



JAGIELLONIAN UNIVERSITY  
IN KRAKOW

# **New porous materials and catalysts – scientific results**

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St. Petersburg  
10-11 June 2013  
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# Plan of presentation

- Investigated compounds
- Description of the methods
- Powder diffraction and its applications
- Typical applications
- Some results obtained so far



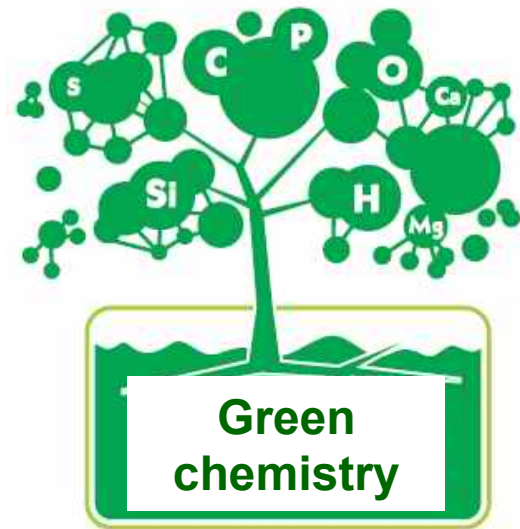
# Investigated compounds

- Catalysts (Mo based)
- Photo-Catalysts
- MOF-related compounds
- Layered materials, sorbents

# Why molybdenum catalysts ?

- Wide range of applicability
- Not expensive
- Not very toxic
- Easy to be synthesised
- Can be converted to peroxocomplexes

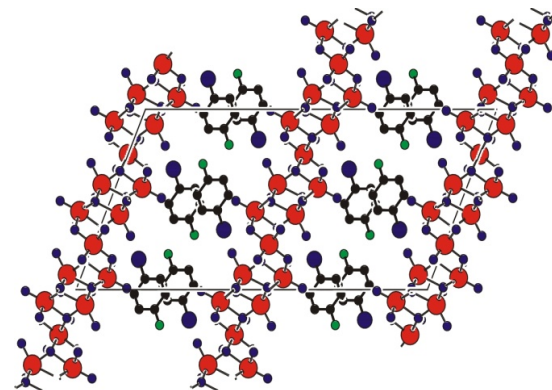
Compounds of Mo and hydrogen peroxide  
important chemicals in 'green chemistry'



# Polyoxometalates

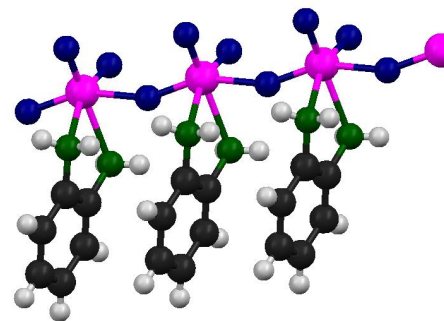
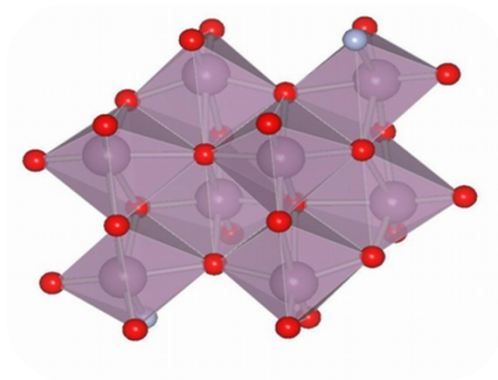
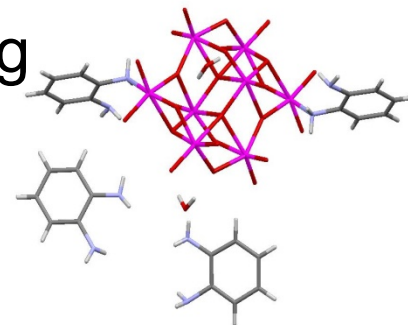
**Polyoxometalates (POM)** - polyatomic ions (anions) which consist of three or more transition metal (V(V), Mo(VI), W(VI)) oxyanions linked together by shared oxygen atoms to form a large, closed 3-dimensional frameworks.

*We investigated a few dozens of new polyoxometalates trying to correlate their properties with their structures.*

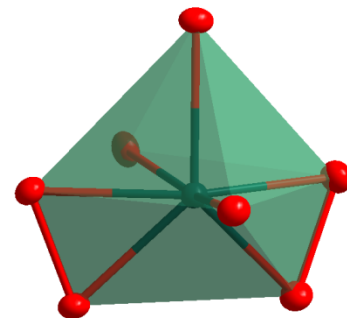


# Polyoxometalates

- Interesting building blocks in crystal engineering
- High oxidation state of central atoms
- Catalyze many chemical reactions
- Show antitumor, antiviral and antibiotic properties
- Exhibit similarity to enzymes



# Peroxometalates



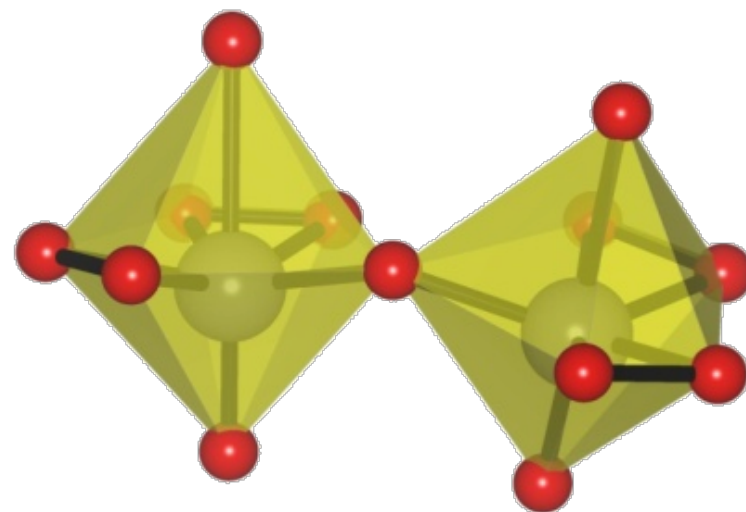
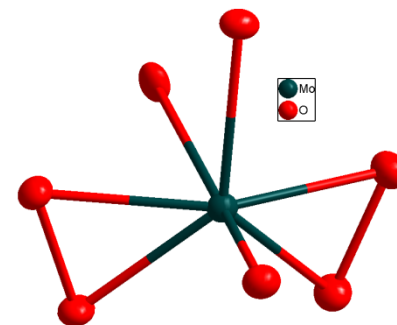
Polyoxometalates may react with hydrogen peroxide giving products in which peroxide group  $\text{O}_2^{2-}$  replaces one or more oxygen atoms.

