

# Chemical Crystallography and Structural Chemistry

VO 270287

Lecture N° 1 — 4<sup>th</sup> March 2021

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# 1 Administrativa

## Contact Details

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- Phone: +43-1-4277-70202
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- my homepage: <https://homepage.univie.ac.at/tim.gruene>

## Course Details

04 <sup>th</sup> March	Lecture N <sup>o</sup> 1	11 <sup>th</sup> March	Lecture N <sup>o</sup> 2
18 <sup>th</sup> March	Lecture N <sup>o</sup> 3	25 <sup>th</sup> March	Lecture N <sup>o</sup> 4
1 <sup>st</sup> April	Easter break	08 <sup>th</sup> April	Easter break
15 <sup>th</sup> April	Lecture N <sup>o</sup> 5	22 <sup>th</sup> April	Lecture N <sup>o</sup> 6
29 <sup>th</sup> April	Lecture N <sup>o</sup> 7	06 <sup>th</sup> May	Lecture N <sup>o</sup> 8
13 <sup>th</sup> May	Lecture N <sup>o</sup> 9	20 <sup>th</sup> May	Lecture N <sup>o</sup> 10
27 <sup>th</sup> May	Lecture N <sup>o</sup> 11	3 <sup>rd</sup> June	Lecture N <sup>o</sup> 12
10 <sup>th</sup> June	Lecture N <sup>o</sup> 13	17 <sup>th</sup> June	Lecture N <sup>o</sup> 14
24 <sup>th</sup> June	Lecture N <sup>o</sup> 15		

- Lectures will be recorded and made available through Moodle
- Interruptions welcome during the lecture
- Lecture notes will be made available online
- <https://homepage.univie.ac.at/tim.gruene/teaching/chemcryst>

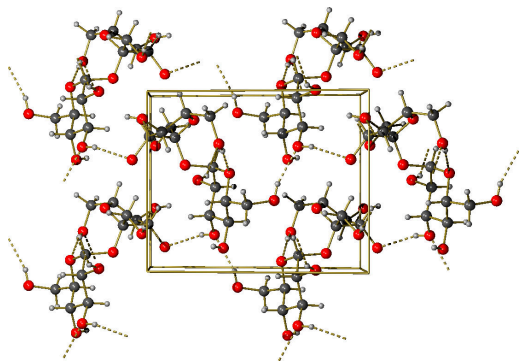
## Examination

There will be an **oral** exam.

## 2 Course Objective

## Chemical Crystallography

Understanding the value of a chemical structure in chemical research

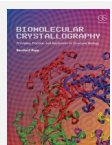


Crystal structure of  
sucrose, with hydrogen  
bonds

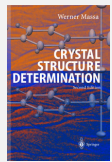
- what do we learn from a crystal structure?
- what are the **limits** of crystallography



### 3 Resources: Literature for Crystallography



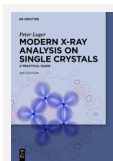
Rupp [1]



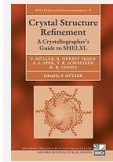
Massa [3]



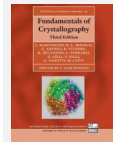
various [5]



Luger [2]

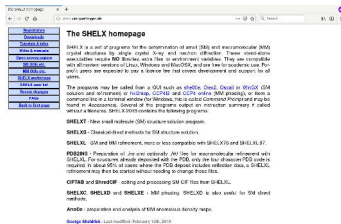


Muller et al. [4]



Giacovazzo [6]

## Online Resources



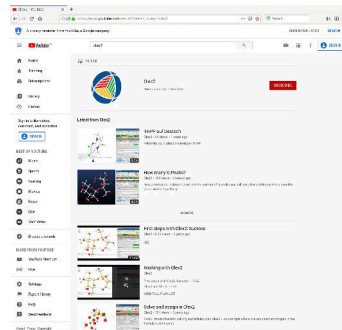
**The SHELX homepage**

SHELX is a set of programs for the determination of small (SHELX) and macromolecular (MAC) crystal structures by single crystal X-ray and neutron diffraction. These stand alone when cluster routine MD-BLASTX acts like an employment assistant. They are compatible with different versions of Linux, Windows and MacOSX, and are free to download. Use Feedback pages are essential to give a reviewer the last word on development and support for all users.

