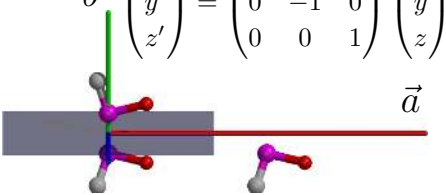
Matrices can be directly applied to atom positions with *fractional coordinates* (as *e.g.* the instruction file for SHELXL).

Symmetry with Translation

Crystal Symmetry (Space group): the translational part has to be expressed with a vector $\vec{t}$

Example: glide mirror plane perpendicular to $\vec{b}$ along $\vec{a}$:

$$\vec{b} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 1/2 \\ 0 \\ 0 \end{pmatrix} = (R, \vec{t}) \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$



A crystal with this type of glide mirror plane with a nitrogen atom at position (x,y,z) has an equivalent nitrogen atom at position (x',y',z')

"symmetric" — What does this mean?

Symmetric molecule (point groups): for every atom at position (x,y,z) of a molecule with a symmetry operator R there is an equivalent atom at position

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = R \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

.

Symmetry in crystals (space groups): for every atom at position (x,y,z) of a molecule with a symmetry operator $(R, \vec{t}$ there is an equivalent atom at position

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = (R, \vec{t}) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = R \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \vec{t}$$

(x, y, z) and (x', y', z') are **equivalent positions** of the crystal.

"symmetric" — What does this mean?

When anyone of the symmetry operators of the space group is applied to **all** atoms in the unit cell, the structure looks the same. Furthermore, the environment of each atom looks the same.

Think of NMR: the NMR spectrum would not change after the application of a symmetry operator to **all** atoms in the unit cell.

Meaning of Symmetry for Structure Determination

The symmetry of a crystal is important because it affects

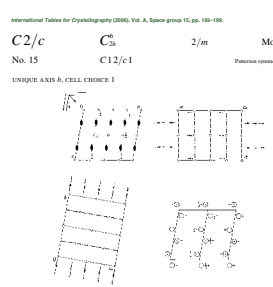
- data acquisition and scaling — more reliable intensities with more robust standard uncertainties
- structure solution
- refinement — wrong space group can sometimes lead to unstable refinement

Presentation of Symmetry in the *International Tables*

The *International Tables for Crystallography* contain a description for each of the 230 space groups.
Each description contains the sections

- **Symmetry Operations**
- **Positions**

Example Space group $C2/c$ (No. 15) (Int. Tables, [5])



International Tables for Crystallography (2006). Vol. A, Space group 15, pp. 192–199.

$C2/c$ C_{2h}^6 $2/m$ Monoclinic

No. 15 $C\,1\,2/c\,1$ Patterson symmetry $C\,1\,2/m\,1$

UNIQUE AXIS *b*, CELL CHOICE 1

Origin at 1 on glide plane *c*

Asymmetric unit $0 \le x \le \frac{1}{4}$; $0 \le y \le \frac{1}{4}$; $0 \le z \le \frac{1}{4}$

Symmetry operations

For (0,0,0)+ set

(1) 1 (2) 2 $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,0,z$

For $(\frac{1}{2},\frac{1}{2},0)$+ set

(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) $2(0,\frac{1}{2},0)$ $\frac{1}{2},y,\frac{1}{4}$ (3) $\bar{1}$ $\frac{1}{2},\frac{1}{2},0$ (4) $n(\frac{1}{2},0,\frac{1}{2})$ $\frac{1}{2},\frac{1}{2},z$

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)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
	(0,0,0)+ $(\frac{1}{2},\frac{1}{2},0)$+	General:
8 f 1	(1) x,y,z (2) $\bar{x},y,\frac{1}{2}-z$ (3) $\bar{x},\bar{y},\bar{z}$ (4) $x,\bar{y},\frac{1}{2}+z$	$hkl:\ h+k=2n$ $0kl:\ k=2n$ $hk0:\ h+k=2n$ $h0l:\ h=2n$ $0k0:\ k=2n$ $00l:\ l=2n$
		Special: as above, plus
4 e 2	$0,y,\frac{1}{4}$ $\frac{1}{2},y,\frac{1}{4}$	no extra conditions
4 d $\bar{1}$	$\frac{1}{4},\frac{1}{4},\frac{1}{2}$ $\frac{3}{4},\frac{3}{4},0$	$hkl:\ k+l=2n$
4 c $\bar{1}$	$\frac{1}{4},\frac{3}{4},\frac{1}{2}$ $\frac{3}{4},\frac{1}{4},0$	$hkl:\ k+l=2n$
4 b $\bar{1}$	$0,\frac{1}{2},0$ $\frac{1}{2},0,\frac{1}{2}$	$hkl:\ l=2n$
4 a $\bar{1}$	$0,0,0$ $\frac{1}{2},0,0$	$hkl:\ l=2n$