*New compounds with different stability,  
oxygen content and oxidizing properties*



# Peroxo-metalates

- 
- Oxidative properties (catalysis, organic chemistry )
- Epoxidation of alkenes and cycloalkenes
- Source of singlet oxygen
- Bleaching processes
- Biochemistry - insulin-like action
- Photodynamic therapy

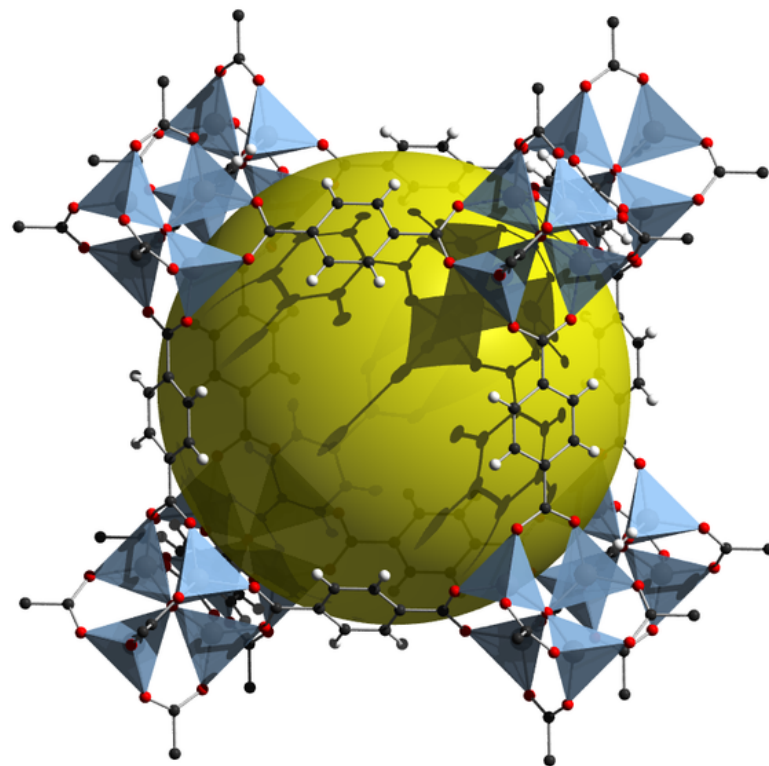




# MOF related compounds

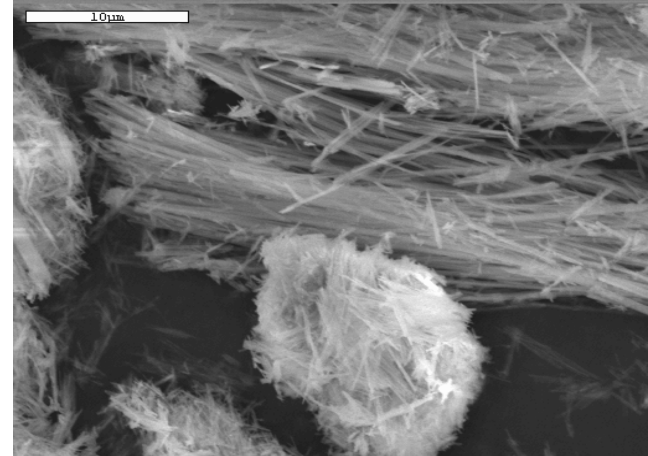
Metals or metal clusters connected by rigid organic groups  
(similarities to zeolites, easy to be synthesized)

- Catalysis
- Gas storage ( $H_2$ )
- Sorption properties
- Drug delivery
- Large, tailored porous systems



# Why powder diffraction ?

- Powerful technique
- Software available
- Rich, thoroughly tested databases (PDF-4+)
- About 50000 diffractometers are working in the world
- Fast measurements, small amount of sample required, non destructive method
- Unstable, very reactive, toxic samples in not typical form (e.g. greasy samples)



# Typical applications of powder diffraction

- Phase analysis (up to 0.1%)
- Size of crystallites
- Crystal structure determination

**Crystal structure** is an important base of properties (e.g. catalytical activity)

We should try all available methods to characterize sample (explore it deeply, to enhance activity)

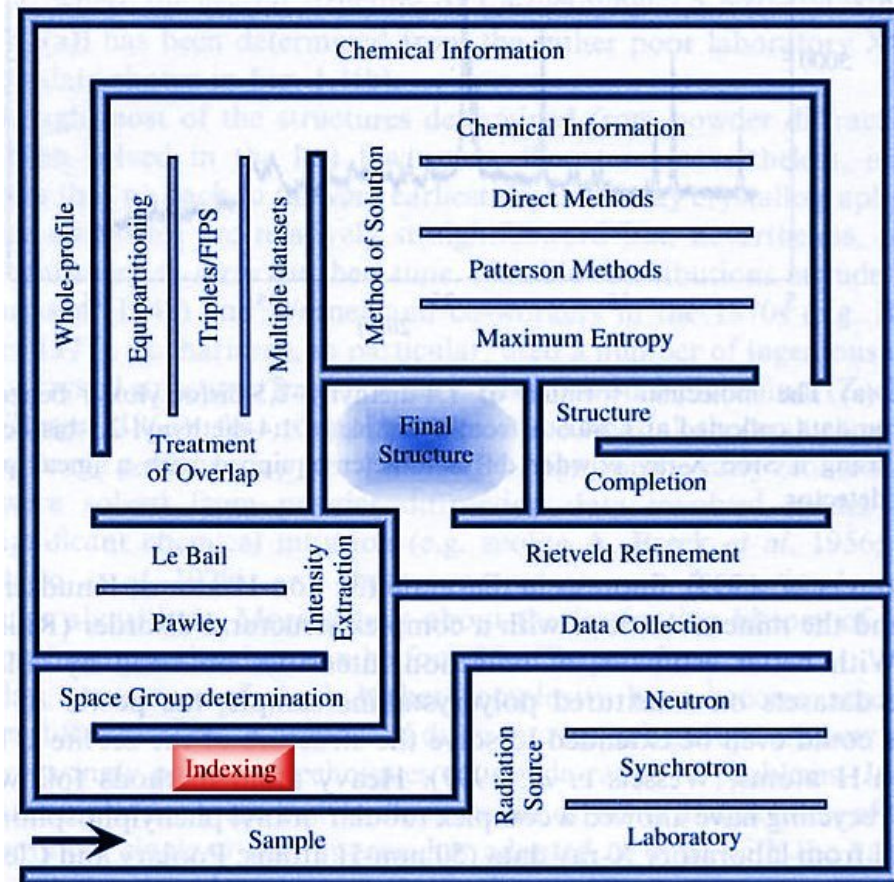
# Why synchrotron ?