The packages may be called from a GUI such as *shelx3 GUI*, *Orbit* or *WinGX GUI* (both on Windows and Macintosh) or *shelx3* and *WinGX* (both on Windows and Macintosh) or from a command line in a terminal window (on Windows, this is called Command Prompt and may be found in Accessories). General info on the program output an instructor summary is called *shelx* or *shelx3*. SHELX contains the following programs:

- SHELXT** - Fast small molecule (SM) structure solution program.
- SHELXD** - Classical indirect methods for SM structure solution.
- SHELXL** - SM and MW refinement, more or less compatible with SHELXT (X) and SHELXL (X).
- POENIN** - Replacement of non-hydrogen atoms in macromolecular refinement with SHELXL. For example already displayed as the PDB, only the four-dimension TCD codes is required. It also offers a GUI where the TCD inputs include reflection data, a SHELXL refinement may then be started without needing to change input files.
- ORFOLD and ShredSM** - editing and processing SM CIF files from SHELXL.
- SHELXD**, **SHELXL** and **WHELXL** - MW refining. SHELXD is also useful for SM check refinement.
- ANADI** - preparation and analysis of MM unrefined density maps.

Source: [shelx.uni-goettingen.de](http://shelx.uni-goettingen.de) Last modified: February 10th, 2019



The screenshot shows the YouTube channel page for 'Olex2'. The channel has 484 subscribers and 53 videos. The video list includes:

- Learn from Olex2** (14:08)
- Shelx and Olex2** (14:08)
- How history of Olex2** (14:08)
- Olex2 for Olex2** (14:08)
- Olex2 for Olex2** (14:08)
- Olex2 for Olex2** (14:08)
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- Olex2 for Olex2** (14:08)

<http://shelx.uni-goettingen.de>

Olex2 etc on youtube

## Journals for Chemical Crystallography

- Acta Crystallographica A–F [journals.iucr.org](https://journals.iucr.org): International Union of Crystallography
- Zeitschrift für Kristallographie, <https://www.degruyter.com/journal/key/ZKRI/html>
- Angewandte Chemie Int. Ed. <http://www.angewandte.org>, GDCh
- JACS, Journal of the American Chemical Society <https://pubs.acs.org/journal/jacsat>

and most other journals for chemistry

## Crystallographic databases

Most journals require the deposition of structural data structures at publicly available data bases. Crystallography has long been a pioneering discipline of open access data.

**Cambridge Structural Database**

**Crystallography Open Database**

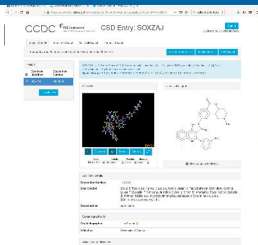
**Inorganic Crystal Structure Database**

**Protein Data Bank**

**CRYSTMET®**

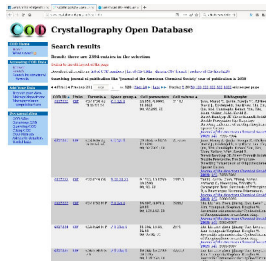
## Cambridge Structural Database (CSD)

- <http://www.ccdc.cam.ac.uk>
- founded 1965
- curated
- Single crystal and powder diffraction
- organic and metal-organic compounds
- > 1,000,000 entries,  $\approx 50,000$ /year
- X-ray, neutron, (and electron diffraction)
- “The world repository of small molecule crystal structures”



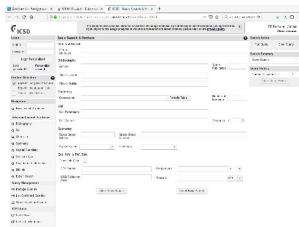
## Crystallography Open Database (COD)

- <http://www.crystallography.net>
- Local version available free of charge
- Can be browsed (by journal, by year,...)
- Organic and inorganic structures (minerals)
- “Open-access collection of crystal structures of organic, inorganic, metal-organics compounds and minerals, excluding biopolymers.”
- All data from IUCr journals, and from American Mineralogist CSD
- > 450,000 entries,  $\approx$  50,000/year



