LECTURE SCHEDULE

	Date		Topic
1.	Wed	28.10.	Course Introduction & Short Review of the Elements
2.	Fri	30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed	11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri	13.11.	Redox Chemistry
6.	Mon	16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed	18.11.	Zn, Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri	20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon	23.11.	Cr, Mo, W & 2D materials
10	Wed	25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri	27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon	30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed	02.12.	Inorganic Materials Chemistry Research

EXAM: Thu Dec 10, 9:00-12:00 Ke1

QUESTIONS: Lecture 8

1. **Explain shortly:**

   Perovskite

   MOF

   MLD

2. **Name the following metal complexes:**

   $K_3[Fe(CN)_6]$

   $[CoN_3(NH_3)_5]SO_4$

   $NH_4[Cr(NCS)_4(NH_3)_2]$

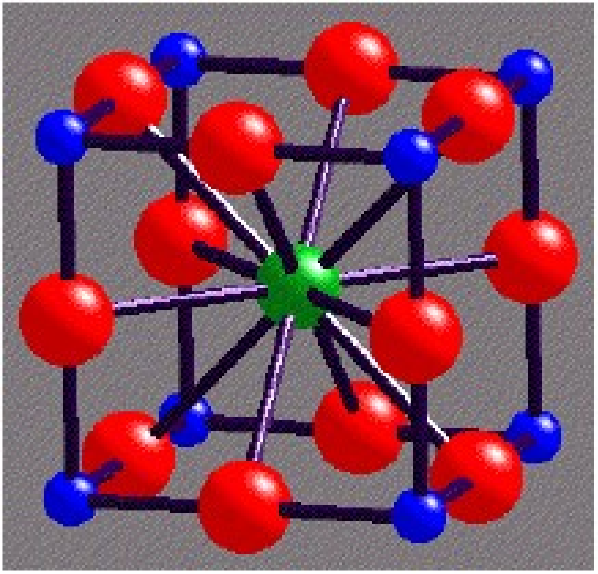
   $[Cr(H_2O)_6]Cl_3$

   $[Al(OH)(H_2O)_5]^{2+}$

APPLICATIONS of NIOBIUM

- **NbN, NbTi, Nb_3Sn and Nb_3Ge (T_c = 10 - 23 K) superconductors** (used in practical applications)
  → strong magnets
  → e.g. MRI, NMR
- **$LiNbO_3$ and $LiTaO_3$:**
  - distorted perovskite structure
  - ferroelectric
    (electrical dipole moment without external electric field)
- **Bronzes: e.g. Sr_xNbO_3 (x = 0.7 - 0.95)**
  - good electrical conductivity
  - *A*-cation deficient ABO_3 perovskite structure
  - ref. Na_xWO_3
- **Additive in steels and metal alloys**
- **Low neutron absorption (ref. Zr)**

ABO_3



PEROVSKITE STRUCTURE

General formula: $ABO_{3-\delta}$

A: large cation

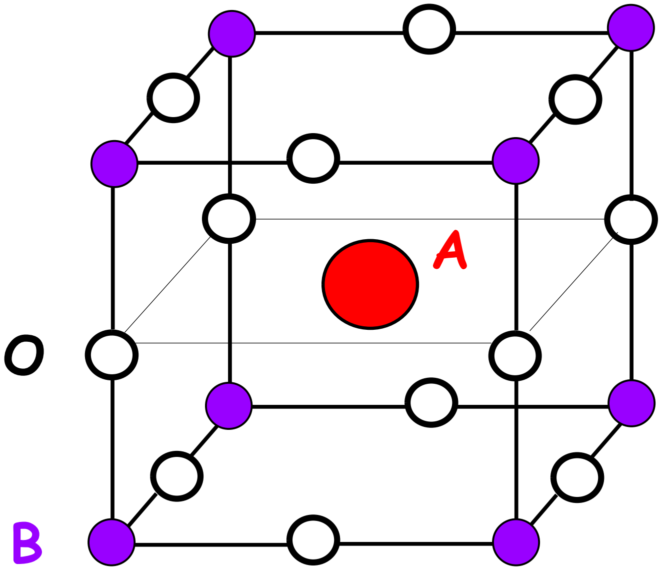
B: small cation (transition metal)

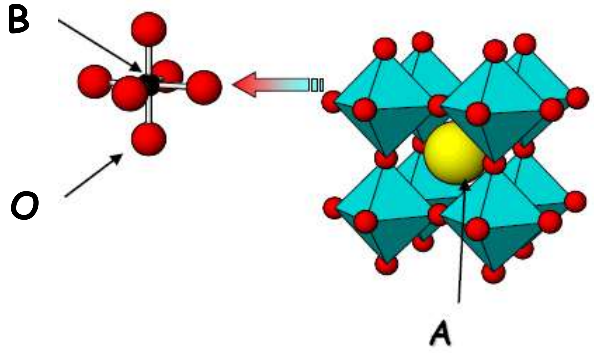
O: oxygen (sometimes halogen)

V(A) + V(B) = 6

e.g. $La^{III}Sc^{III}O_3$, $Sr^{II}Ti^{IV}O_3$, $Na^{I}Nb^{V}O_3$

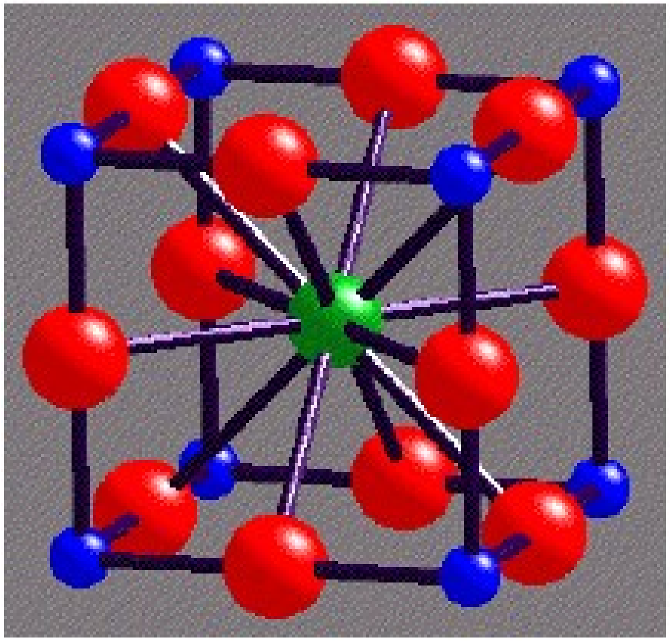
CN(A)=12, CN(B)=6, CN(O)=6



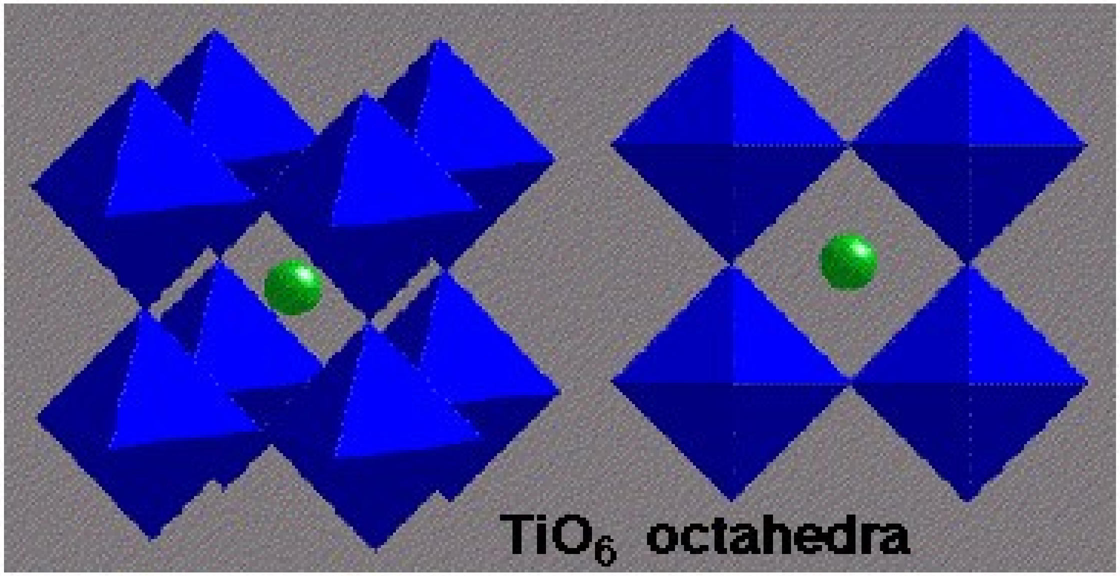


Mineral Perovskite: $CaTiO_3$

- Named after Russian mineralogist, Count Lev Aleksevich von Perovski
- Discovered by Gustav Rose in 1839 from samples found in Ural Mountains



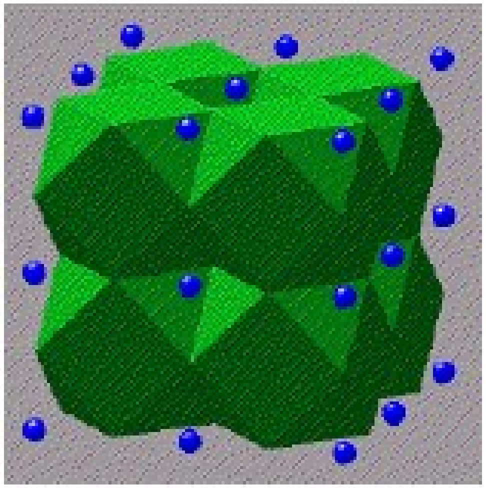
A-Cell



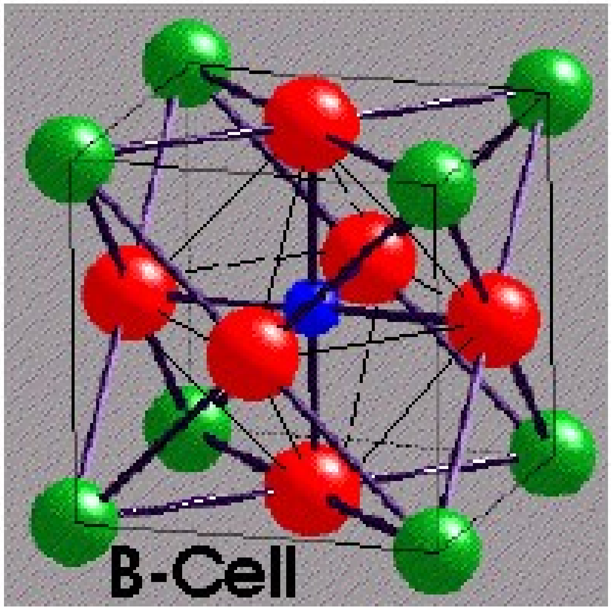
Perovskite

$CaTiO_3$

● Ca ● Ti ● O



CaO_{12} cuboctahedra



Perovskite – Multifunctional structure

Perovskite
ABO_3

Ion conductor
$La(Co,Ga)O_3$

Electric insulator
$SrTiO_3$

Superconductor
$CuBa_2YCu_2O_{6+z}$

Magnetoresistor
$LaMnO_3$

Record-high melting point
$Ba_3MgTa_2O_9$

Major constituent of earth
$MgSiO_3$

Catalyst
$La(Co,Mn)O_3$

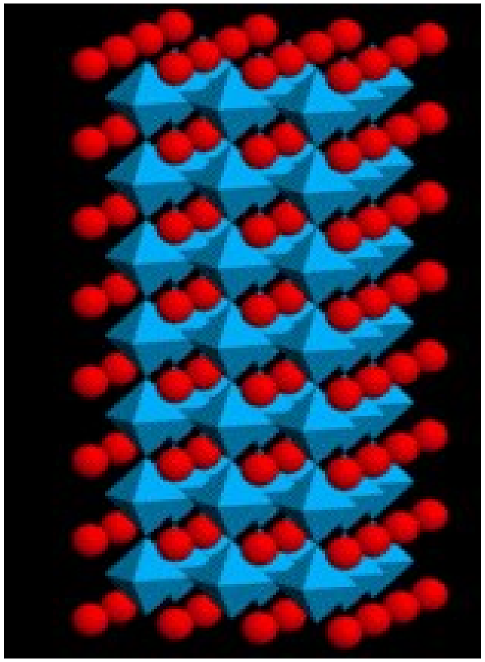
Metallic conductor
$LaCrO_3$

Piezoelectric material
$Pb(Zr,Ti)O_3$

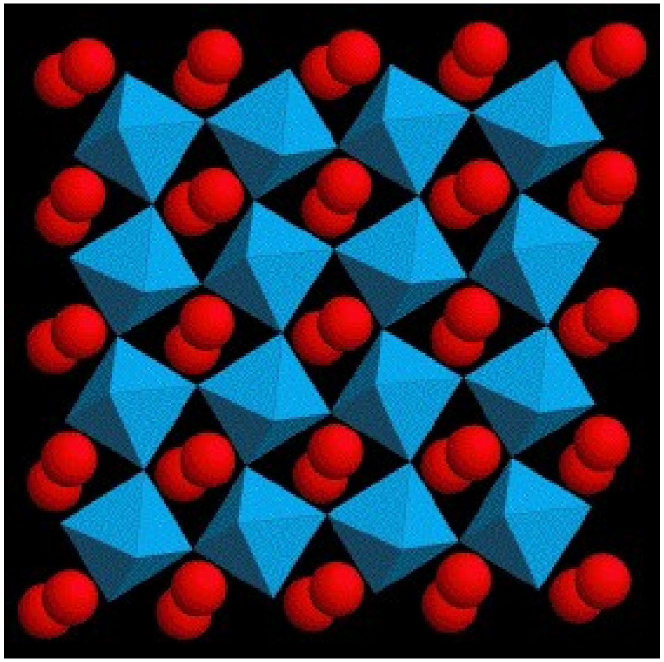
Capasitor
(high dielectric constant)
$BaTiO_3$