Symmetry of special projections

Along [001] *c*2*mm* — $\mathbf{a}=\mathbf{a}$ $\mathbf{b}=\mathbf{b}$ — Origin at 0,0,*z*

Along [100] *p*2*gm* — $\mathbf{a}=\mathbf{b}$ $\mathbf{b}=\mathbf{c}$ — Origin at 0,0,0

Along [010] *p*2 — $\mathbf{a}=\mathbf{a}$ $\mathbf{b}=\mathbf{c}$ — Origin at 0,*y*,0

Maximal non-isomorphic subgroups

I [2] $C1c1$ (C_s, 9); [2] $C1\bar{1}$ (C_i, 2) (1; 4)+ (1; 3)+ (1; 2)+ (1, $\frac{1}{2}$, 0)+

IIa [2] $P2/c$ ($P2_1/m$, 11); [2] $P2_1/c$ ($P2_1/m$, 11); [2] $P2/c1$ ($P2/m$, 10); [2] $P12/c1$ ($P2/c$, 13); [2] $P12_1/c1$ ($P2_1/c$, 14); [2] $P2_1/c11$ ($P2_1/m$, 11); [2] $P12/c1$ ($P2/c$, 13); [2] $P12_1/c1$ ($P2_1/c$, 14) (1; 2; 4)+ $\mathbf{a}=\mathbf{a}$ $\mathbf{b}=\mathbf{b}$; (1; 2; 3)+ $\mathbf{a}=\mathbf{a}$ $\mathbf{b}=\mathbf{b}$; 1; 2; 3; 4

IIb none

Maximal isomorphic subgroups of lowest index

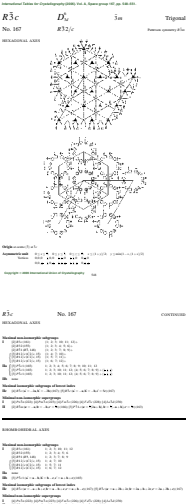
IIc [2] $C\,1\,2/c\,1$ ($\mathbf{a}=2\mathbf{a}$) ($C12/c$, 15); [2] $C\,1\,2/c\,1$ ($\mathbf{c}=2\mathbf{c}$) ($C2/c$, 15); [2] $C\,1\,2/c\,1$ ($\mathbf{a}=\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{c}$, $\mathbf{c}=-\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{c}$) ($C2/c$, 15)

Minimal non-isomorphic supergroups

I [2] $Cmcm$ (63); [2] $Cmce$ (64); [2] $Cccm$ (66); [2] $Ccce$ (68); [2] $Fddd$ (70); [2] $Ibam$ (72); [2] $Ibca$ (73); [2] $Immm$ (74); [2] $I4_1/amd$ (141); [3] $P\bar{3}1c$ (163); [3] $P\bar{3}c1$ (165); [3] $R\bar{3}c$ (167)

II [3] $P\,12/m1$ ($C2/m$, 12); [3] $C\,12/m1$ ($\mathbf{c}=\frac{1}{2}\mathbf{c}$) ($C2/m$, 12); [3] $P\,12/c1$ ($\mathbf{a}=2\mathbf{a}$, $\mathbf{b}=\mathbf{b}$) ($P2/c$, 13)

Example Space group $R\bar{3}c$ (No. 167) (Int. Tables, [5])



Example Space group $R\bar{3}c$ (No. 167) (Int. Tables, [5])