# Inorganic Crystal Structure Database (ICSD)

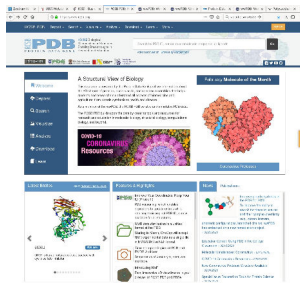
- <https://icsd.fiz-karlsruhe.de/>
- inorganic and intermetallic structures
- only licensed access
- > 215,000 entries



## Protein Data Bank (PDB)

<https://www.pdb.org>

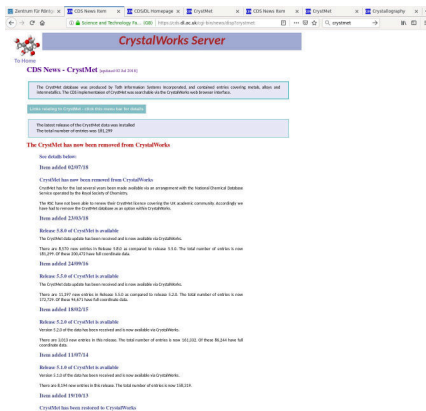
- Search from
  - [www.rcsb.org](http://www.rcsb.org)
  - <https://www.ebi.ac.uk/pdbe>
  - <https://pdj.org> (Japanese)
- polypeptides (proteins) and polysaccharides (nucleic acids)
- Crystal structures, NMR structures, EM structures
- Since 2007: data **must** be submitted along with coordinates
- > 160,000 structures





# CrystMET

- <https://cds.dl.ac.uk/cds/datasets/cryst/mdf/1lmdf.html>
- Crystal structure data for metals and alloys
- licensed access only



The screenshot shows a web browser window displaying the 'CrystalWorks Server' website. The page title is 'CDS News - CrystMet' and it features a list of news items regarding updates and releases of the CrystMet database. The news items are as follows:

- Release 5.0.0 of CrystMet is available:** The CrystMet database was updated to include information from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Crystallography (IUCr). The total number of entries is now 101,200.
- Release 4.0.0 of CrystMet is available:** The CrystMet database was updated to include information from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Crystallography (IUCr). The total number of entries is now 101,200.
- Release 3.0.0 of CrystMet is available:** The CrystMet database was updated to include information from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Crystallography (IUCr). The total number of entries is now 101,200.
- Release 2.0.0 of CrystMet is available:** The CrystMet database was updated to include information from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Crystallography (IUCr). The total number of entries is now 101,200.
- Release 1.0.0 of CrystMet is available:** The CrystMet database was updated to include information from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Crystallography (IUCr). The total number of entries is now 101,200.

# 4 Structure, Data, Data Formats, and Visualisation Software

## Structural Data: the CIF-file


- Main file format for published structures
- available from CSD, COD, ICSD, journal web-sites, etc
- pure text file
- Can and should contain both structure information (coordinates) and experimental data (hkl-file)

# Example: CSD entry UQACEW, CIF-file: 984199.cif

Dalle et al. [7]

ShelXle Download Page X uebergang - Translati... X Wikipedia, the free en... X Pauling's rules - Wikip... X Search Results - Acces... X Weakly Coupled Blo... X

https://www.ccdc.cam.ac.uk/structures/Search?Author=gruene&Database=... ov3022

CCDC  FIZ Karlsruhe CSD Entry: UQACEW [Sign In](#)

Simple Search Structure Search Unit Cell Search Formula Search

Your query was: Authors: gruene and the search returned 23 records. [Back to Search List](#) [Modify Search](#) [New Search](#)

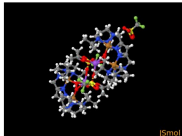
Results

Database Identifier	Deposition Number
<input type="checkbox"/> UQACEW	984199

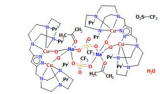
[Download](#)