“Distortions and Imperfections” in Perovskite Structure

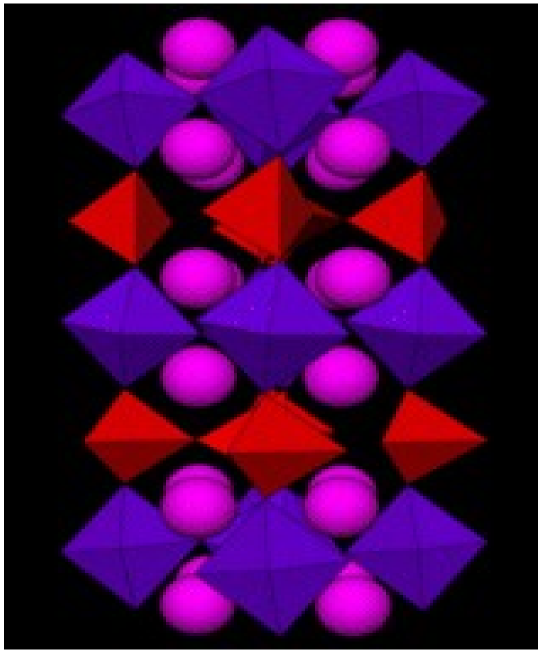
- often the source of the desired properties



IDEAL

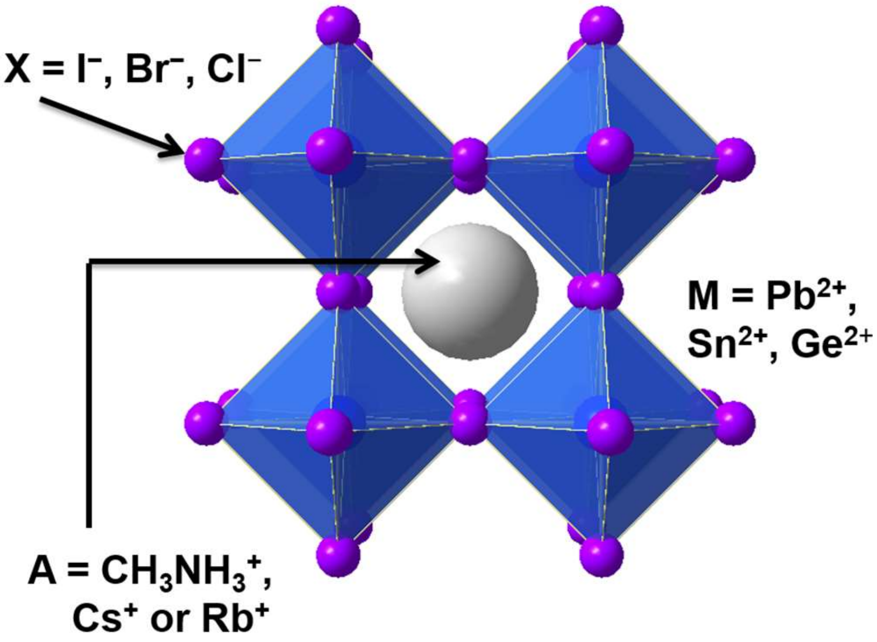


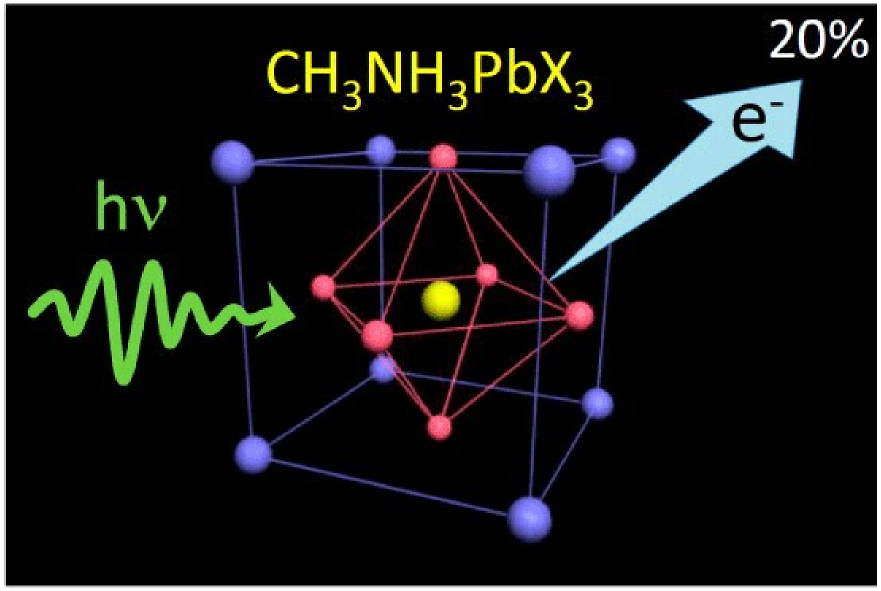
Changes in atomic positions

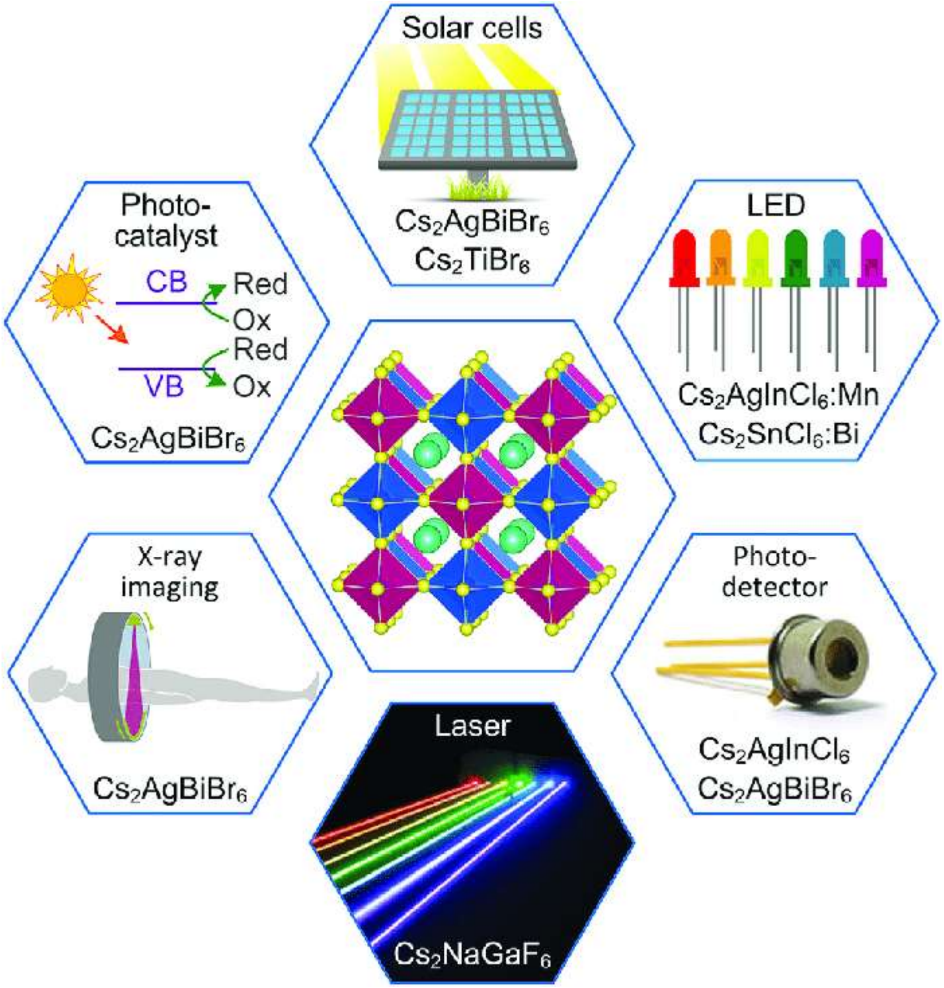


Oxygen deficiency

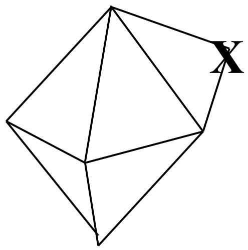
“Perovskite Solar Cell”



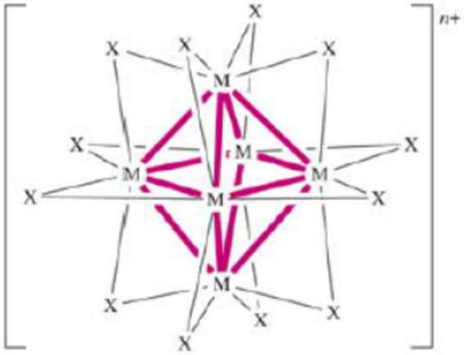




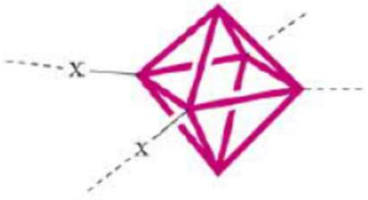
METAL CLUSTER COMPOUNDS



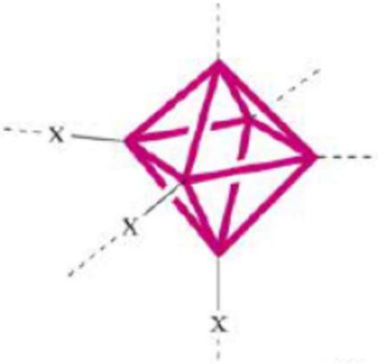
- Metal cluster: metal-metal bonds
- Typical for Nb and Ta (with low oxidation states and d electrons)
- general formula $[M_6X_{12}]^{n+}$
  - metals (M) form octahedra
  - halides (X) at edges and bonded to two metals



- each basic unit can bond via halide atoms:
  - to four similar units
    - 2D sheets
    - average formula $MX_{2.3}$
    - diamagnetic

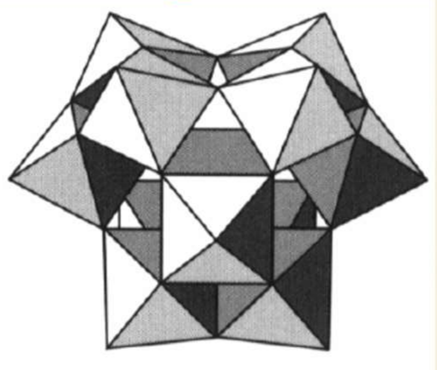


  - to six similar units
    - 3D networks
    - average formula $MX_{2.5}$
    - paramagnetic



ISO- and HETEROPOLYANIONS

- ”Coordination compounds” (V, Nb, Ta, Mo, W)
- Also called PolyOxoMetallates (POMs)
- First synthesized in 1826: $[PMo_{12}O_{40}]^{3-}$
- *M* metal at its highest oxidation state
  → OXOPHILIC
- Basic structure unit: MO_6
- IsoPolyAnion (IPA): $[M_nO_y]^{p-}$
- HeteroPolyAnion (HPA): $[X_zM_nO_y]^{q-}$ $(z \leq n)$
- Dissolve as distinct units
- Many applications in chemistry, catalysis and medicine



$[PMo_{12}O_{40}]^{3-}$

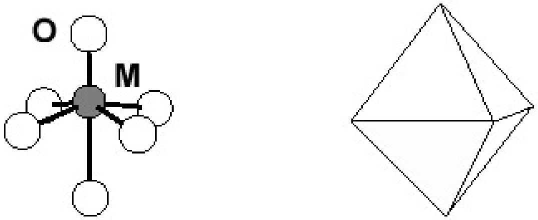


Figure 1.1. Ball-and-stick and polyhedral representations of the fundamental unit MO_6. Note that the M atom is displaced off the geometrical centre of the octahedron towards one of the oxygens, thus giving rise to a distorted C_{4v} unit.