CONTINUED No. 167 $R\bar{3}c$

Symmetry operations

For $(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$ set

(1) $t(\frac{2}{3},\frac{1}{3},\frac{1}{3})$ (2) $3^-(0,0,\frac{1}{3})$ $\frac{1}{3},\frac{1}{3},z$ (3) $3^-(0,0,\frac{1}{3})$ $\frac{1}{3},0,z$
(4) $2(\frac{1}{3},\frac{1}{3},0)$ $x,x-\frac{1}{6},\frac{5}{12}$ (5) $2(\frac{1}{3},0,0)$ $x,\frac{1}{6},\frac{5}{12}$ (6) 2 $\frac{1}{3},y,\frac{5}{12}$
(7) $\bar{1}$ $\frac{1}{3},\frac{1}{3},\frac{1}{3}$ (8) $\bar{3}^+$ $\frac{1}{3},-\frac{1}{3},z$; $\frac{1}{3},-\frac{1}{3},\frac{1}{6}$ (9) $\bar{3}$ $\frac{1}{3},\frac{1}{3},z$; $\frac{1}{3},\frac{1}{3},\frac{1}{3}$
(10) $g(\frac{1}{3},-\frac{1}{6},\frac{2}{3})$ $x+\frac{1}{3},\bar{x},z$ (11) $g(\frac{1}{6},\frac{1}{3},\frac{2}{3})$ $x+\frac{1}{3},2x,z$ (12) $g(\frac{1}{3},\frac{1}{3},\frac{2}{3})$ $2x,x,z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{3},\frac{1}{3},\frac{1}{3})$; (2); (4); (7)

Positions

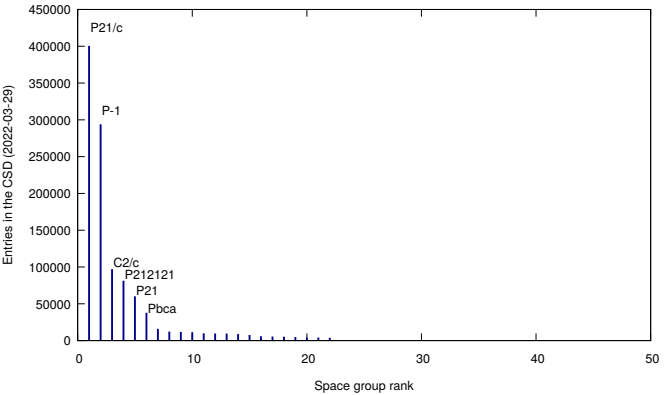
Multiplicity, Wyckoff letter, Site symmetry		Coordinates			Reflection conditions
		$(0,0,0)+$	$(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$	$(\frac{1}{3},\frac{2}{3},\frac{2}{3})+$	
36	f 1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$	General:
		(4) $y,x,\bar{z}+\frac{1}{2}$	(5) $x-y,\bar{y},\bar{z}+\frac{1}{2}$	(6) $\bar{x},\bar{x}+y,\bar{z}+\frac{1}{2}$	
		(7) $\bar{x},\bar{y},\bar{z}$	(8) $y,\bar{x}+y,\bar{z}$	(9) $x-y,x,\bar{z}$	$hkil$: $-h+k+l=3n$
		(10) $\bar{y},\bar{x},z+\frac{1}{2}$	(11) $\bar{x}+y,y,z+\frac{1}{2}$	(12) $x,x-y,z+\frac{1}{2}$	$hki0$: $-h+k=3n$
					$hh\bar{2}hl$: $l=3n$
					$h\bar{h}0l$: $h+l=3n$, $l=2n$
					$000l$: $l=6n$
					$hh\bar{h}00$: $h=3n$
					Special: as above, plus
18	e .2	$x,0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$ $0,\bar{x},\frac{1}{2}$ $x,x,\frac{1}{2}$
					no extra conditions

Example Space group $R\bar{3}c$ (No. 167) (Int. Tables, [5])

- Symmetry operation number (10): glide mirror plane $g(1/6, -1/6, 5/6)\ x+1/2, \bar{x}.z$:
  1. mirror all points of the unit cell at the plane $x + 1/2, \bar{x}, z$
  2. translate the points by the fractional vector $(1/6, -1/6, 5/6)$
- The "General position" number (10), $\bar{y}, \bar{x}, z + 1/3$:

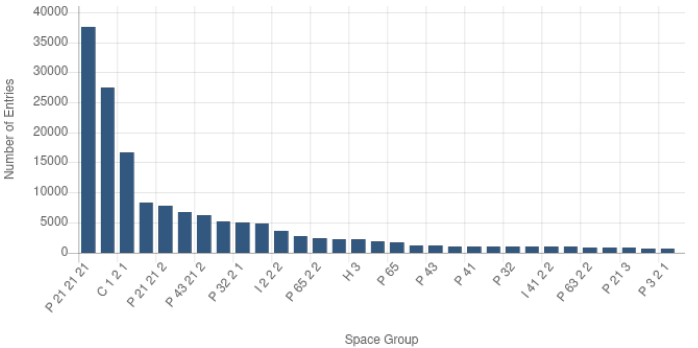
$$x' = R_{11}x + R_{12}y + R_{13}z + t_1$$
$$y' = R_{21}x + R_{22}y + R_{23}z + t_2$$
$$z' = R_{31}x + R_{32}y + R_{33}z + t_3$$
$$\begin{pmatrix} \bar{y} \\ \bar{x} \\ z+1/3 \end{pmatrix} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 1/3 \end{pmatrix}$$

Freuency of space groups for chemical compounds (CSD, March 2022)



http://www.ccdc.cam.ac.uk/

Frequency of space groups for Macromolecules (PDB, March 2022)



http://www.rcsb.org

5 Choosing the Unit Cell

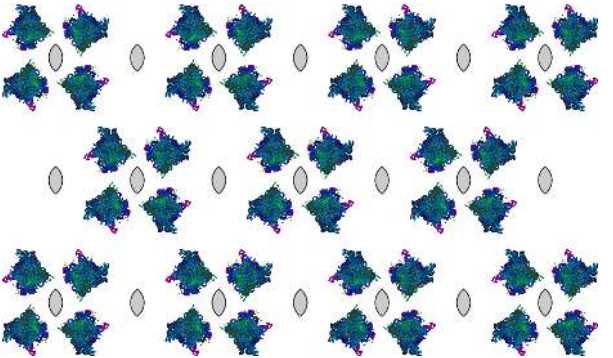
Unit Cell

- the entire crystal can be created by translations of the unit cell
- the unit cell is described by the three unit cell lengths a, b, c and the respective angles α, β, and γ.
- the unit cell is not unique

Unit Cell — Overview

- the primitive cell
- the asymmetric unit
- 7 crystal classes
- 14 Bravais lattices

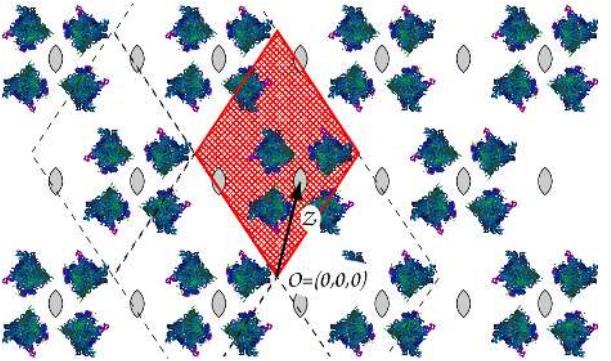
Choice of Unit Cell



The space group and the symmetry of the crystal is given by the crystal.

- The position of the molecules determines the position of the symmetry operators
- Here: **2-fold** rotation axes (not 4-fold!)

Choice of Unit Cell

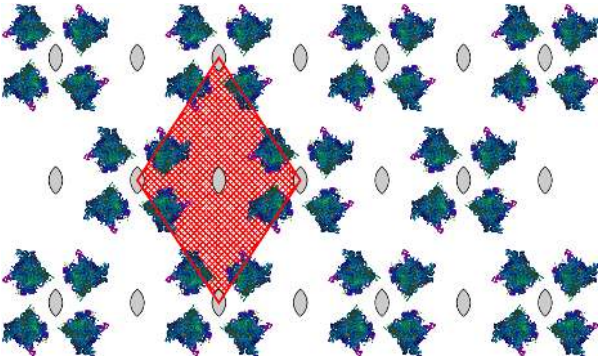


- Uni cell: Mathematical construct, molecules are “ignorant” of the unit cell
- Condition for unit cell: integer translations cover the entire crystal