UQACEW: bis(p-peroxido)-bis( $\mu$ -3,5-bis(4,7-dipropen-2-yl)-1,4,7-triazonan-1-ylmethylpyrazol-1-ido)-bis( $\mu$ -trifluoromethanesulfonato)-bis(acetone)-di-sodium-tetra-copper(II)-bis(trifluoromethanesulfonato) monohydrate  
Space Group: P T (2), Cell: a 10.336(5)Å b 12.803(3)Å c 17.594(10)Å,  $\alpha$  72.65(6)°  $\beta$  89.27(7)°  $\gamma$  85.81(4)°

3D viewer



Chemical diagram



View group symbols key

Additional details

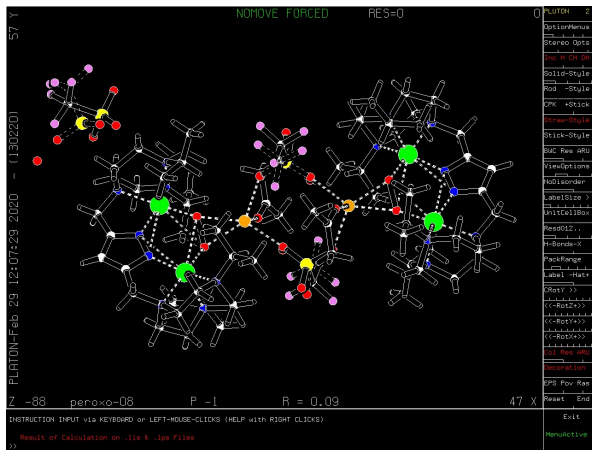
Deposition Number	984199
Data Citation	K. Dalle, T. Gruene, S. Descheri, S. Dimeshko, F. Meyer CCDC 984199: Experimental Crystal Structure Determination, 2016, DOI: 10.5517/ccdc.csd.ccl1214cm

## Structural Data: the RES-file

- RES/INS text file: chemical structure in computer language
- developed by George Sheldrick (SHELX programs), late 1960s
- still the most sophisticated format for chemical compounds
- “work” format: refinement and model building

# Platon: Validation, format conversion

<http://www.cryst.chem.uu.nl/spek/platon>



→ 984199\_sx.ins and 984199\_sx.hkl

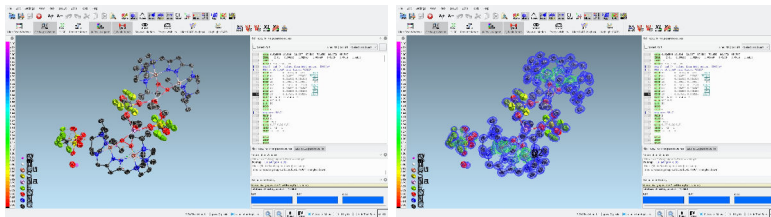
## ShelXle: Visualisation and Modelling

<https://www.shelxle.org/shelx>

```
#> shredcif 984199.cif
```

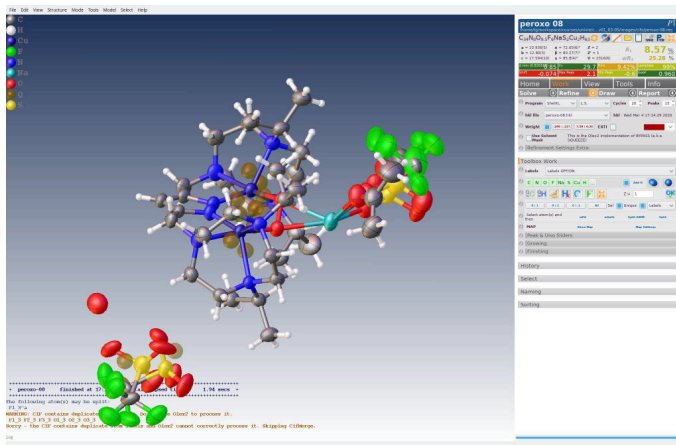
```
peroxo-08.res extracted, checksum O.K.
```

```
peroxo-08.hkl extracted, checksum O.K.
```