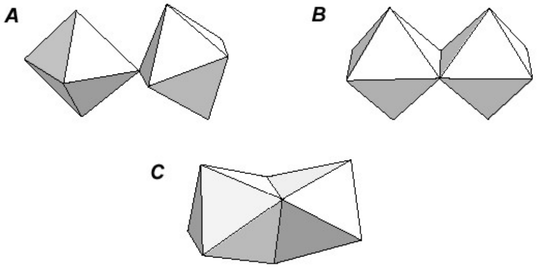
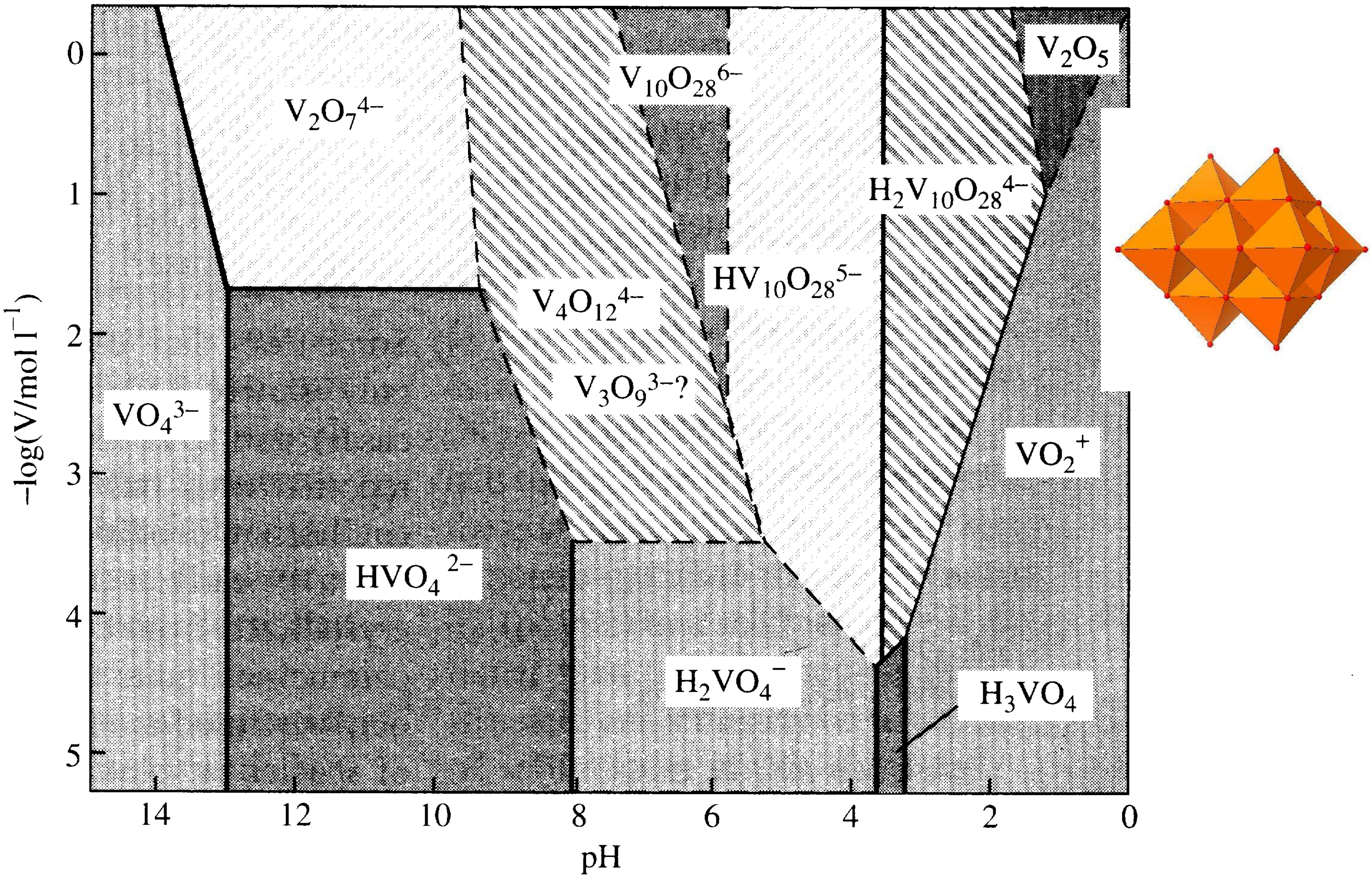


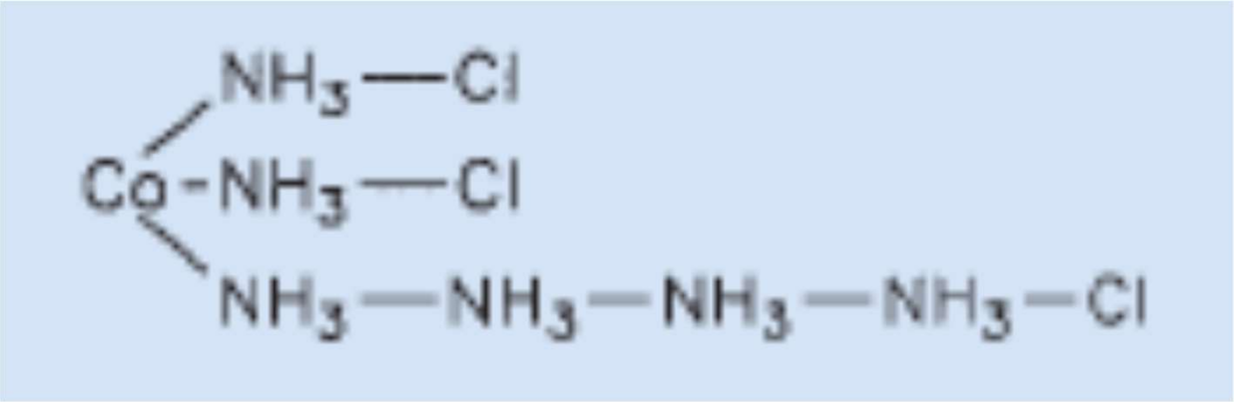
Figure 1.2. The polyhedral models represent the three possible unions between two MO_6 octahedral units. A) corner-sharing, B) edge-sharing and C) face-sharing. Each corner represents an oxygen position.



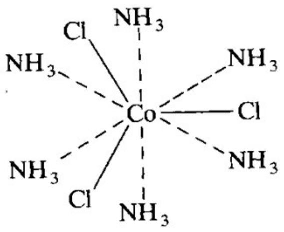
Occurrence of various vanadate and polyvanadate species as a function of pH and total concentra of vanadium.

HISTORY of COORDINATION COMPLEXES

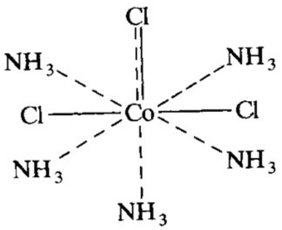
- Prussian blue: $KFe[Fe(CN)_6]$
  - synthesized in 1704 in Berlin
  - used as a pigment in Prussian army uniform
- Tassaert 1798: $CoCl_3$ x 6 NH_3
  - cobolt chloride + ammonia → brownish red product
- Blomstrand-Jörgensen chain theory:
  - derived from organic chemistry:
    ammine-chains + chlorine at the ends



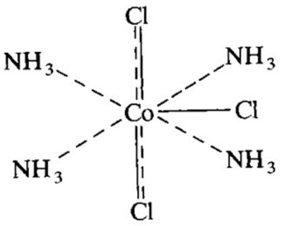
(1) $CoCl_3 \cdot 6NH_3$

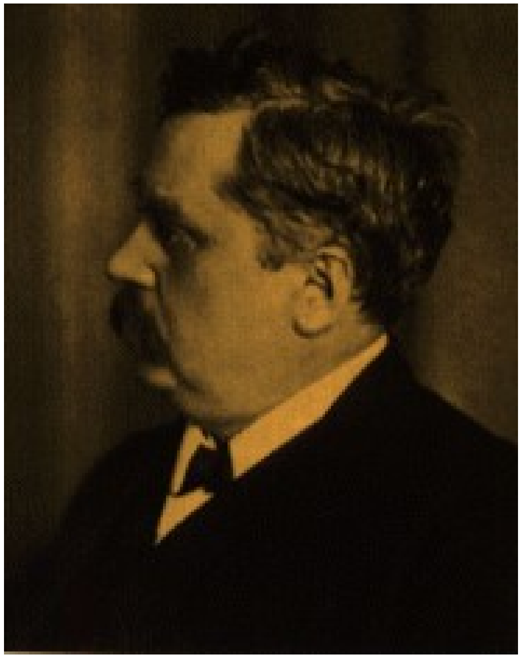


(2) $CoCl_3 \cdot 5NH_3$



(3) $CoCl_3 \cdot 4NH_3$





Alfred Werner
(1866-1919)
Nobel 1913

WERNER COORDINATION THEORY

- Alfred Werner 1892 (University of Zurich)

- Two “valences”
  - primary valence (*hauptvalenz*) ≈ oxidation state (___)
  - secondary valence (*nebenvalenz*) ≈ coordination number (-----)

MODERN COORDINATION THEORY

- **central cation (Co; prefers 6-coordination = ”secondary valence 6”)**
- **coordinated ligands (e.g. NH_3) within the brackets**
- **Cl^- ions within the brackets belong to the coordination sphere**
- **Cl^- ions outside of the brackets (so-called counter ions) contribute to the oxidation state only (primary valence 3)**
- **Outside-of-brackets Cl^- ions can be removed in water solutions**

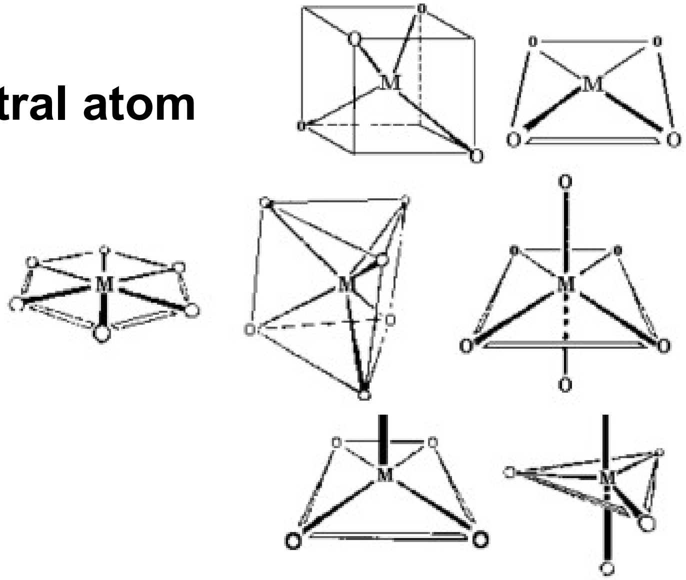
(1) $CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$
(2) $CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$
(3) $CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4]Cl_2]Cl$
(4) $CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$

These complexes differ in colour and electrical conductivity

- $[Pt(NH_3)_6]Cl_4$ has relatively high conductivity (more ions)
- $[Pt(NH_3)_5Cl]Cl_3$ has decreasing conductivity
- $[Pt(NH_3)_4Cl_2]Cl_2$ has decreasing conductivity
- $[Pt(NH_3)_3Cl_3]Cl$ has decreasing conductivity
- $[Pt(NH_3)_2Cl_4]$ has zero conductivity

COORDINATION CHEMISTRY

- **Metal complex: $[ML_n]X_y$ tai $A_b[ML_n]$**
- **Central atom (M): metal cation or neutral metal atom**
- **Ligands (L; lat. *ligare* = to bind = sitoa):**
  - molecules or ions around the central atom
  - infinite/integer number (n)
  - ligands form the coordination sphere of the central atom



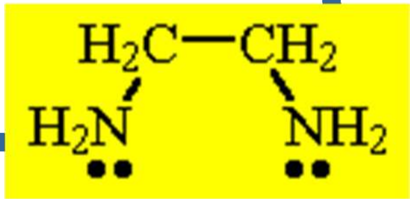
- **Metal-ligand bond: $M \leftarrow :L$**
  - each ligand gives an electron pair to the central atom
  - COVALENT COORDINATION BOND
- **Coordination number (CN = n):**
  - typically 4 (tetrahedron or square-plane) or 6 (octahedron)
  - sometimes 5 (pyramid or trigonal bipyramid)
- **Counter ion: anion (X) or cation (A)**
- **Typical for metal complexes: bright colours & magnetism**

DENTICITY and CHELATE EFFECT

- Monodentante: ligand bonds to the central atom via one atom
- Multidentante: ligand bonds to the central atom via multiple atoms
- Ambidentate (changing):