- If placed arbitrarily: matrix description becomes awkward:

$$(x'y'z') = R\big((xyz) - Z\big) + Z$$

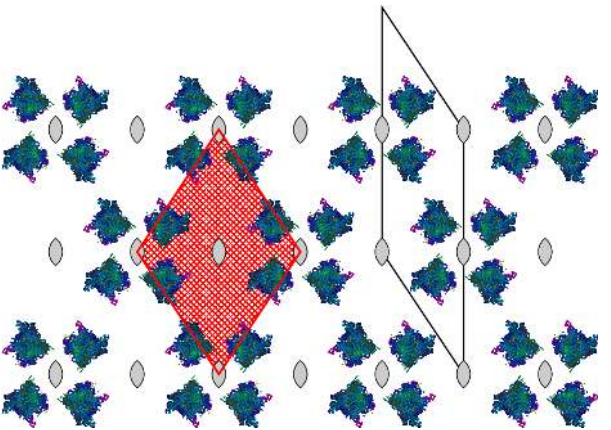
Choice of Unit Cell



- Place origin of unit cell with position of one of the symmetry elements: simplifies matrix description:

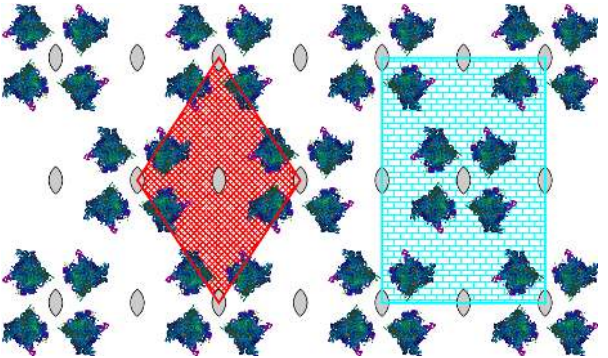
$$(x'y'z') = R(xyz)$$

Choice of Unit Cell



Every crystal possesses a unit cell with no symmetry element *inside* the cell. This unit cell is named the **primitive cell**.

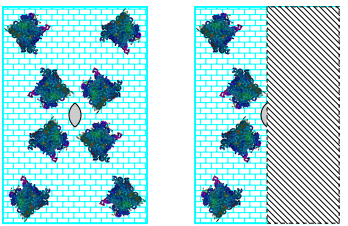
Choice of Unit Cell



- The **primitive cell** does not necessarily reflect the crystal symmetry
- here: 2-fold axes, but angles $\neq 90°$
- By convention: choose as unit cell the smallest cell which reflects the symmetry, *e.g.* trigonal (3-fold rotation axis) or hexagonal (6-fold rotation axis) system : $\gamma = 120°$

Asymmetric unit

The unit cell is the smallest box that creates the entire crystal solely by integer translations.



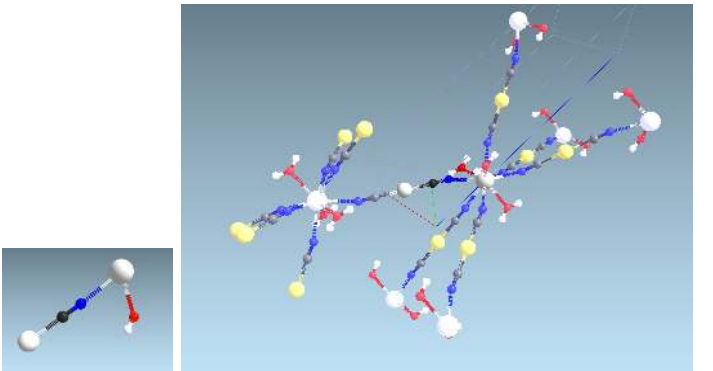
The **asymmetric unit** is the smallest box that creates the entire crystal from integer translations and all symmetry operations of the space group.

All atoms and molecules inside the asymmetric unit are independent from each other and never symmetry related

Crystallography determines the atom positions only inside the unit cell. Everything else is derived.

Example: $La[Au(CN)_2]_3 \cdot 3H_2O$, Space group: $P6_3/mcm$ [6]

The asymmetric unit does not always make chemical sense:



6 7 Crystal Systems [4]

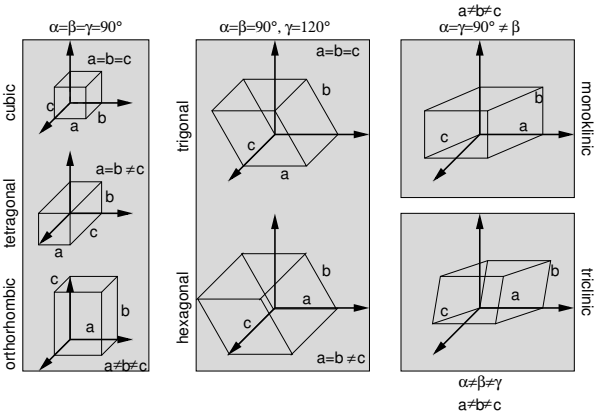
The 7 crystal systems [4]