## Olex2: Visualisation and Modelling

<https://www.olexsys.org/>





## 5 Crystals and Crystal Growth

## Crystal Types

- Crystal = Solid state compound with regular composition
- interactions responsible for crystallisation
  1. ionic bond
  2. metallic bond
  3. covalent bond
  4. van-der-Waals interaction
- often not a clear cut between these types
- crystallography can characterise bond types

## Ionic Crystals

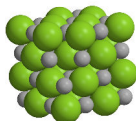
- Composed of anions (negative charge) and cations (positive charge)
- Geometry according to Pauling's rules

Simple example:  $NaCl$ :

- cubic lattice
- energy difference  $Na + Cl \rightarrow Na^+ + Cl^-: -6.4eV$

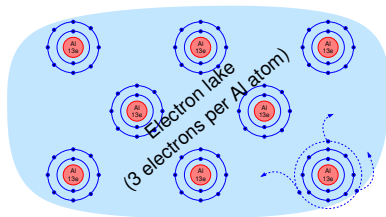


Chrome alum,  
*i.e.* Chromium(III) potassium sulfate  
 $KCr(SO_4)_2$



cubic lattice of  $NaCl$

## Metallic Crystals



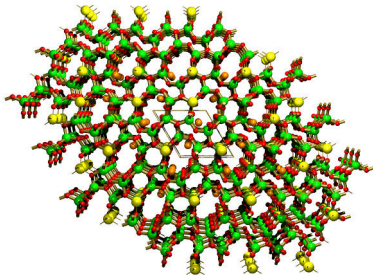
various forms of iron [8]

Valence electrons dissociate from individual atoms and form an **electron lake** (conduction band)

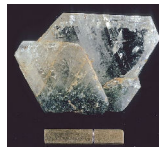
- electrical conductivity
- thermal conductivity (copper)
- shiny surface
- plasticity

## Covalent bond

- Two atoms share an electron to reach noble gas configuration.
- Examples: zeolites, MOFs, diamond, quartz
- $\Rightarrow$  high stability
- The entire crystal is a single molecule



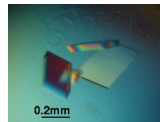
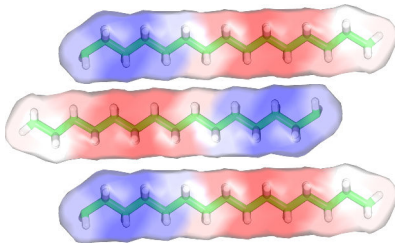
Feldspar Albite  $NaAlSi_3O_8$  [9]



Albite crystals [10]

## van-der-Waals interaction

- typical for organic and macromolecular compounds
- stochastic charge distribution (dipole moments) causes mutual attraction between molecules
- weak (“soft”) interaction



protein crystals in mother liquor

## Crystals in Crystallography

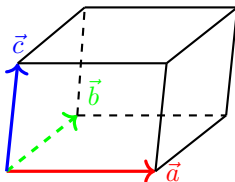
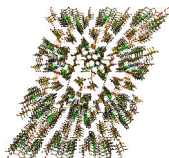
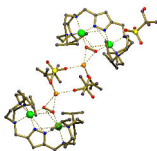
### Definition *International Union of Crystallography*:

“A material is a crystal if it has essentially a sharp diffraction pattern.”

### Crystal in the context of this lecture:

A crystal is composed of a chemical compounds that repeats periodically in all three directions.

## Crystals in Crystallography



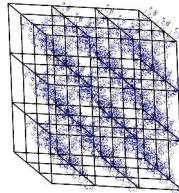
- The periodicity results in the diffraction pattern of the crystal
- The periodicity acts like a signal amplifier
- The smallest unit of the periodicity is an inclined box. It is called the **unit cell of the crystal**.