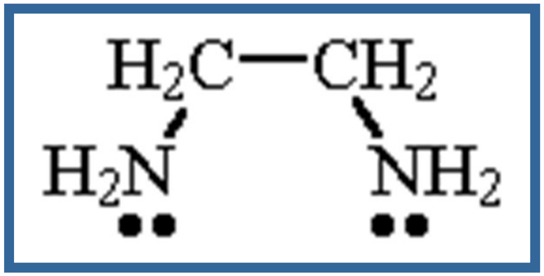
  depending on conditions, ligand may bond via different atoms to the central atom, e.g.:
  - CN (cyano) and NC (isocyano)
  - SCN (thiocyanato) and NCS (isothiocyanato)
  - NO_2 (nitro) and ONO (nitrito)

- Chelate: complex compound in which multidentante ligands
- CHELATE EFFECT:
  - chelates are unusually stable
  - e.g. $[Ni(en)_3]^{2+}$ ca. 10 times more stable than $[Ni(NH_3)_6]^{2+}$

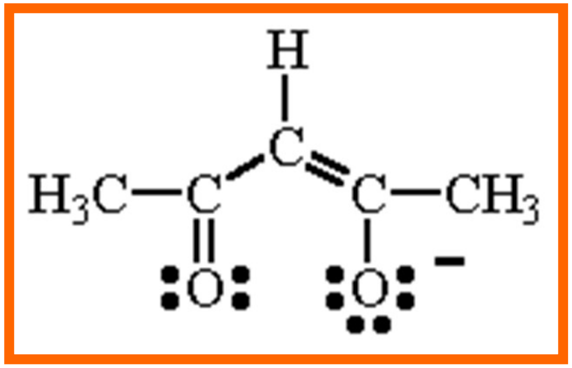


Ethylenediamine (en)

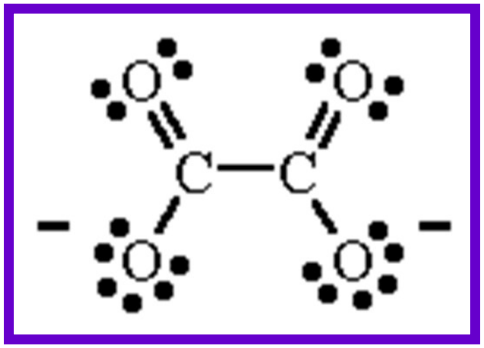
Examples of 2-dentante ligands



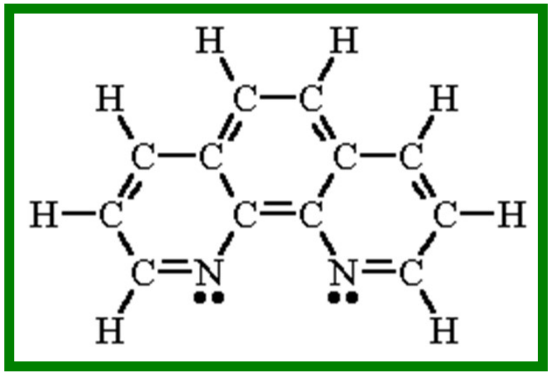
Ethylenediamine (en)



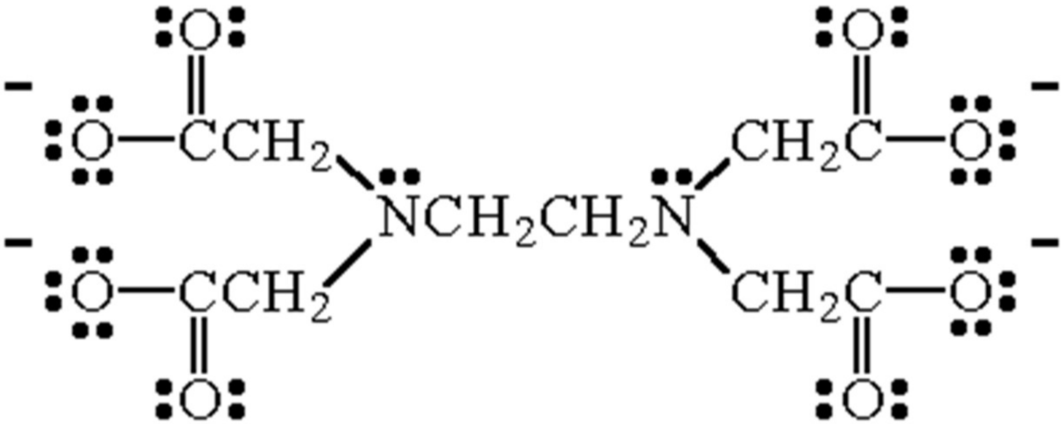
Asetyleneacetonato (acac)

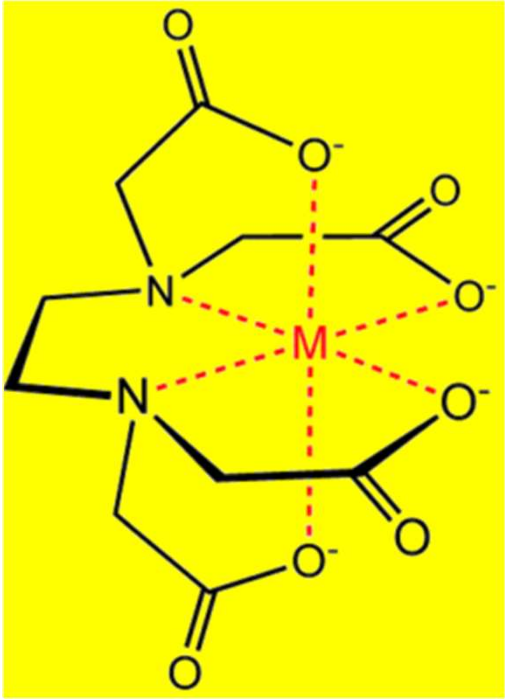


Oxalato (ox)



Phenantroline (phen)





EDTA^{4-}

- 6-dentante
- extremely stable complexes with most of the transition metal
- typically octahedral structures
- bonds via 2 N-atoms and 4 negatively charged O-atoms

NAMING

- **Ligand names:**

(1) negative ligand: o-ending

F^- fluoro
Cl^- chloro
Br^- bromo
I^- iodo
O^{2-} oxo
OH^- hydroxo
NO_2^- nitro
CN^- cyano

(2) neutral ligand: name of the molecule without changes

(3) positive ligand: ium-ending (e.g. hydratsinium $NH_2NH_3^+$)

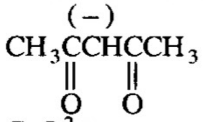
(4) trivial names:

- aqua H_2O
- ammine NH_3
- carbonyl CO
- nitrosyl NO

(5) ambidentante ligands:

- nitro NO_2^- and nitrito ONO^-
- thiocyanato SCN^- and isothiocyanato NCS^-

(6) bridging ligands: μ-

F^-	fluoro		
Br^-	bromo		
I^-	iodo		
CO_3^{2-}	carbonato		
NO_3^-	nitrato		
SO_3^{2-}	sulfito		
$S_2O_3^{2-}$	thiosulfato		
SO_4^{2-}	sulfato	Common bridging ligands	
CO	carbonyl		
Cl^-	chloro		
O^{2-}	oxo		
O_2^{2-}	peroxo		
OH^-	hydroxo		
NH_2^-	amido		
CN^-	cyano		Ambiden ligands
SCN^-	thiocyanato		
NO_2^-	nitro		
H_2O	aquo		
NH_3	ammine		
CH_3NH_2	methylamine		
$P(C_6H_5)_3$	triphenylphosphine		
$As(C_6H_5)_3$	triphenylarsine		
N_2	dinitrogen		
O_2	dioxygen		
NO	nitrosyl		
C_2H_4	ethylene		
C_5H_5N	pyridine		
	Multidentate ligands		
$NH_2CH_2CH_2H_2$	ethylenediamine (en)	(2)	
 $CH_3\underset{\underset{O}{\|}}{C}\overset{(-)}{CH}\underset{\underset{O}{\|}}{C}CH_3$	acetylacetonato (acac)	(2)	
$C_2O_4^{2-}$	oxalato	(2)	
$NH_2CH_2COO^-$	glycinato (gly)	(2)	
$NH_2CH_2CH_2NHCH_2CH_2NH_2$	diethylenetriamine (dien)	(3)	
$N(CH_2COO)_3^{3-}$	nitrilotriacetato (NTA)	(4)	
$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$	ethylenediaminetetraacetato (EDTA)	(6)	

■ Naming of complexes/complex compounds:

(1) cation first, then anion

(2) ligands in alphabetical order (prefix does NOT affect) before central atom

(3) number of similar ligands:

prefix: di-, tri-, tetra-, penta-, hexa-

- monoatomic ligands
- polyatomic ligands with short name
- neutral ligands with trivial names

prefix: bis-, tris-, tetrakis-

- ligands with prefix di-, tri- …
- neutral ligands (no trivial name)
- ionic ligands with very long names

(4) anionic complex: central atom with ate-ending (cuprate, ferrate, …)

(5) oxidation state of central atom with Roman numerals in parentheses

EXAMPLES

- $[Co(NH_3)_4Cl_2]Cl$

  - ligands in alphabetical order: NH_3 neutral (trivial) → ammine
    Cl negative → chloro
  - 4 ammine ligands and 2 chloro ligands → tetraamminedichloro
  - Cl is anion, complex is cation, cobalt oxidation state +3 → cobalt(III)

  tetraamminedichlorocobalt(III)chloride

- $(NH_4)_2[Pt(NCS)_6]$

  - 6 negative NCS ligands (bonding via N) → hexaisothiocyanato
  - NH_4 cation → ammonium
  - complex is anion, platinum oxidation state +4 → platinate(IV)

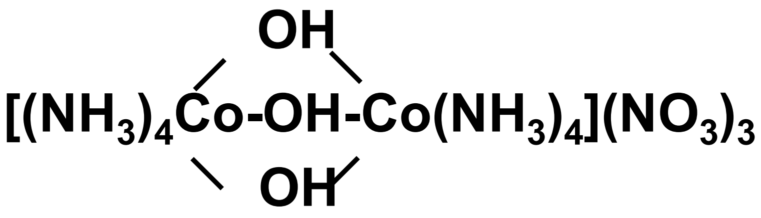
  ammoniumhexaisothiocyanatoplatinate(IV)

- $[Cu(NH_2CH_2CH_2NH_2)_2]SO_4$

  bis(ethylenediamine)copper(II)sulphate

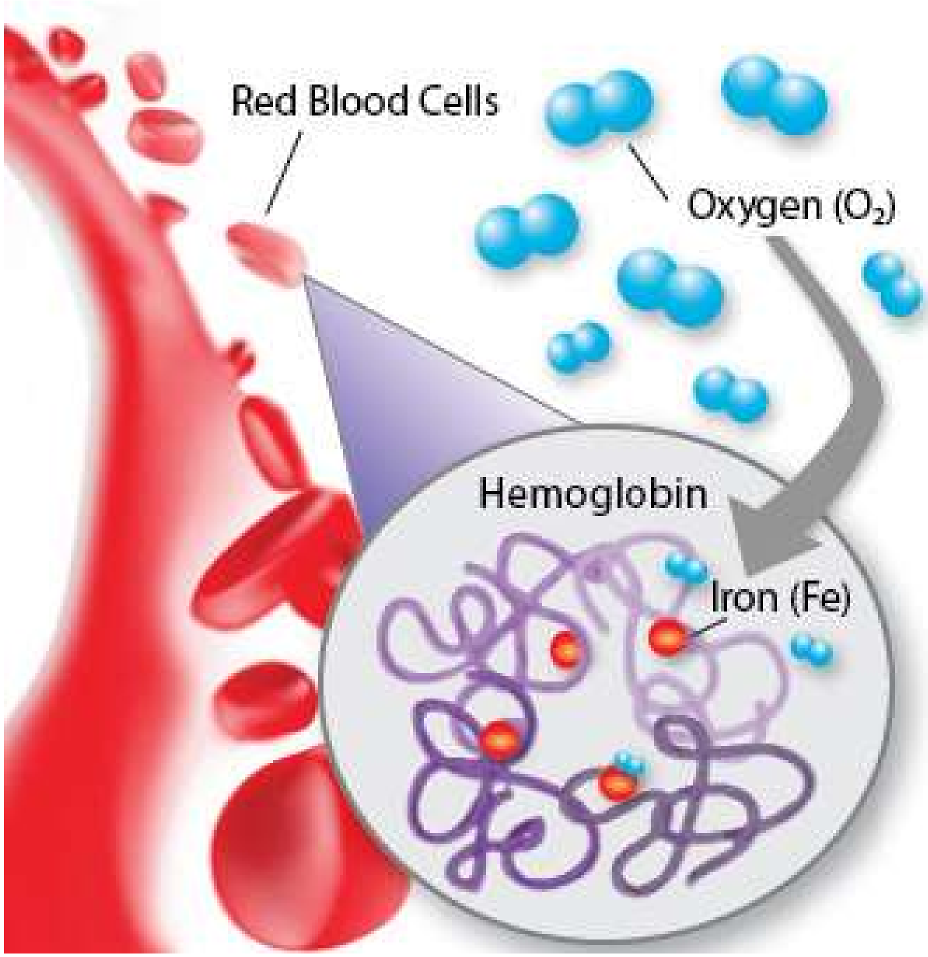
- $[Ag(CH_3NH_2)_2]\ [Mn(H_2O)_2(C_2O_4)_2]$

  bis(methylamine)silver(I)diaquadioxalatomanganate(III)

