TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory & Jahn-Teller Effect
9.	Wed	06.10.	V, Nb, Ta & Metal Complex & POM, MOF, MLD
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
12.	Wed	13.10.	EXTRA
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021

PRESENTATION TOPICS/SCHEDULE

Wed	06.10.	Nb:	Toivonen
Fri	08.10.	Mo:	Ahmed, Shamshad
Mon	11.10.	Mn:	Majaniemi, Thakur, Ahkiola
		Ru:	Ichanson, Locqueville, Olsio
Wed	13.10.	Co:	Ekholm, Olander, Syväniemi
		Cu:	Kolawole, Nguyen, Munib
Fri	15.10.	In:	Kovanen, Ogunyemi, Svinhufvud
		Te:	Huhtakangas, Wallin, Kaarne
Mon	18.10.	Eu:	Sonphasit, Tuisku
		Nd:	Jussila, Siuro, Perttu
		U:	Sinkkonen, Wennberg, Partanen

QUESTIONS: Lecture 9

1. Which one(s) of the followings may involve both inorganics and organics; please explain shortly.

   - Perovskite

   - POM

   - MOF

   - MLD

2. Name the following metal complexes:

   $K_3[Fe(CN)_6]$

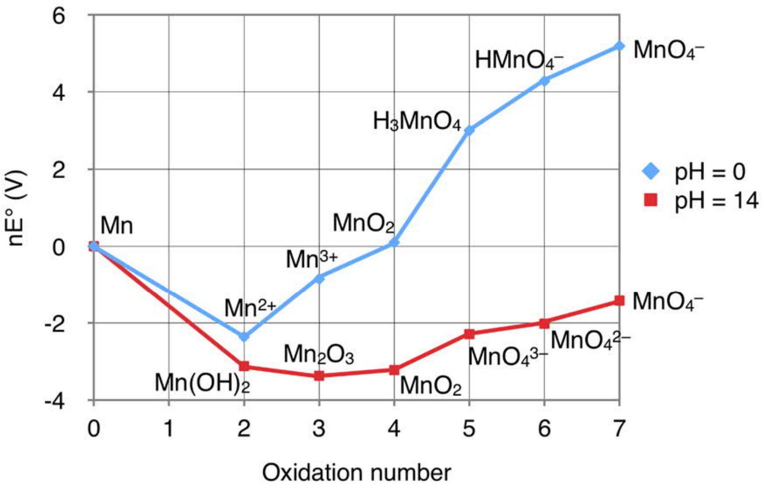
   $[CoN_3(NH_3)_5]SO_4$

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

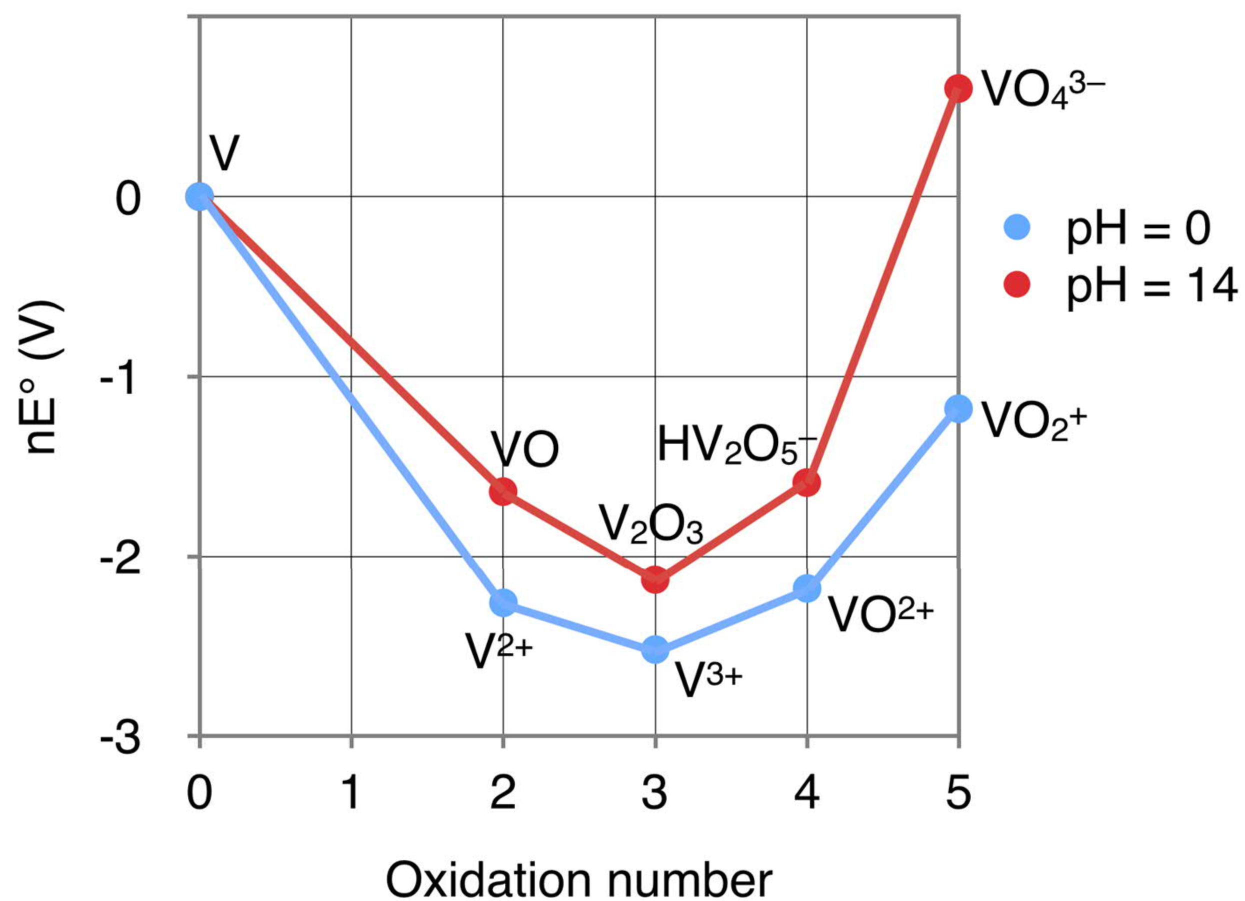
   $[Cr(H_2O)_6]Cl_3$

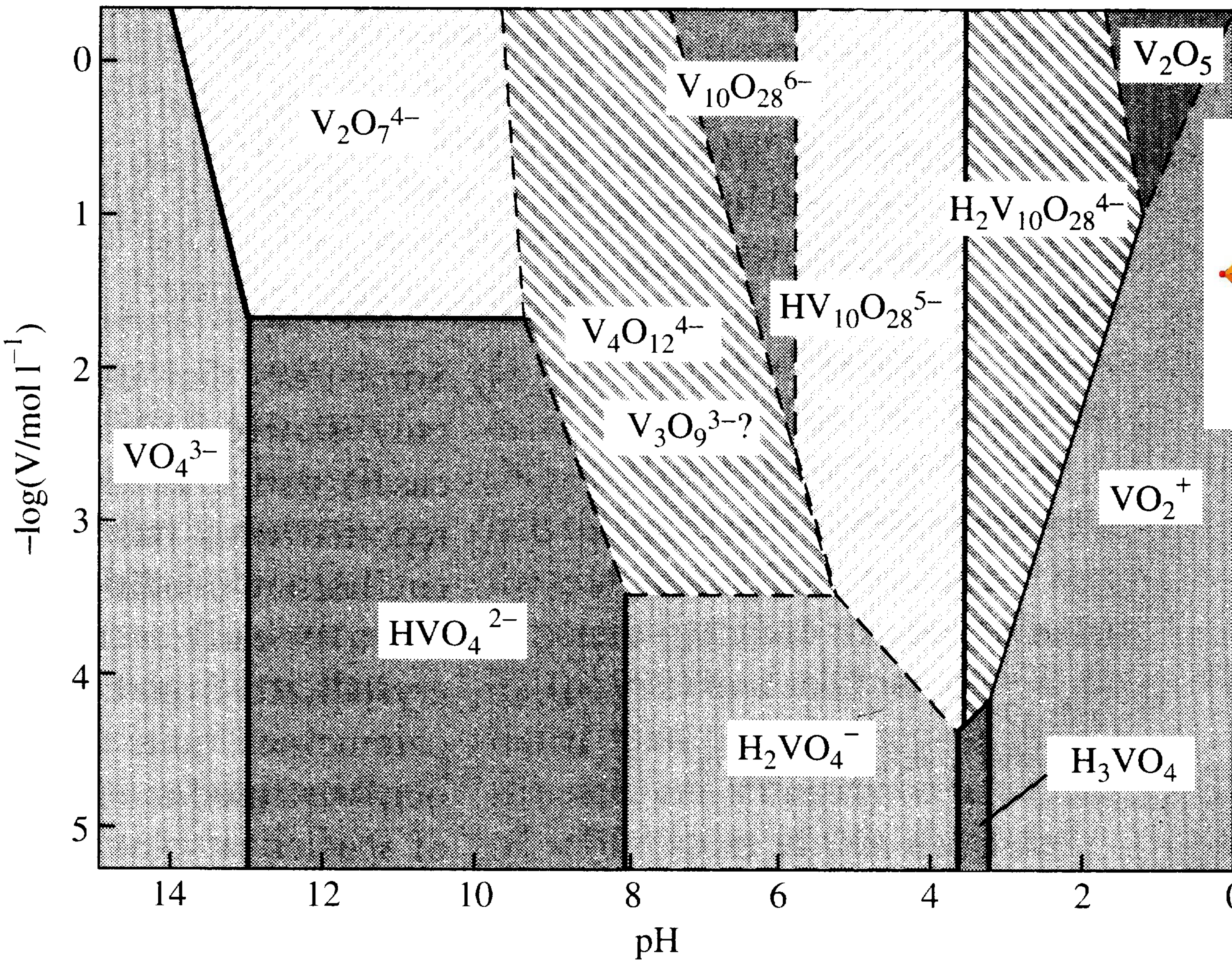
   $[Al(OH)(H_2O)_5]^{2+}$

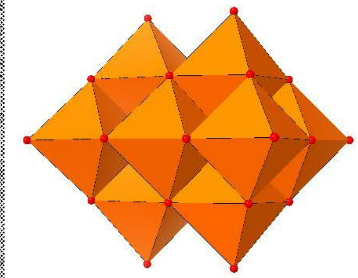
Frost diagram for manganese



Frost diagram for vanadium

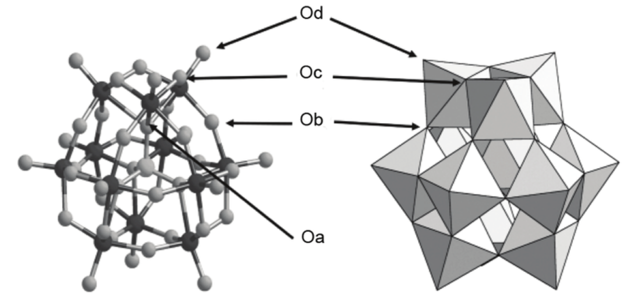






Occurrence of various vanadate and polyvanadate species as a function of pH and total concentra
of vanadium.

PolyOxoMetallite (POM)



- Discrete anionic metal oxygen clusters