Indepently from the content of the unit cell, the unit cell parameters $a, b, c, \alpha, \beta, \gamma$, can be classified according to regularity. These classifications result in the **seven crystal systems**

System		Conditions lengths	Conditions angles
triclinic	a	none	none
monoclinic	m	none	$\alpha = \gamma = 90°$
trigonal	h	$a = b = c$	$\alpha = \beta = 90°$ $\gamma = 120°$
hexagonal	h	$a = b$	$\alpha = \beta = 90°$ $\gamma = 120°$
orthorhombic	o	none	$\alpha = \beta = \gamma = 90°$
tetragonal	t	$a = b$	$\alpha = \beta = \gamma = 90°$
cubic	c	$a = b = c$	$\alpha = \beta = \gamma = 90°$

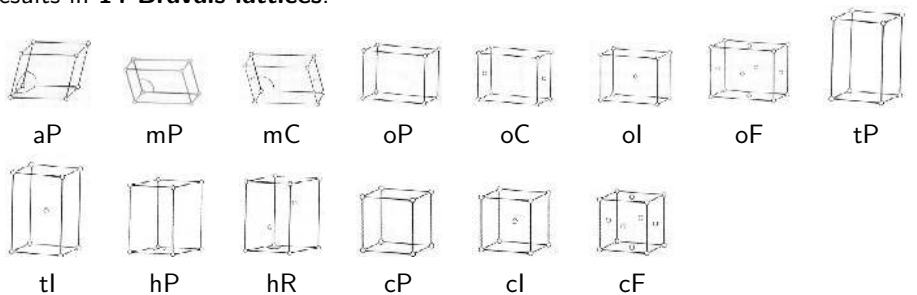
The 7 crystal systems [4]

Indepently from the content of the unit cell, the unit cell parameters $a, b, c, \alpha, \beta, \gamma$, can be classified according to regularity. These classifications result in the **seven crystal systems**



14 Bravais lattices [4]

7 crystal systems plus the requirement that the unit cell reflects the symmetry results in **14 Bravais lattices**:



Dots: Positions of symmetry elements

14 Bravais lattice — naming conventions

- lower case letters (a, m, h, o, t, c): crystal system (shape of cell).
- upper case letters (P, C, F, I, R): Symmetry. They present positions of symmetry elements within the unit cell in addition to the unit cell corners.

  P **p**rimitiv, symmetry elements only at corners

  C **C**-centred: Symmetry element at centre of C-faces (spanned by $\vec{a}$ and $\vec{b}$); (correspondingly: A- and B)

  F **f**ace centred (centred at each face)

  I body centred: at the centre of the cell (German: **i**nnenzentriert)

  R **r**hombohedral

- the (P, C, F, I, R) are the same as in the Hermann-Mauguin names for space groups ($P2_12_12$, $C2/c$, ...)

References

[1] *Parliament Clock Westminster*. URL: https://commons.wikimedia.org/wiki/File:Parliament_Clock_Westminster.jpg (visited on 23/03/2021).

[2] Philip M. Cook et al. 'Oxidative-addition reaction of platinum acetylacetonate with iodine in solid state and solution. Crystal structure and equilibrium studies of trans-bis(acetylacetonato)di-iodoplatinum(IV)'. In: *J. Chem. Soc., Dalton Trans.* (1973), pp. 294–301. DOI: 10.1039/DT9730000294.

[3] Wikipedia contributors. *Crystallographic point group*. 2022. URL: https://en.wikipedia.org/wiki/Crystallographic_point_group (visited on 29/03/2022).

[4] W. Massa. *Crystal Structure Determination*. Springer Verlag Berlin, Heidelberg, 2002.

[5] Th Hahn, ed. *International Tables of Crystallography*. Vol. A. Wiley, 2006.

[6] Julie Clarissa F. Colis et al. 'Structural studies of lanthanide ion complexes of pure gold, pure silver and mixed metal (gold–silver) dicyanides'. In: *Dalton Trans.* (2005), pp. 675–679. DOI: 10.1039/B413967D.