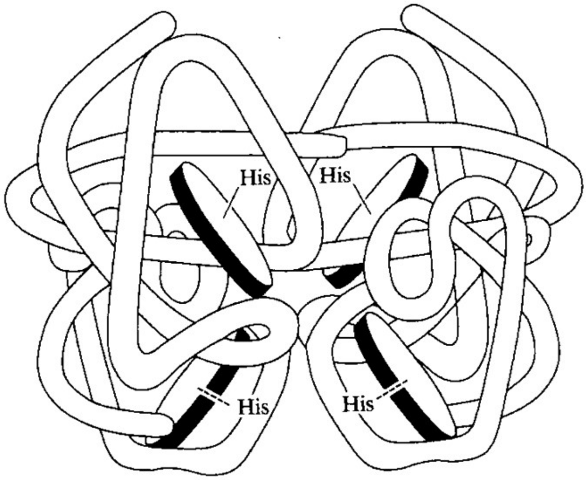
- 

  $[(NH_3)_4Co\text{-}OH\text{-}Co(NH_3)_4](NO_3)_3$

  tetraamminecobalt(III)-μ-trihydroxotetraamminecobalt(III)nitrate

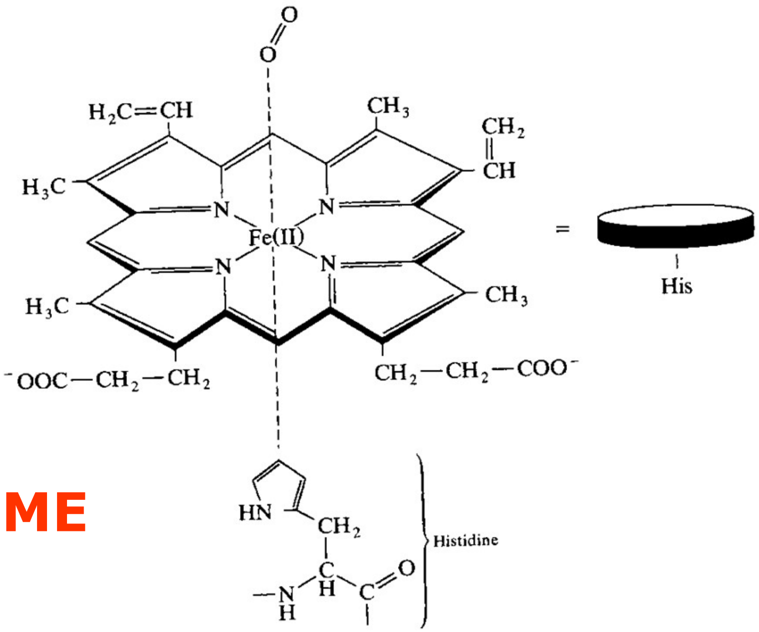


GLOBIN



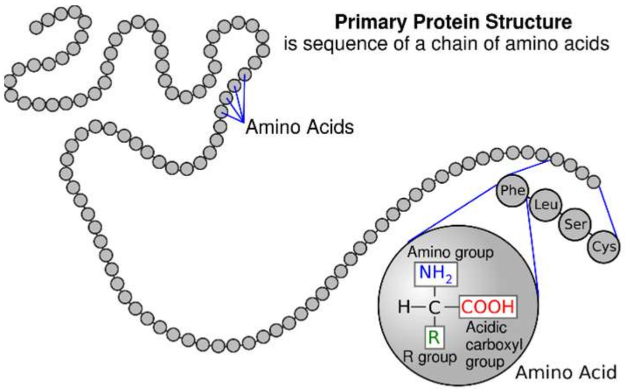
(a)

HEME

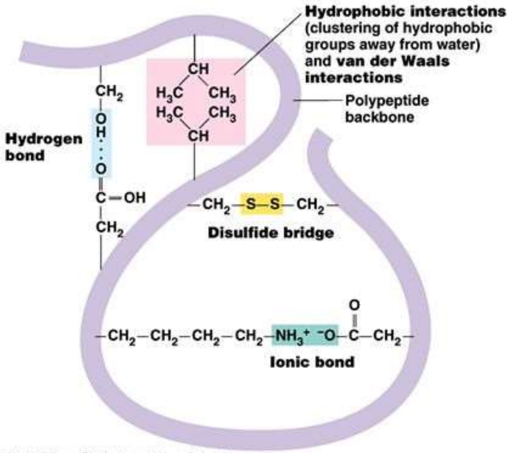


(b)

LEAD POISONING



- **Lead (and other heavy metals):**
  - **readily binds to aminoacids (of proteins)**
- **EDTA first aid:**
  - **binds effectively Pb, but also other metals (e.g. Ca)**
- **Penicillamine treatment:**
  - **binds via S more selectively to Pb**



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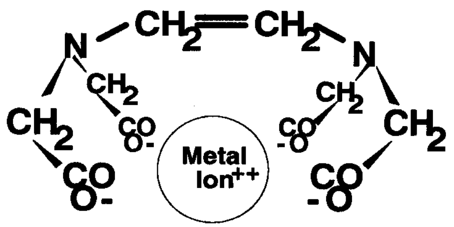
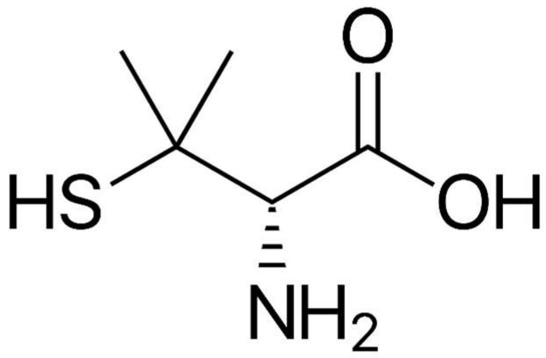
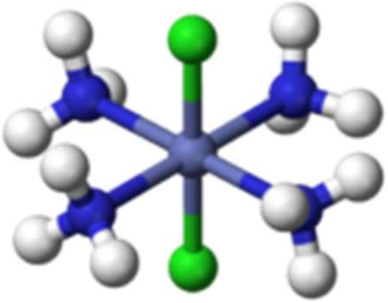


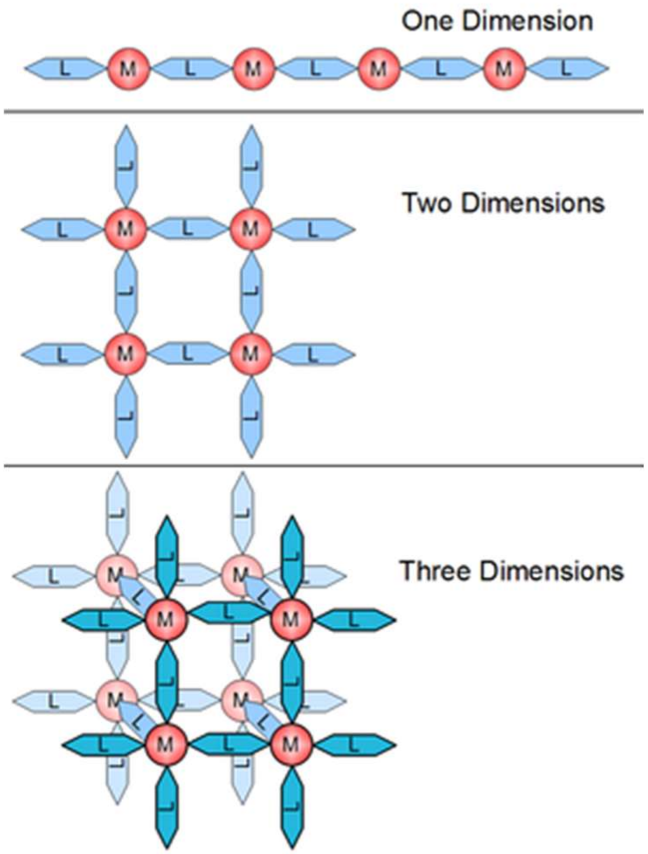
Ethylenediaminetetraacetic acid (EDTA) chelates a metal ion

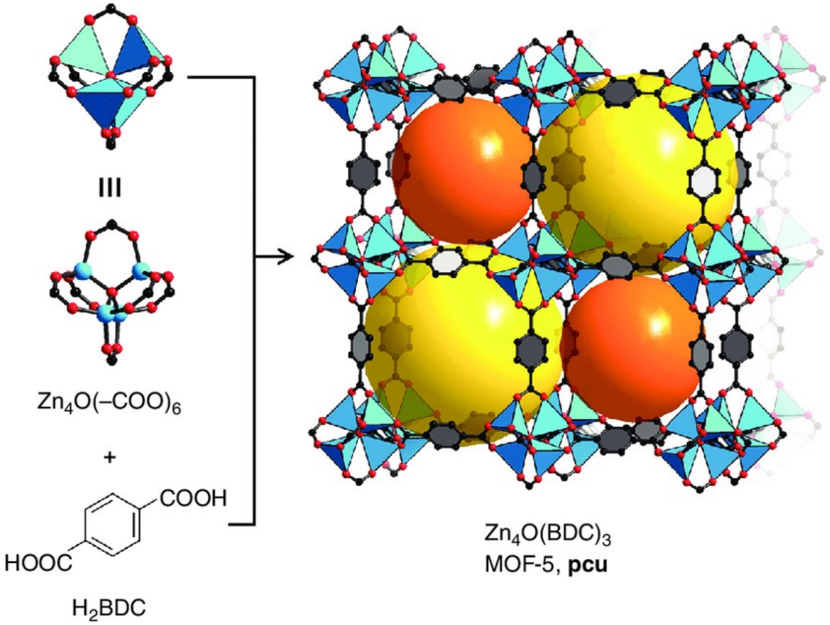


Inorganic-Organic Materials

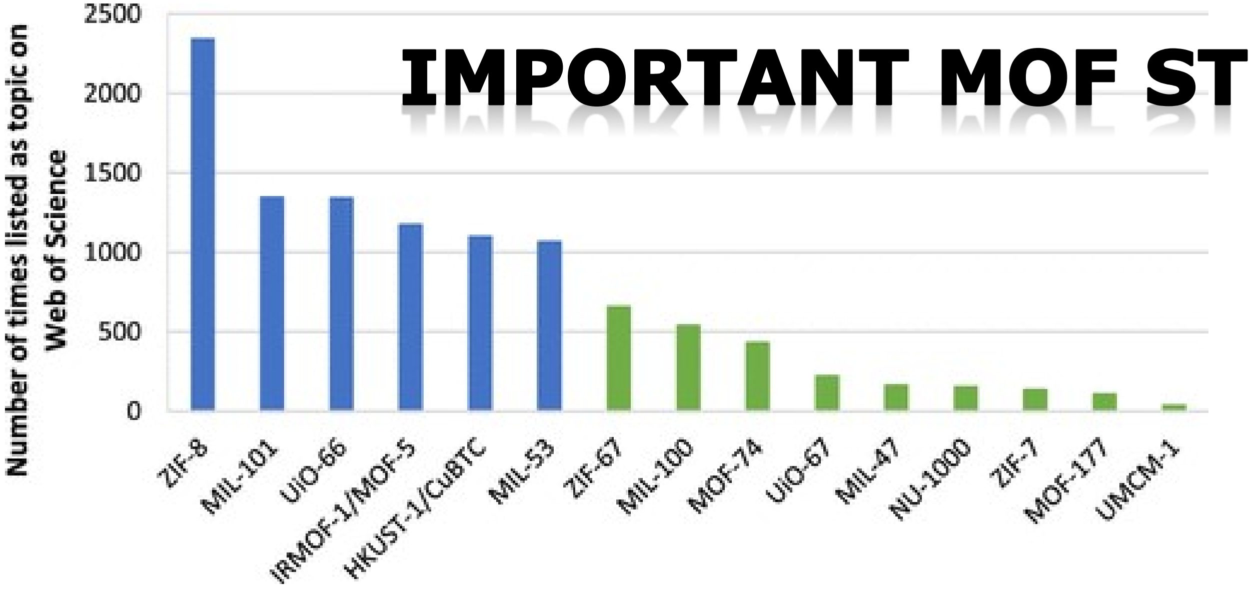
- **Compound NOT Composite**
- **Coordination Complex: central metal ion + (organic) ligands**
- **Coordination Polymer/Network: ligands act as bridges**
- **Metal-Organic Framework (MOF): highly porous**