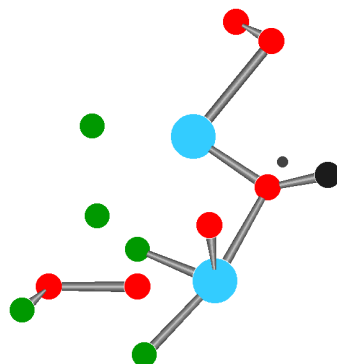
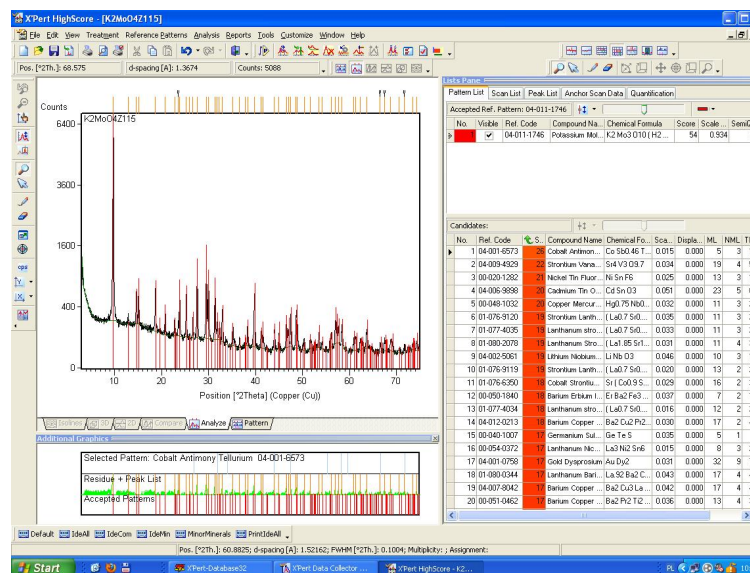
- Excellent quality powder-diffraction data
- Wavelength can be adjusted and a sample can be thoroughly penetrated
- ‘Time resolved’ measurements (during fast reaction) can be performed
- Faster, much better than conventional diffractometer



# Typical way of investigations

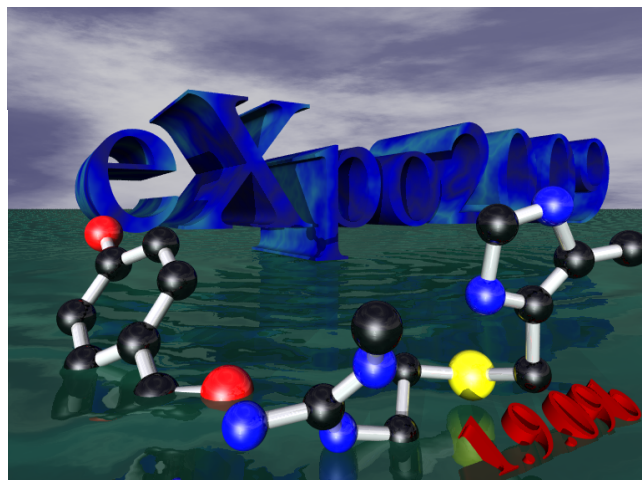
- Measurements (as good as possible)
- Search in databases (ICSD, CSD)
- Indexing (lattice parameters)
- Space group determination
- Structure solution (finding a structure model)
- Classical methods
- New methods





$$I_{hkl} = I_p m_k |F_{hkl}|^2 A T$$

$$\rho(xyz) = 1/V \sum_h \sum_k \sum_l F(hkl) \exp(-2\pi i(hx + ky + lz))$$



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# New methods – direct space methods

When direct methods fail (poor quality data - peaks overlap, weak resolution, etc...) the only solution can be '**direct space methods**'

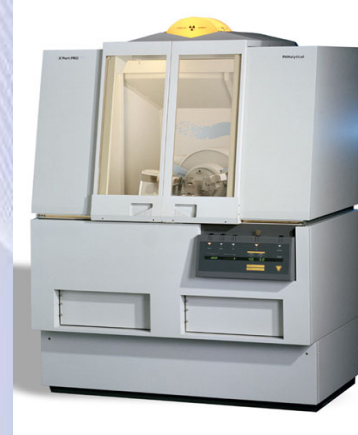
In these methods subsequent 'configurations/structure models' are build and tested (against diffraction data) until satisfactory solution will be found.

Structure is described using the largest building blocks, constructed using all *apriori* information about connectivity of the atoms to reduce number of degrees of freedom DOF, (number of variables/parameters)

Several optimisation algorithms can be used PT or SA

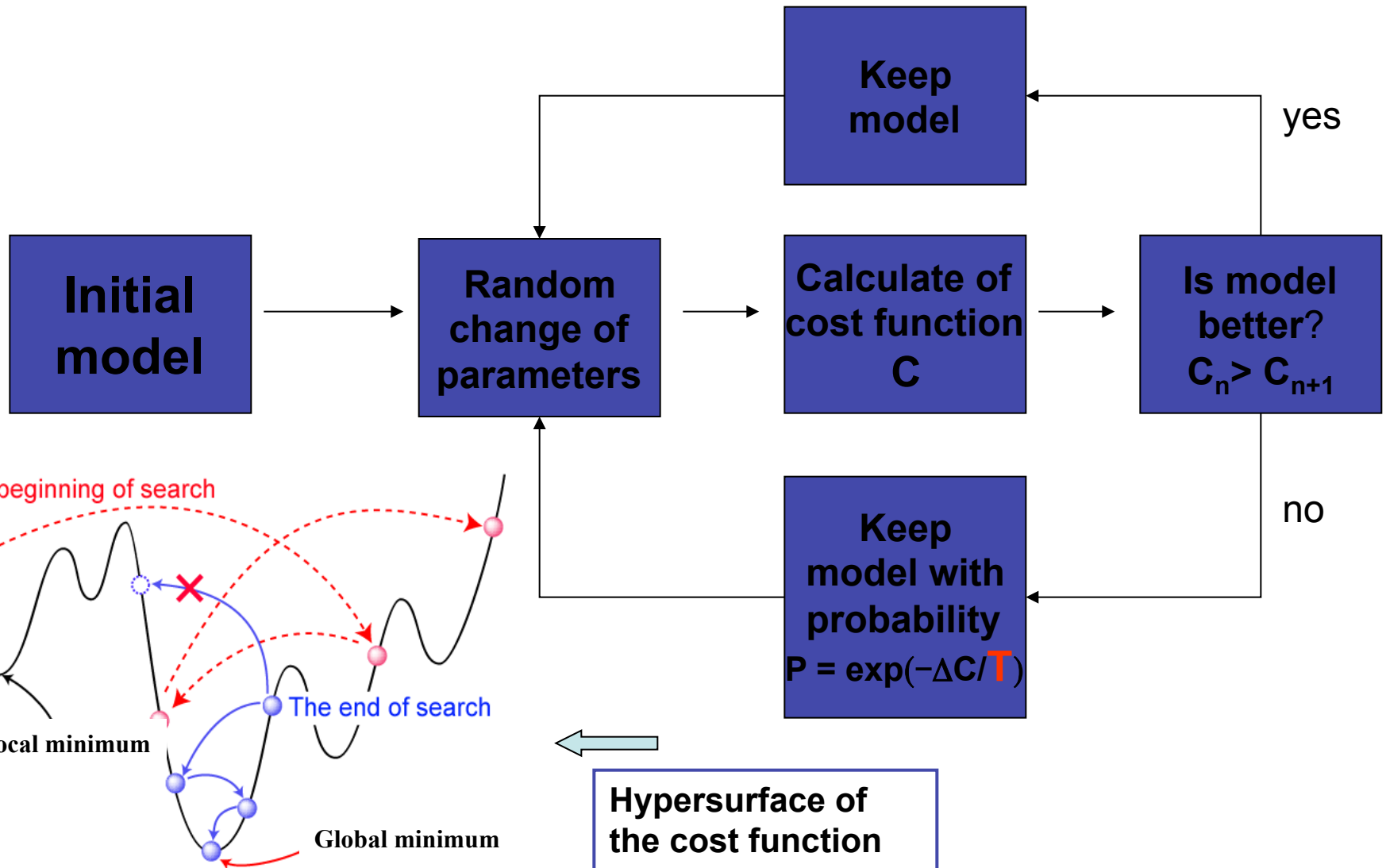
- It is possible to use jointly all available data sets:

XRD & ND, single crystal data and powder data





# How does it work?



# FOX – dialog window

File Objects Help

Crystals Powder Diffraction Single Crystal Diffraction Global Optimization

List of all Crystals

Crystal Change Me!