## Crystal Growth

Crystals are

1. solid state materials
2. highly ordered, *i.e.* their entropy is very low compared to amorphous material



Especially for large molecules: weak interaction, *i.e.* low energy gain through crystallisation  $\Rightarrow$  Crystal growth can be difficult

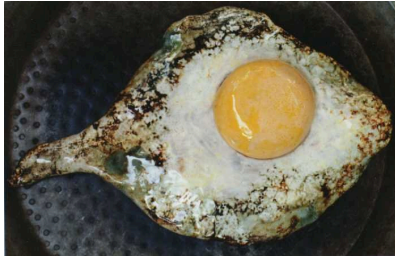
## Crystal Growth

Usually: Precipitation from solution

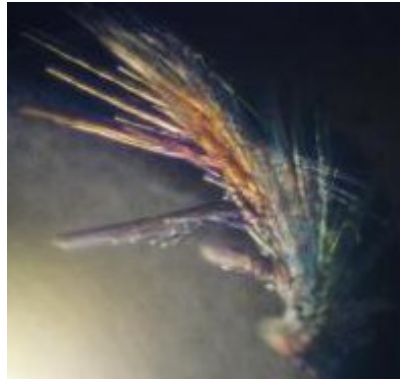
Some means for precipitation (*cf.* LeChatelier's principle)

- Changes in temperature or pressure
  - sugar: better soluble in warm water
- precipitant
  - sugar: ethanol
  - high salt concentrations

## Preliminaries for structure determination



crystallisation (instead of amorphous precipitation)

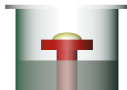


crystallisation as single crystal

## Examples for Crystallisation

1. Dissolve in Tetrahydrofuran (THF) in glass vial
2. Cover with parafilm: slow evaporation of THF
3. Store at  $-80^{\circ}\text{C}$

1. Dissolve in organic solvent (EtOH, Isopropanol, ...)
2. Store sealed on water reservoir
3. Uptake of water (vapour) reduces solubility of compound



Twinned structures (cf. end of term) can often be improved with elevated temperature during crystal growth ( $30\text{-}40^{\circ}\text{C}$ ).

(see e.g. W. Massa, *Crystal Structure Determination*, Ch. 7)

## 6 X-rays and Diffraction

end of lecture, continued in lecture N° 2

## References

- [1] B Rupp. *Biomolecular Crystallography*. 1st ed. Garland Science, 2009.
- [2] P. Luger. *Modern X-ray Analysis on Single Crystals*. Walter de Gruyter, Berlin, 2014.
- [3] W. Massa. *Crystal Structure Determination*. Springer Verlag Berlin, Heidelberg, 2002.
- [4] P. Muller et al., eds. *Crystal Structure Refinement. A Crystallographer's Guide to SHELXL*. Oxford University Press, 2006. ISBN: 9780198570769.
- [5] various, ed. *International Tables of Crystallography*. Vol. A–I. International Tables of Crystallography. Wiley, 2016. URL: <https://it.iucr.org/>.
- [6] C. Giacovazzo, ed. *Fundamentals of Crystallography*. Oxford University Press, 1985.
- [7] K. Dalle et al. 'A weakly coupled biologically relevant  $Cu_2^{II}(\mu - \eta^1 : \eta^1 - O_2)$  cis-peroxo adduct that binds side-on to additional metal ions'. In: *J. Am. Chem. Soc.* 136 (2014), pp. 7428–7434. DOI: 10.1021/ja5025047.
- [8] Alchemist-hp. *Iron electrolytic and 1cm3 cube*. URL: [https://commons.wikimedia.org/wiki/File:Iron\\_electrolytic\\_and\\_1cm3\\_cube.jpg](https://commons.wikimedia.org/wiki/File:Iron_electrolytic_and_1cm3_cube.jpg) (visited on 03/03/2020).

- [9] E. Fröjdh et al. 'Discrimination of Aluminum from Silicon by Electron Crystallography with the JUNGFRÄU Detector'. In: *Crystals* 10 (2020), p. 1148. DOI: 10.3390/cryst10121148.
- [10] Rock Courier. *Albite - Crete (Kriti) Island, Greece*. URL: [https://commons.wikimedia.org/wiki/File:Albite\\_-\\_Crete\\_\(Kriti\)\\_Island,\\_Greece.jpg](https://commons.wikimedia.org/wiki/File:Albite_-_Crete_(Kriti)_Island,_Greece.jpg) (visited on 03/03/2020).