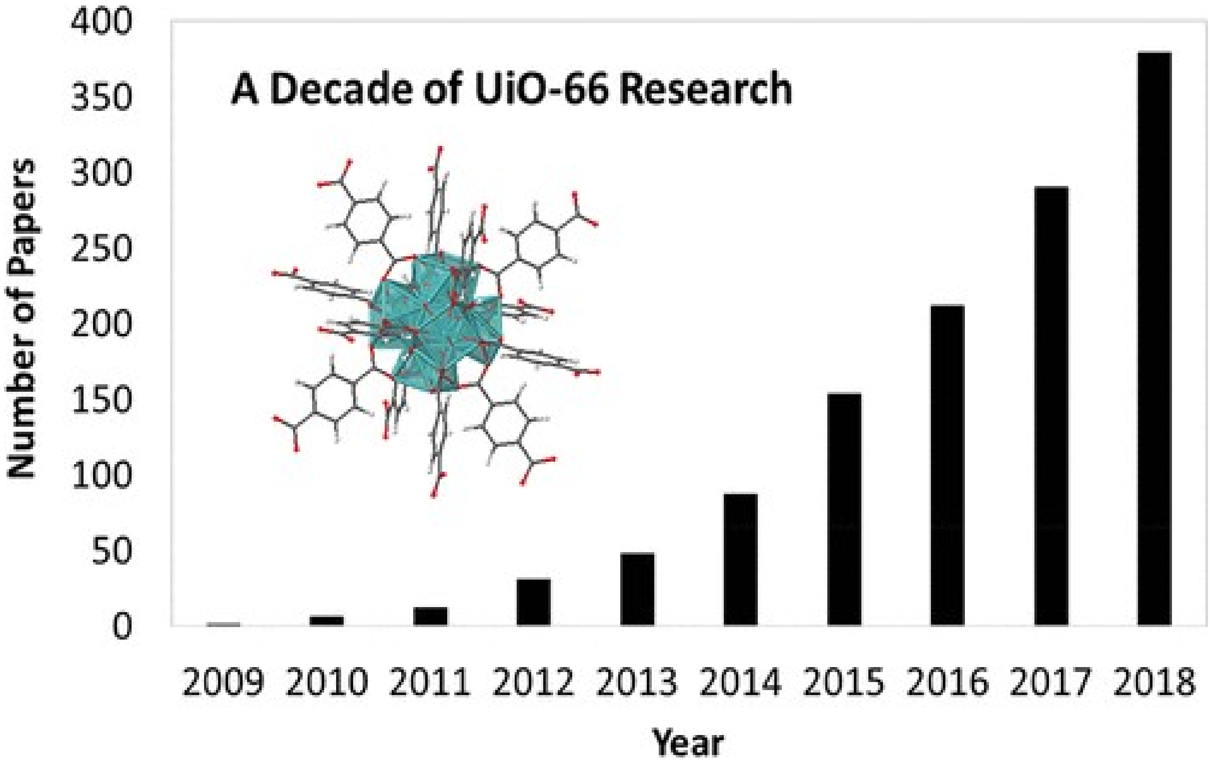




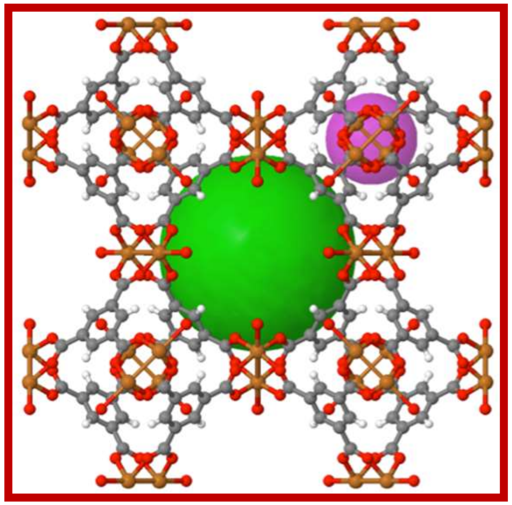


IMPORTANT MOF STRUCTURES

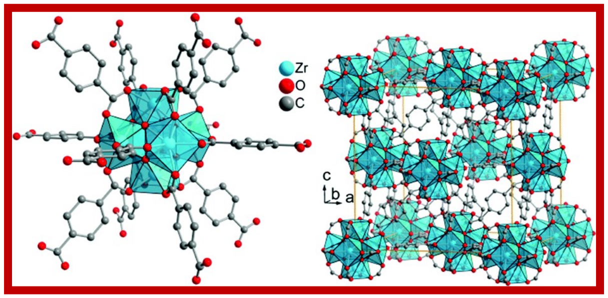


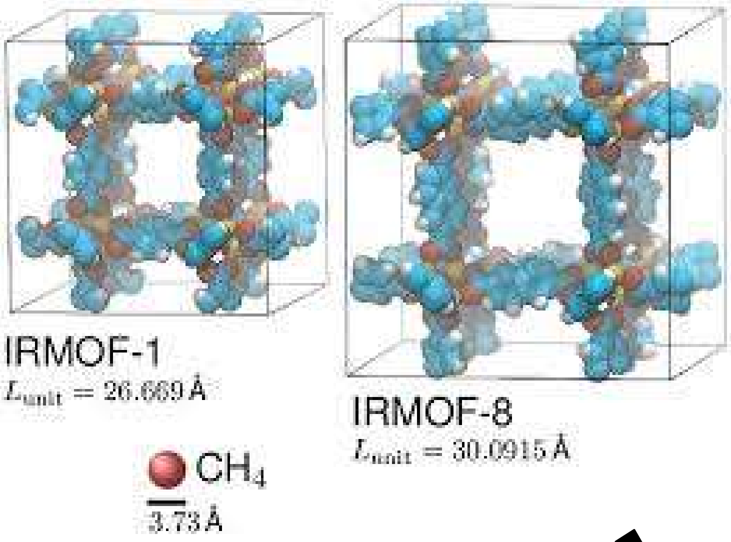


HKUST-1

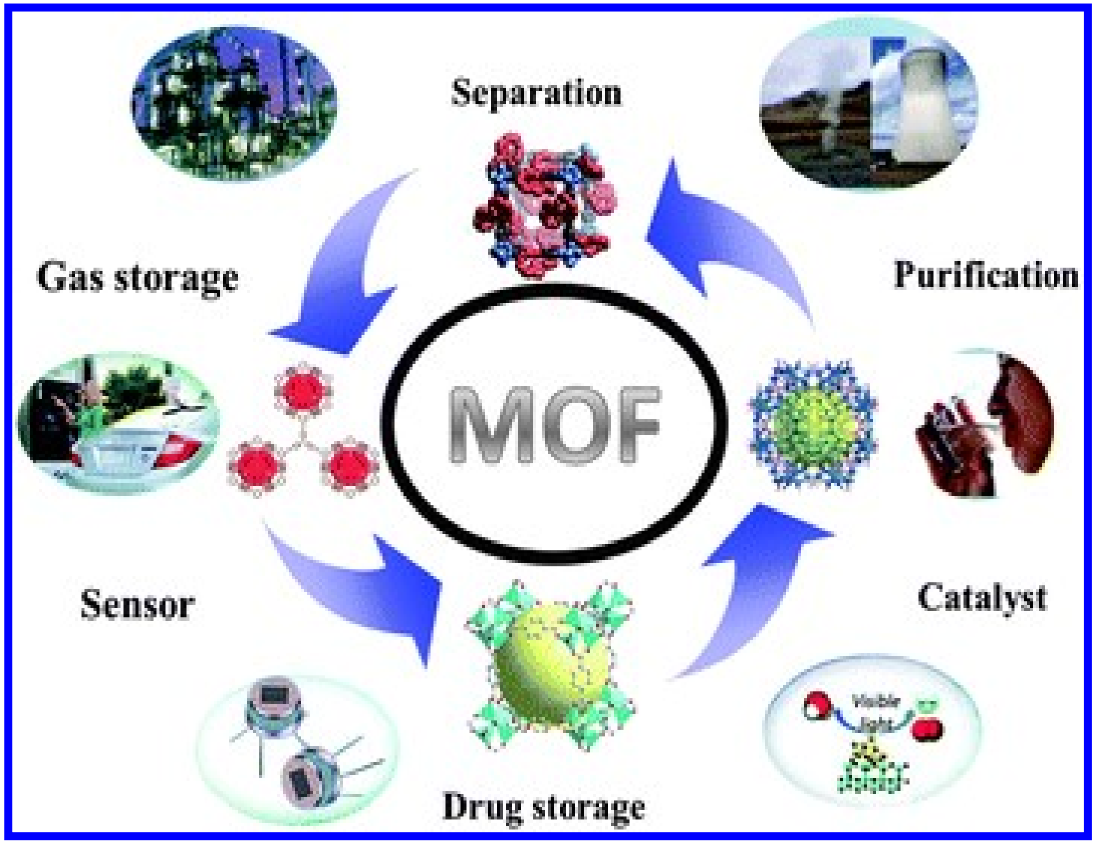


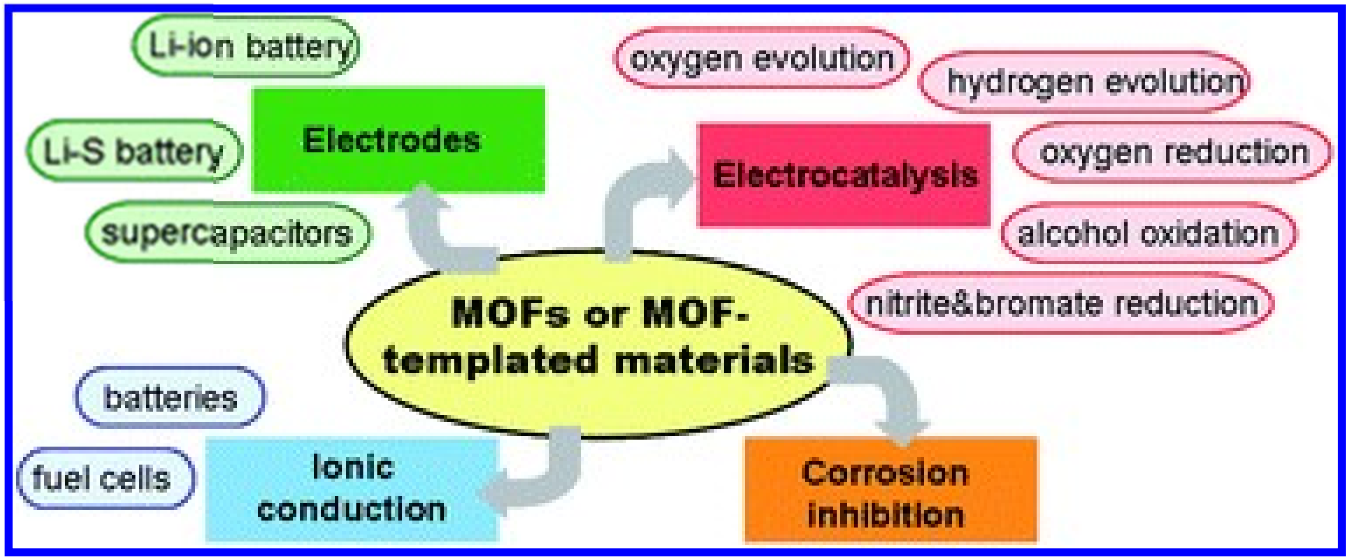
UiO-66





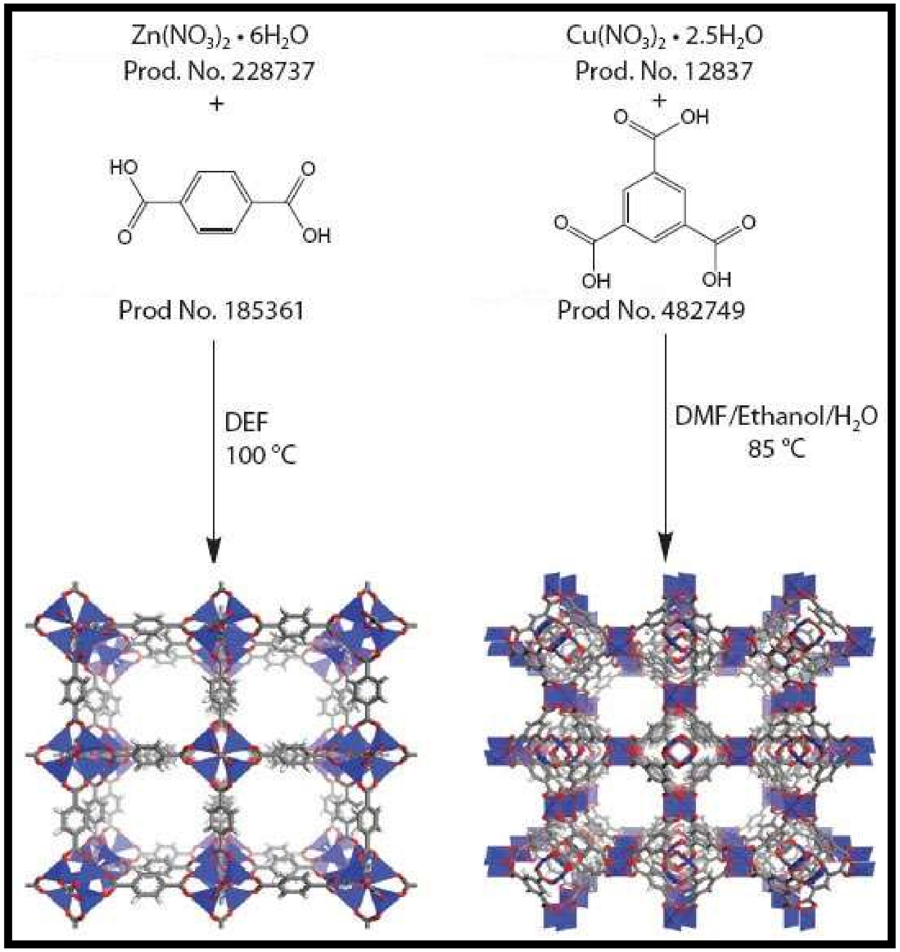
MOF THIN FILMS!