File Parameters Scatterers Display

Constrain Lattice to SpaceGroup Symmetry Yes (Default)

Use Dynamical Occupancy Correction Yes

Display Enantiomer No

AntiBump 0.000000 Scale 1.0000C

Bond Valence Coef 0.000000 Scale 1.0000C

aR ☒ L 8.2124C bR ☒ L 14.024E cR ☒ L 3.9944C

betaR ☒ L 99.271E

SpaceGroup: P2<sub>1</sub>/m

List of Crystal ScatteringPowers

| ScatteringPowerAtom | Symbol |
|---------------------|--------|
| N                   | N      |
| C                   | C      |
| S                   | S      |
| O                   | O      |
| Ag                  | Ag     |
| Change me           | H      |

List of Crystal Scatterers

ZScatterer Change Me!

Import/Export Parameters Atom

xR ☒ L 0.7600S yR ☒ L 0.3170T zR ☒ L 0.2016E OccupancyR ☒ L 1.0000C

PhiR ☒ L 282.27S ChiR ☒ L 103.79A PsiR ☒ L 296.01S

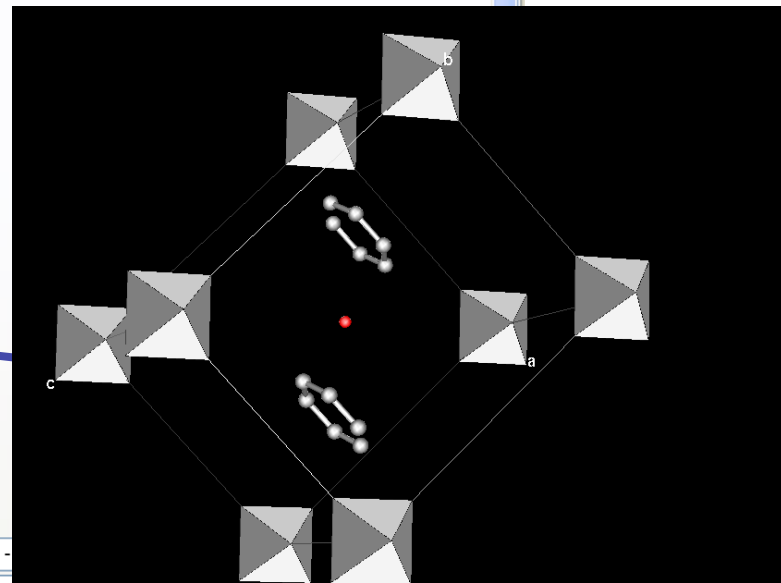
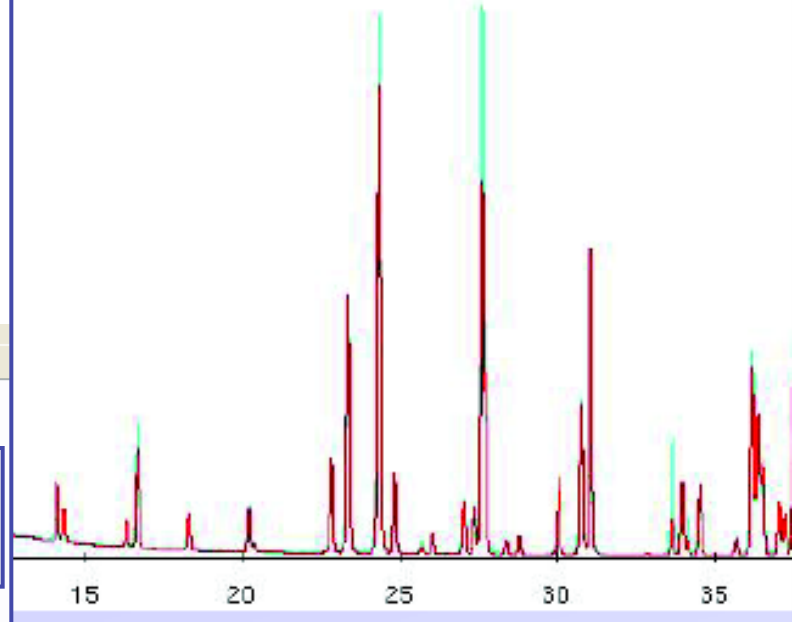
List of ZAtoms

| Atom | Type | Bond(w/N1)R                                   | Angle(w/N1)R                                  | Occup.R                                       |
|------|------|---|---|---|
| N1   | N    |   |   | <input checked="" type="checkbox"/> L 1.0000C |
| C2   | C    | <input checked="" type="checkbox"/> L 1.3708E |   | <input checked="" type="checkbox"/> L 1.0000C |
| S3   | S    | <input checked="" type="checkbox"/> L 1.74372 | <input checked="" type="checkbox"/> L 111.761 | <input checked="" type="checkbox"/> L 1.0000C |
| C4   | C    | <input checked="" type="checkbox"/> L 1.81921 | <input checked="" type="checkbox"/> L 92.6822 |   |
| C5   | C    | <input checked="" type="checkbox"/> L 1.5112E | <input checked="" type="checkbox"/> L 106.25E |   |

Unit cell and  
space group

Scatters

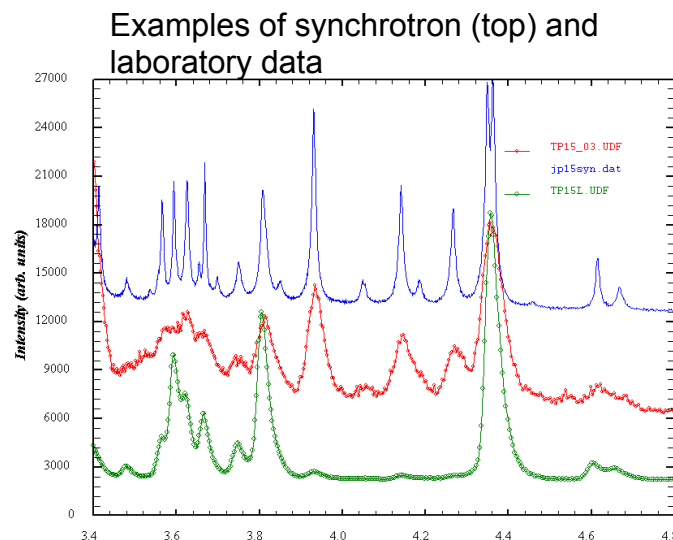
Molecule



# Obtained results

# Why did we need synchrotron ?

- All attempts of solving crystal structures with the use of laboratory data failed
- We needed better data with:
  - Sharper and narrower peaks
  - Better monochromatization
  - Smaller texture