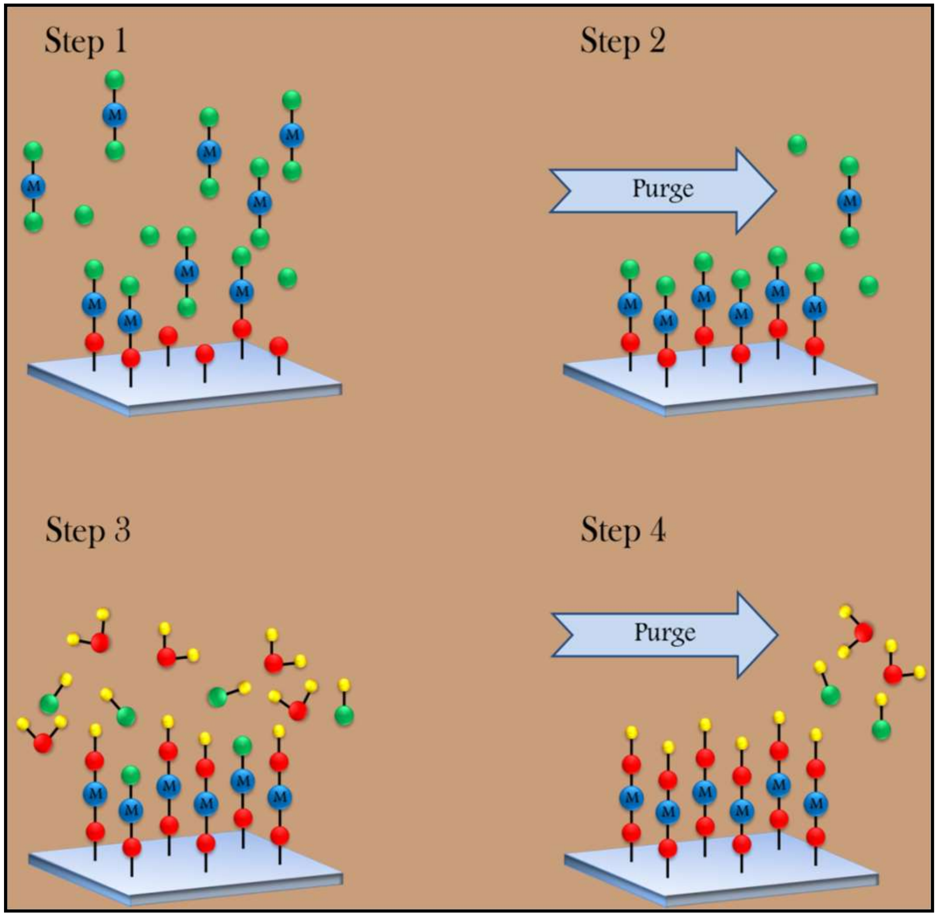




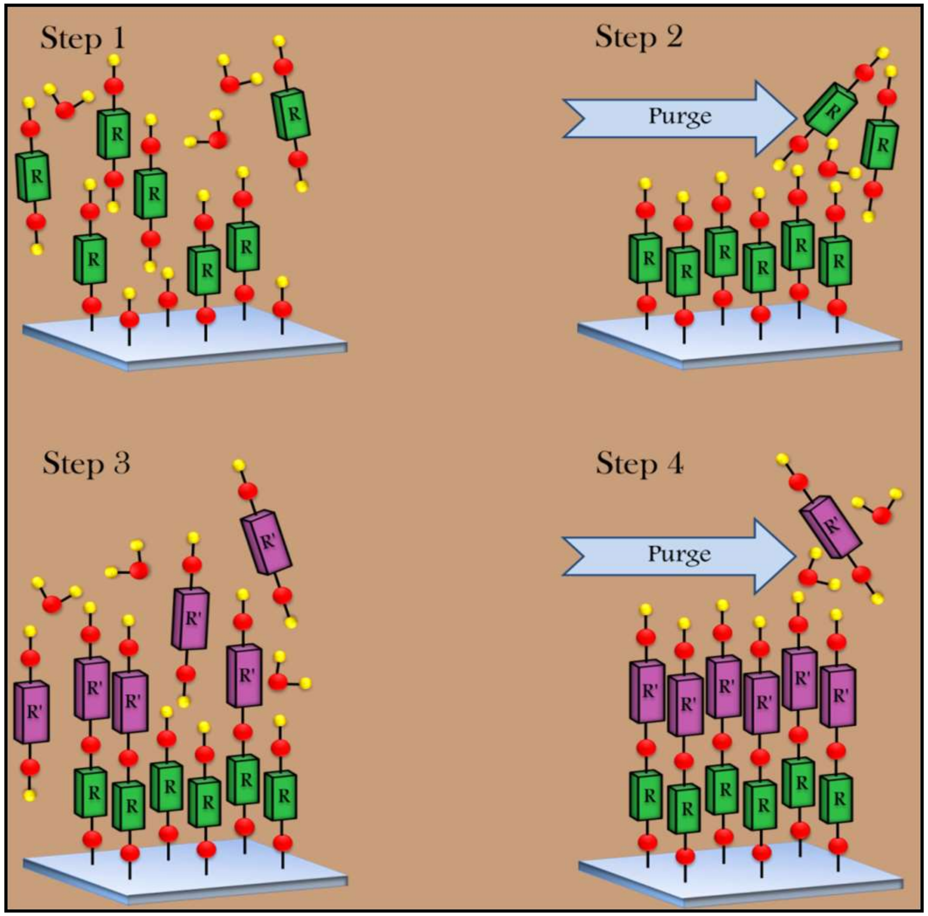
Synthesis of MOFs

- Synthesized most often in bulk form via solution techniques
- Porous structure → MOFs absorb readily/unintentionally solvent molecules
- Many prospective applications would require high-quality thin films
- No gas-phase deposition techniques (before ALD/MLD) !





ALD (Atomic Layer Deposition)



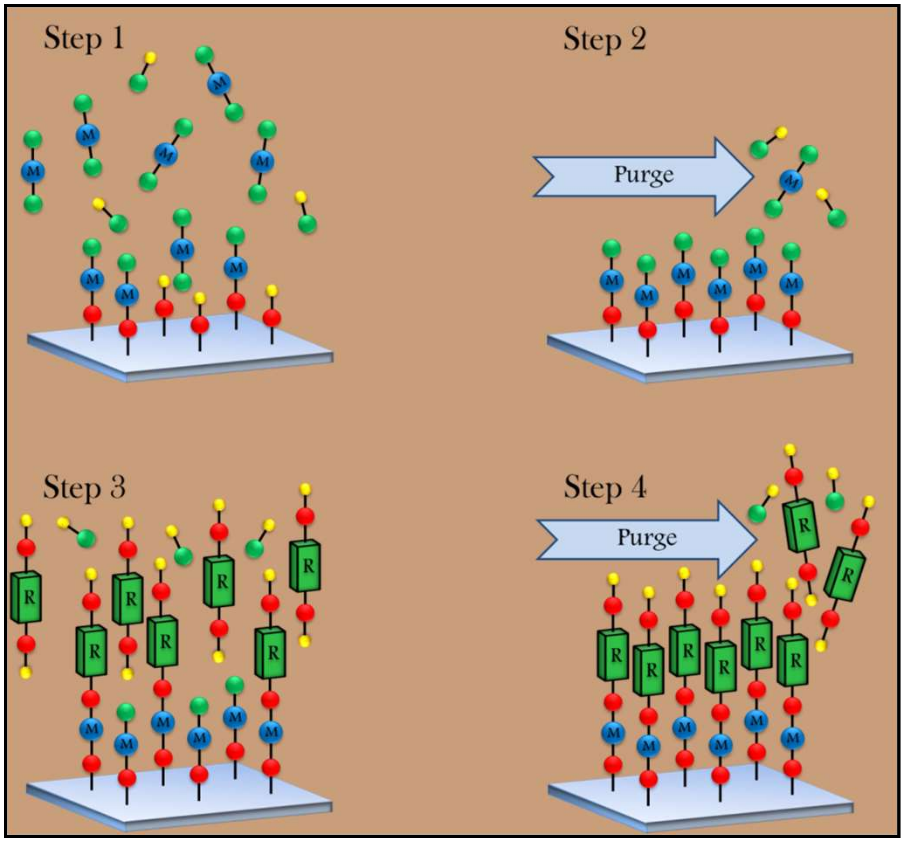
MLD (Molecular Layer Deposition)

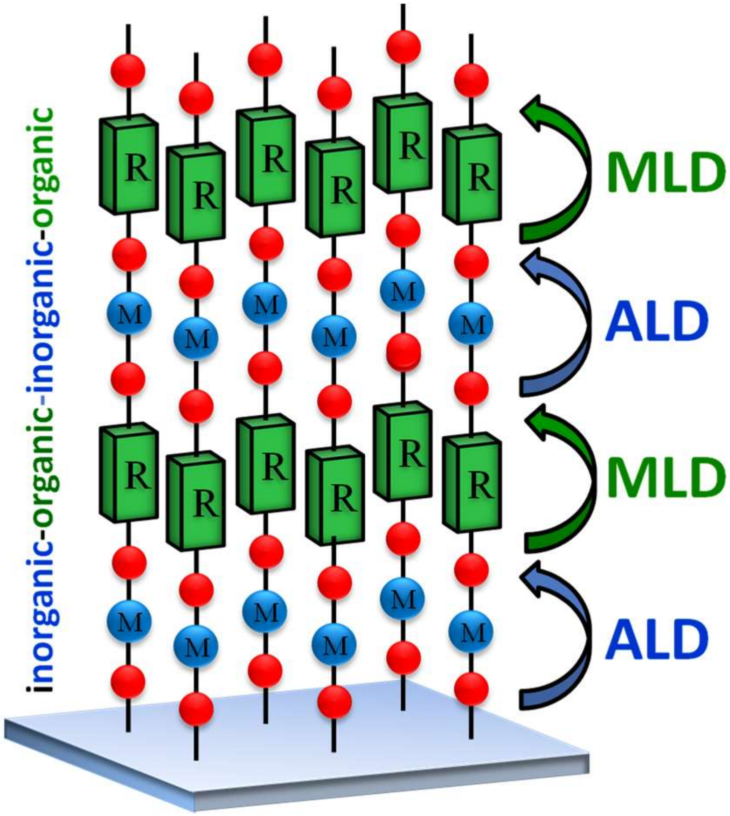
High-quality
INORGANIC thin films
with atomic level control

ORGANICS !

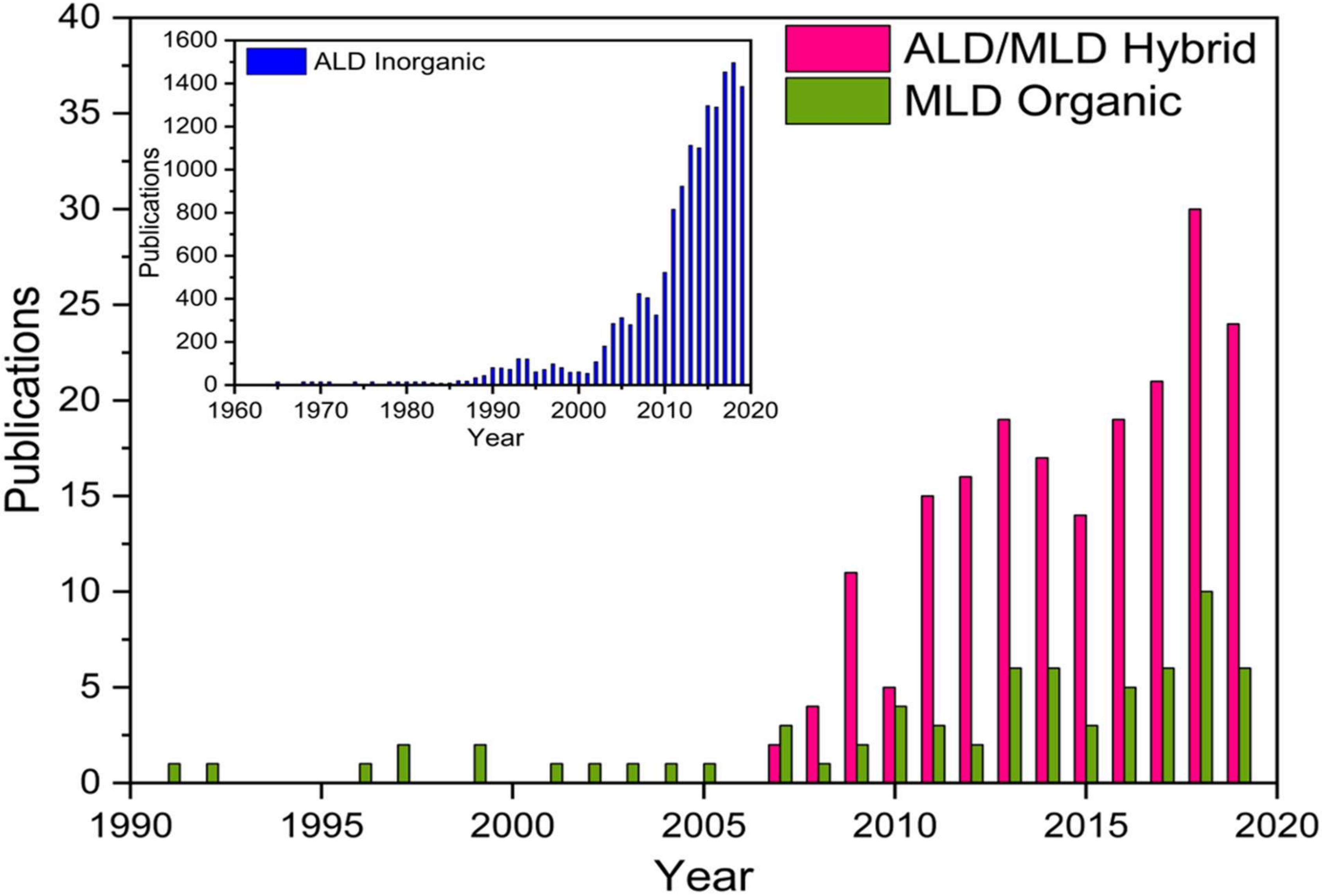
(in 1990s)

Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD





MULTIFUNCTIONAL SINGLE-PHASE HYBRID (compound) MATERIALS !!!



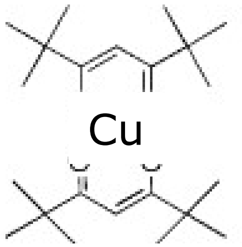
Publications
Year
1990
1995
2000
2005
2010
2015
2020
0
5
10
15
20
25
30
35
40
ALD/MLD Hybrid
MLD Organic
ALD Inorganic
Publications
Year
1960
1970
1980
1990
2000
2010
2020
0
200
400
600
800
1000
1200
1400
1600

OXIDES (Al_2O_3, ZnO, TiO_2, ZrO_2 & HfO_2) & ALD (atomic layer deposition) thin-film technology

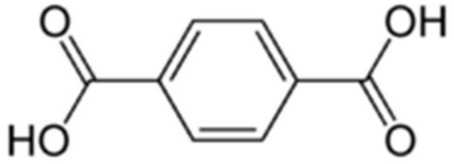
EXAMPLES of APPLICATIONS

- ALD-HfO_2 (amorphous): high-k dielectrics
- ALD-ZrO_2 (amorphous): barrier coating
- ALD-TiO_2 (crystalline): photovoltaics
- ALD-ZnO (crystalline): thermoelectric material
- ALD-Al_2O_3 (amorphous): barrier and protective coating

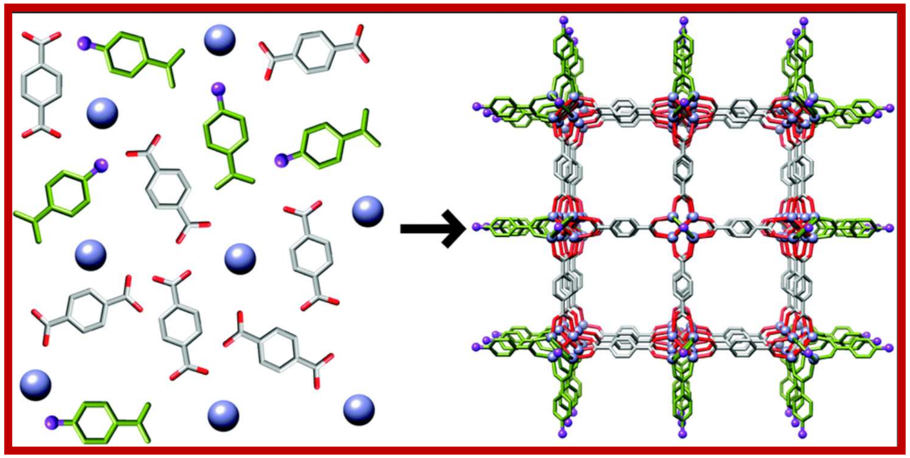
PRECURSORS for ALD/MLD



Cu(thd)$_2$



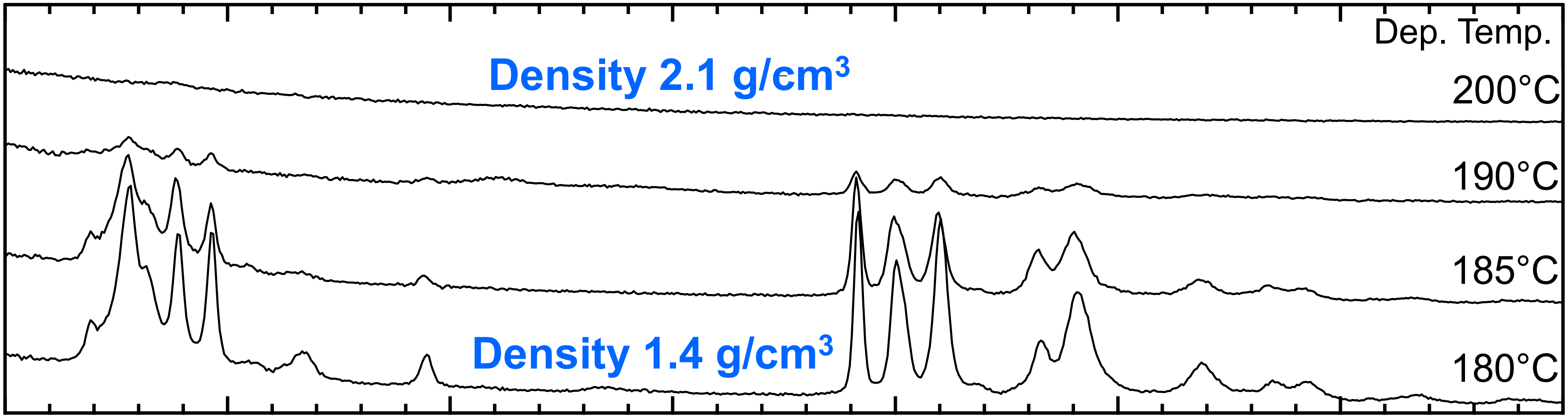
Terephthalic acid (TPA)

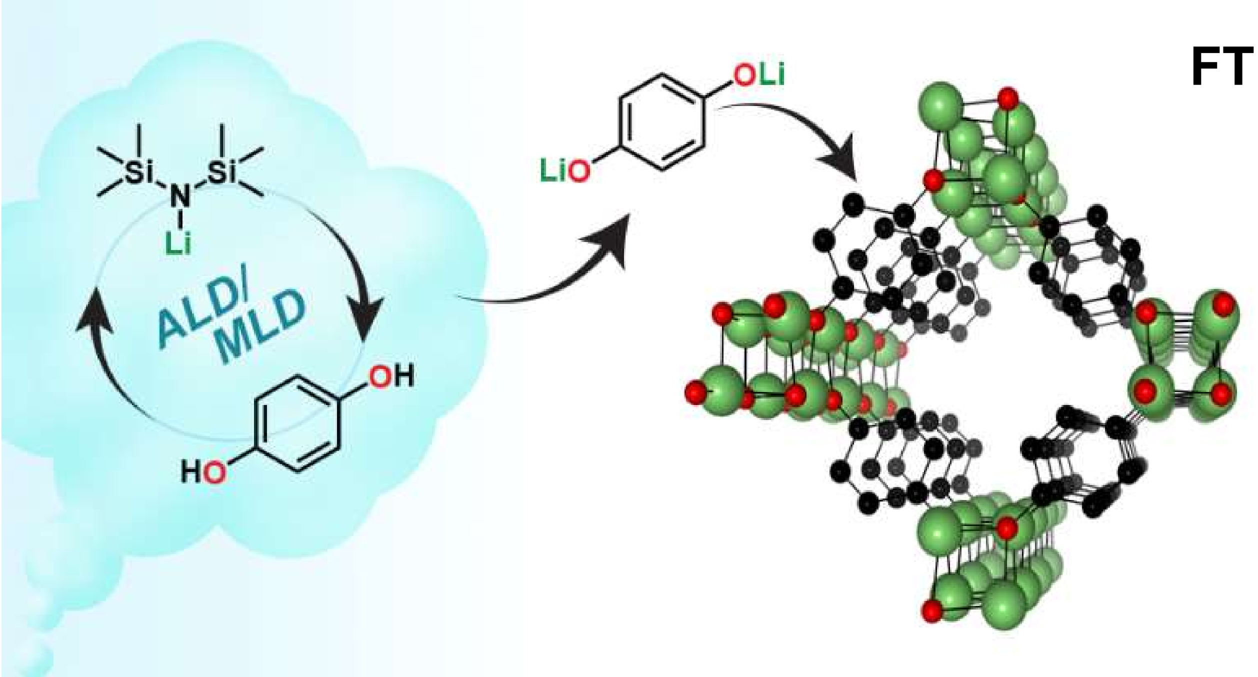


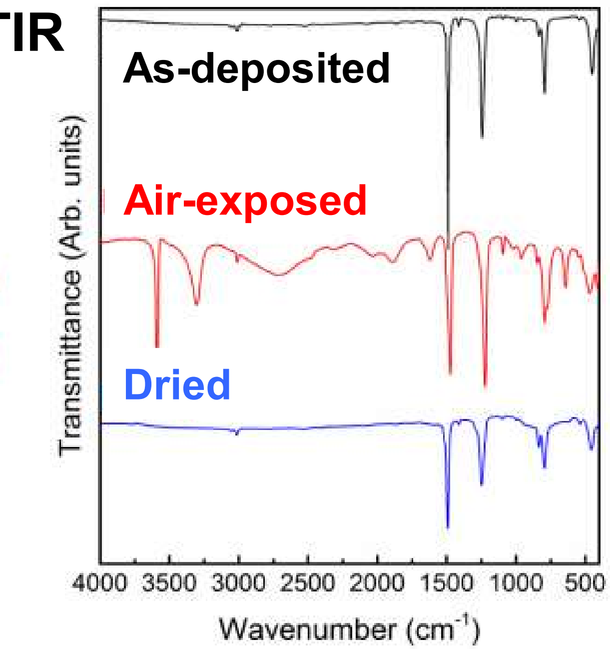
MOF

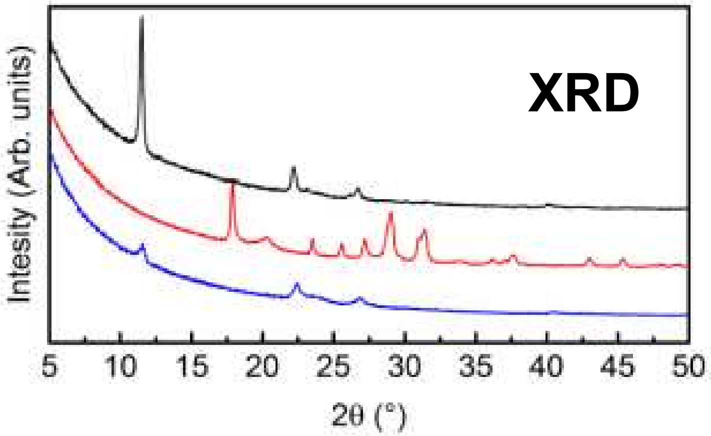
METAL-ORGANIC FRAMEWORK

E. Ahvenniemi & M. Karppinen, Chem. Commun. **52**, 1139 (2016).









Structure predicted by DFT

Li + Hydroquinone

- **Crystalline films**
- **NOT synthesized by any other technique**
- **Under-coordinated Li-site**
- **Reversible water absorption (gas absorption)**
- **Potential application: Li-ion battery cathode**

M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chemistry – A European Journal* **23**, 2988 (2017).