# Layered compounds – coordination polymers we have studied:

- **CdCl – 1,4 –butane**
- **CdBr – 1,4-butane**
- **CdCl<sub>2</sub> – 1,6-diaminohexane**
- **CdCl<sub>2</sub> – 1,6-diaminohexane**
- **CdCl<sub>2</sub> + 1,4-phenylenediamine**
- **CdI<sub>2</sub> + 1,4-phenylenediamine**
- **dilithium glutarate**

# Coordination polymers

We are working on the final elaboration of the structural data of several compounds of  $\text{MeX}_2(\text{NH-R})_2$  or  $\text{MeX}_2(\text{NH-R-NH})$  type. Depending on the type of the central atom and X anion we may obtain:

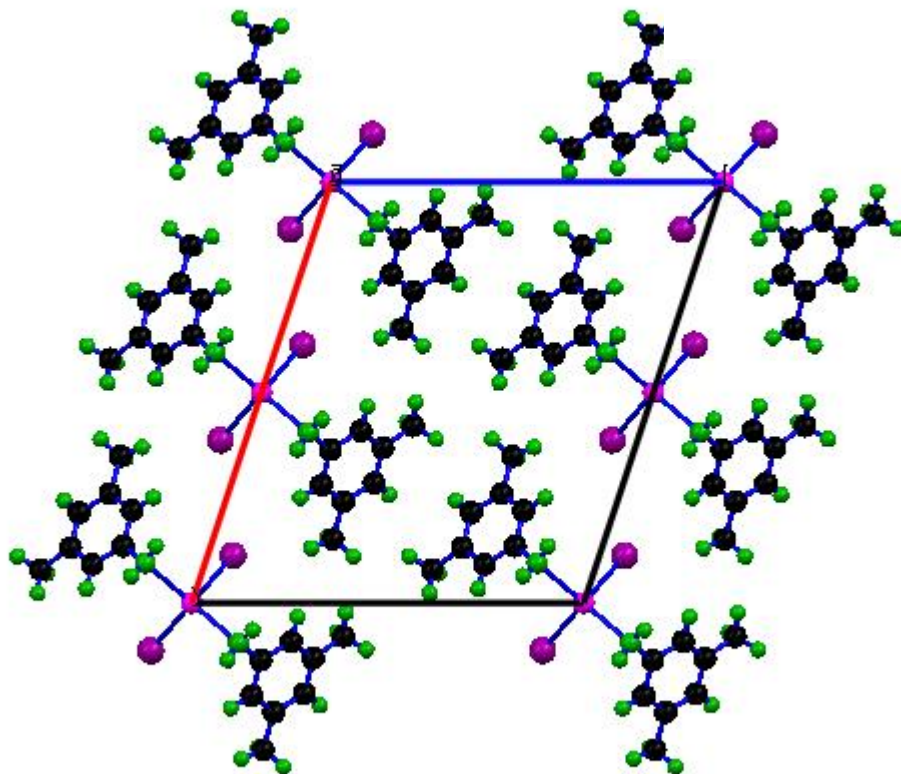
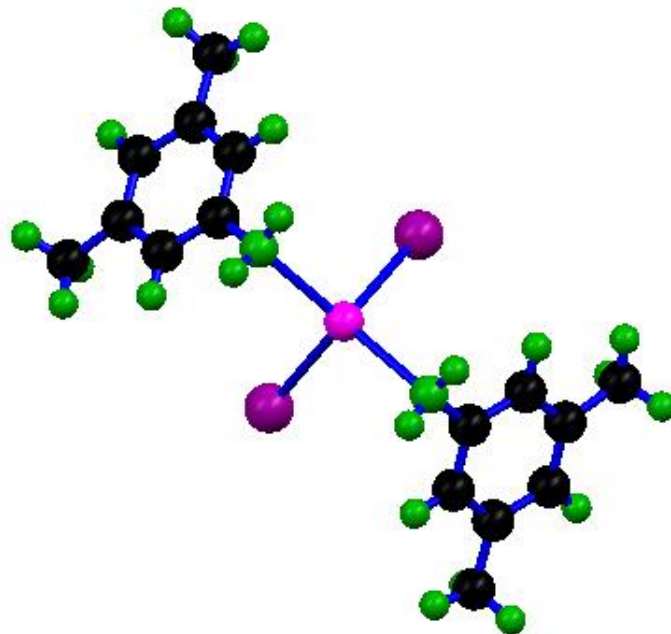
- Isolated molecules similar to cis-platinum
- Isolated polymer chains
- Polymer chains combined in layers (not always flat, with not uniform thickness)
- Three-dimensional structure



Isolated molecules  
'related to cis-platinun

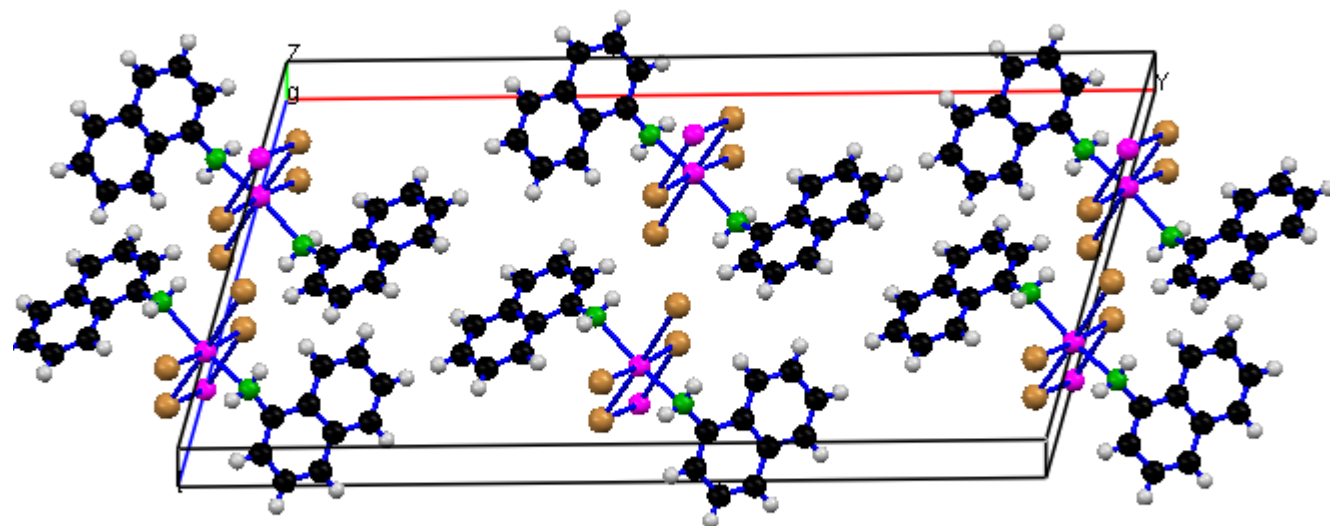
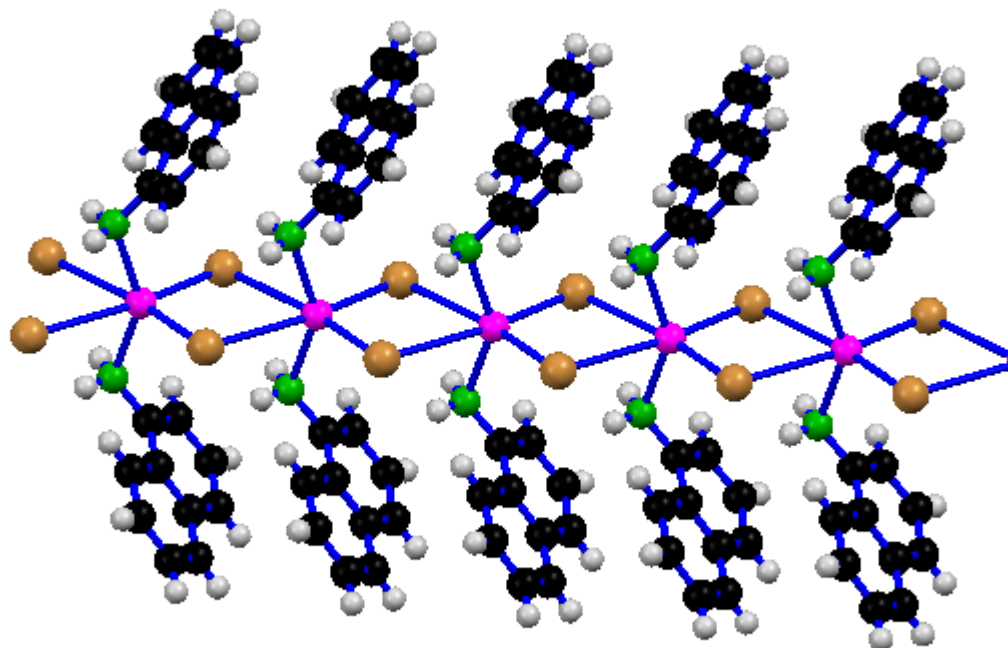
$\text{Cd} - \text{I} = 2.75 \text{ \AA}$

$\text{Cd} \cdots \text{I} = 4.12 \text{ \AA}$



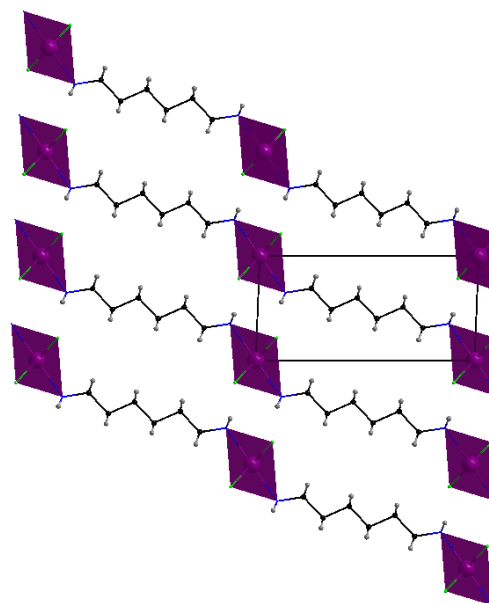
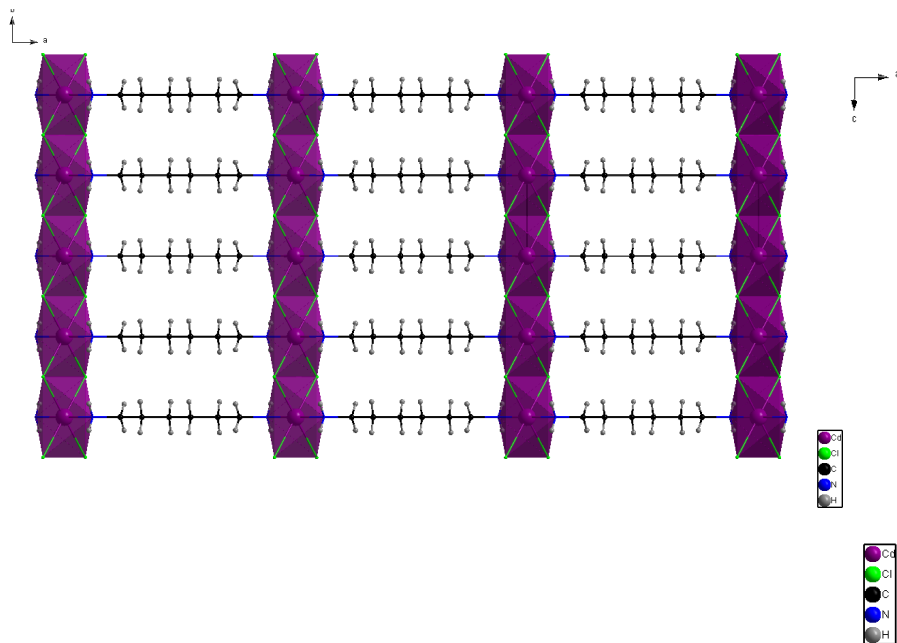
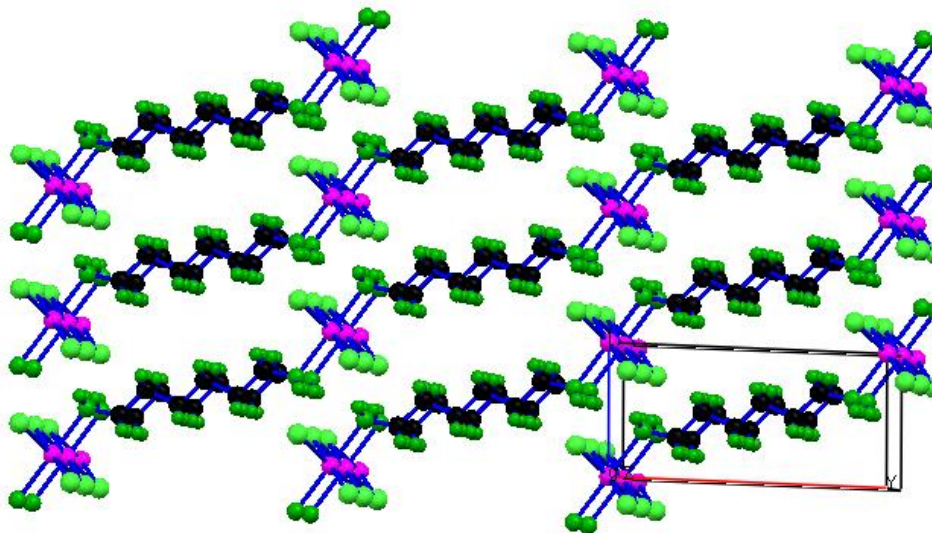


# Isolated polymer chains

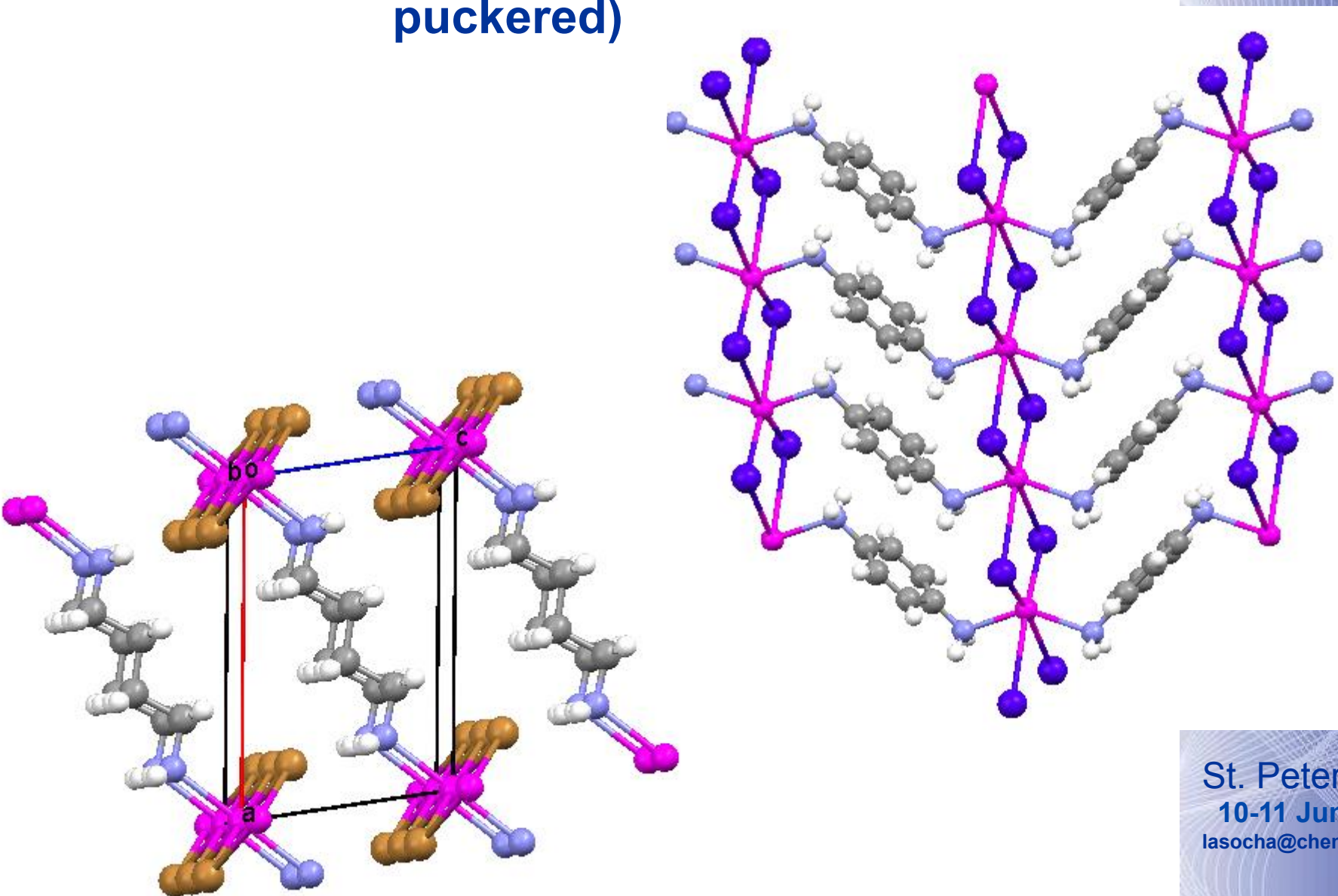


# Isolated polymer chains

**CdCl<sub>2</sub> – 1,6-diaminohexane**

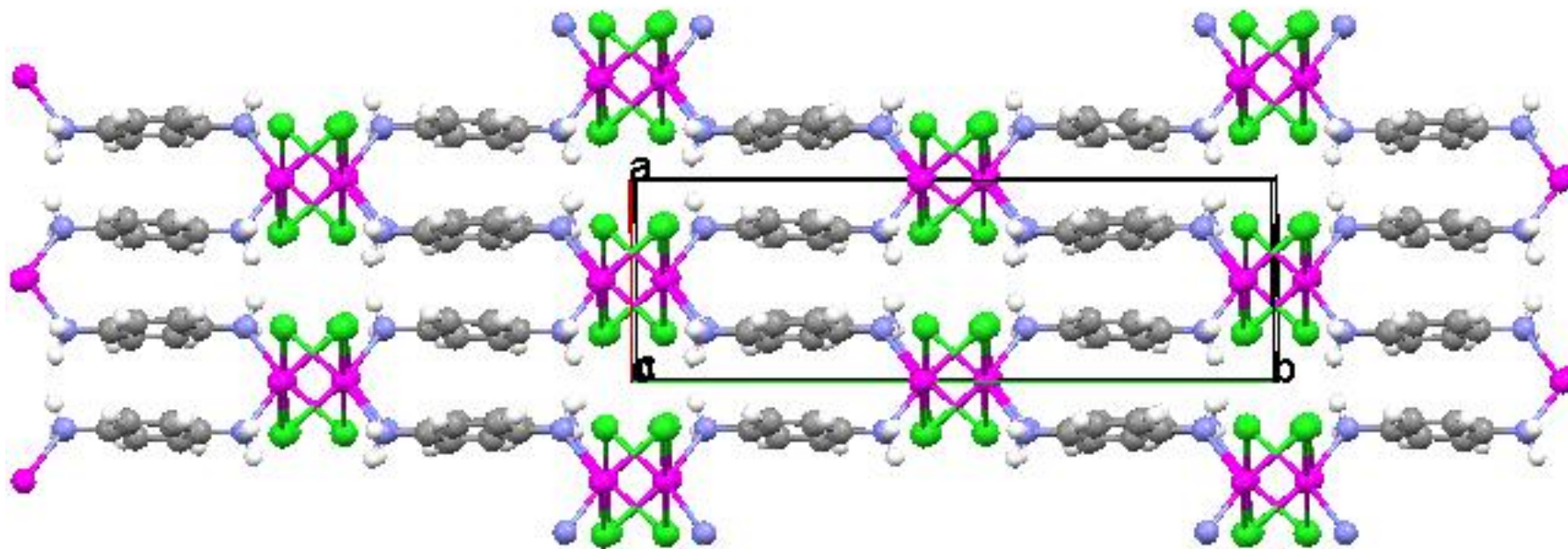


# Polymer chains combined into layers (not always of equal thickness, puckered)



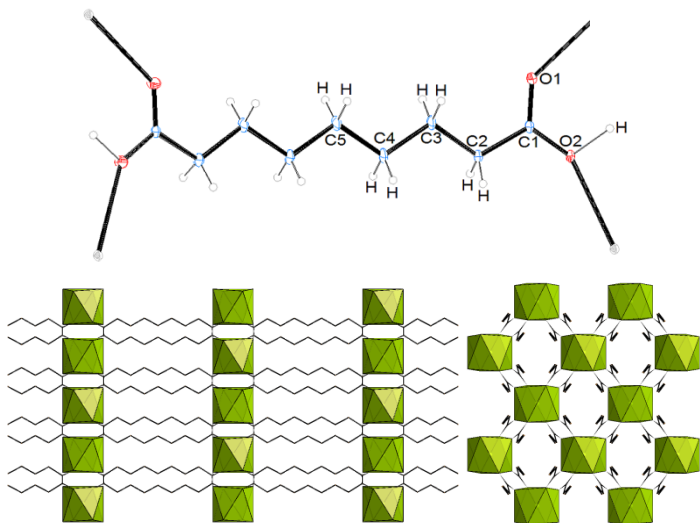


# Three-dimensional structures can be formed

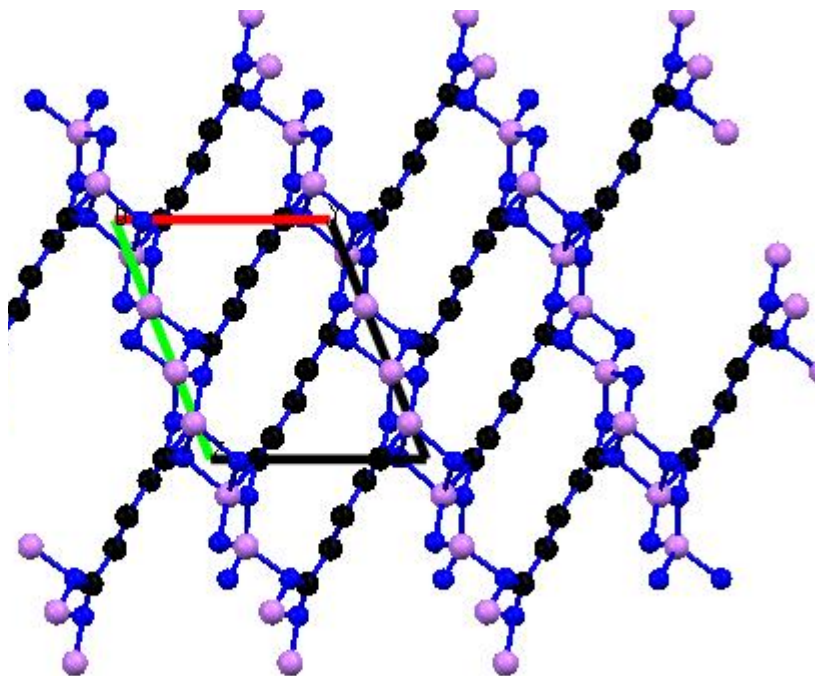


We are trying to create new: 1 -, 2 - or 3-dimensional materials, looking for porous materials with a given geometry of channels, etc..

# Salts of dicarboxylic acids



Dilithium glutarate

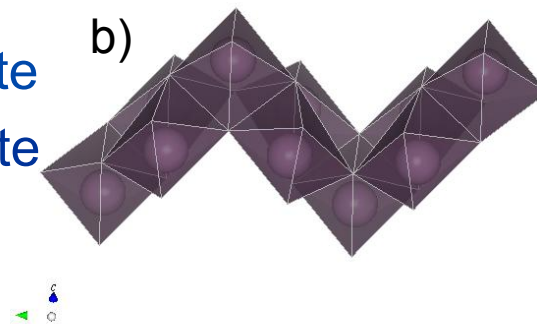


# Polymolybdates – Mo based catalysts

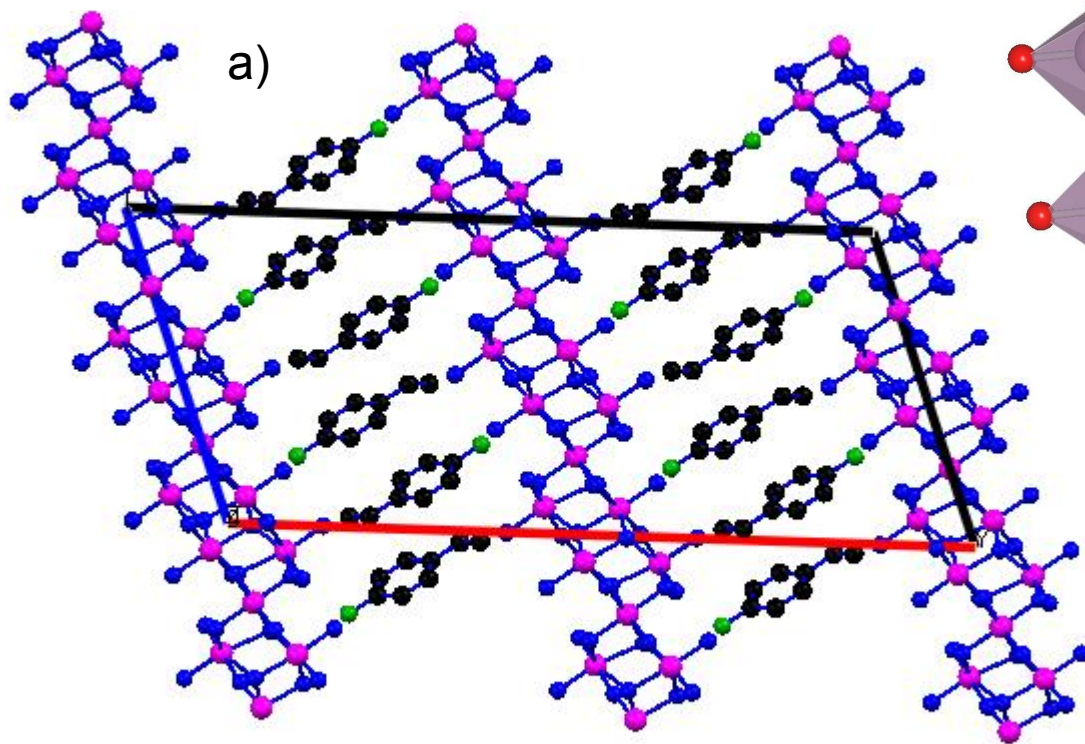
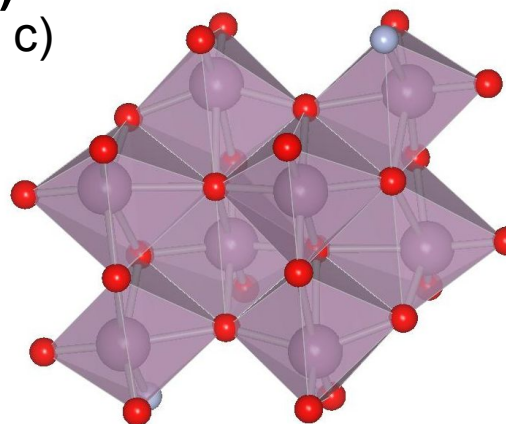
- Barium trimolybdate
- Bis(4-hydroksyanilinium) trimolybdate hydrate
- Bis(4-ethylanilium) pentamolybdate



- a) Bis(4-ethylanilinium) pentamolybdate
- b) Bis(4-hydroksyanilinium) trimolybdate
- c) Barium molybdate



**We are trying to correlate the type of anion and properties (e.g catalytic)**





# Results obtained so far...

- We have already finished investigations of 15 samples
- Their crystal structures have been solved by powder diffraction methods; tests of other structures are in progress...
- We have started also investigations based on pair distribution functions formalism (pdf)
- We have gathered experience with the synthesis of porous or layered materials
- Catalytic and photocatalytic tests are in progress...

## Co-workers:

- Synchrotron measurements:
  - **Graham Appleby**, DESY, Hamburg
- Structure solution
  - **Marta Grzesiak-Nowak**, IC PAS
  - **Anna Szymańska**, IC PAS
  - **Marcin Oszejca**, JU
  - **Marcin Koziół**, JU
- Applications
  - **Zbigniew Miara (FAMAR)**
  - **Alicja Rafalska-Łasocha** JU



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**Thank you very much for  
your attention**

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