- Basic structure unit: MO_6
- Typical for: V, Nb, Ta, Mo, W
- *M* metal at its highest oxidation state → **Oxophilic**
- First synthesized in 1826 (Berzelius), structure 1934 (Keggin): $[PMo_{12}O_{40}]^{3-}$
- IsoPolyAnion: $[M_nO_y]^{p-}$
- HeteroPolyAnion: $[X_zM_nO_y]^{q-}$
- APPLICATIONS: - redox catalysis (oxidation of organics)
  - medicine (antiviral/antitumor)
  - molecular electronics (unique magnetic properties)

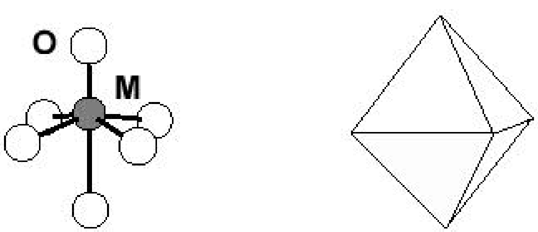


Figure 1.1. Ball-and-stick and polyhedral representations of the fundamental unit MO_6. Note that the M atom is displaced off the geometrical centre of the octahedron towards one of the oxygens, thus giving rise to a distorted C_{4v} unit.

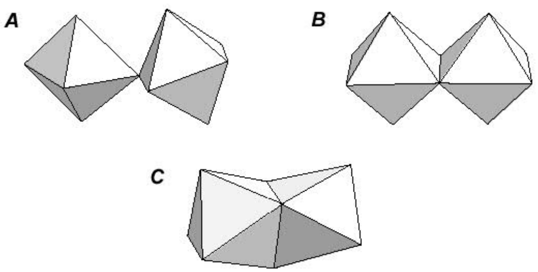
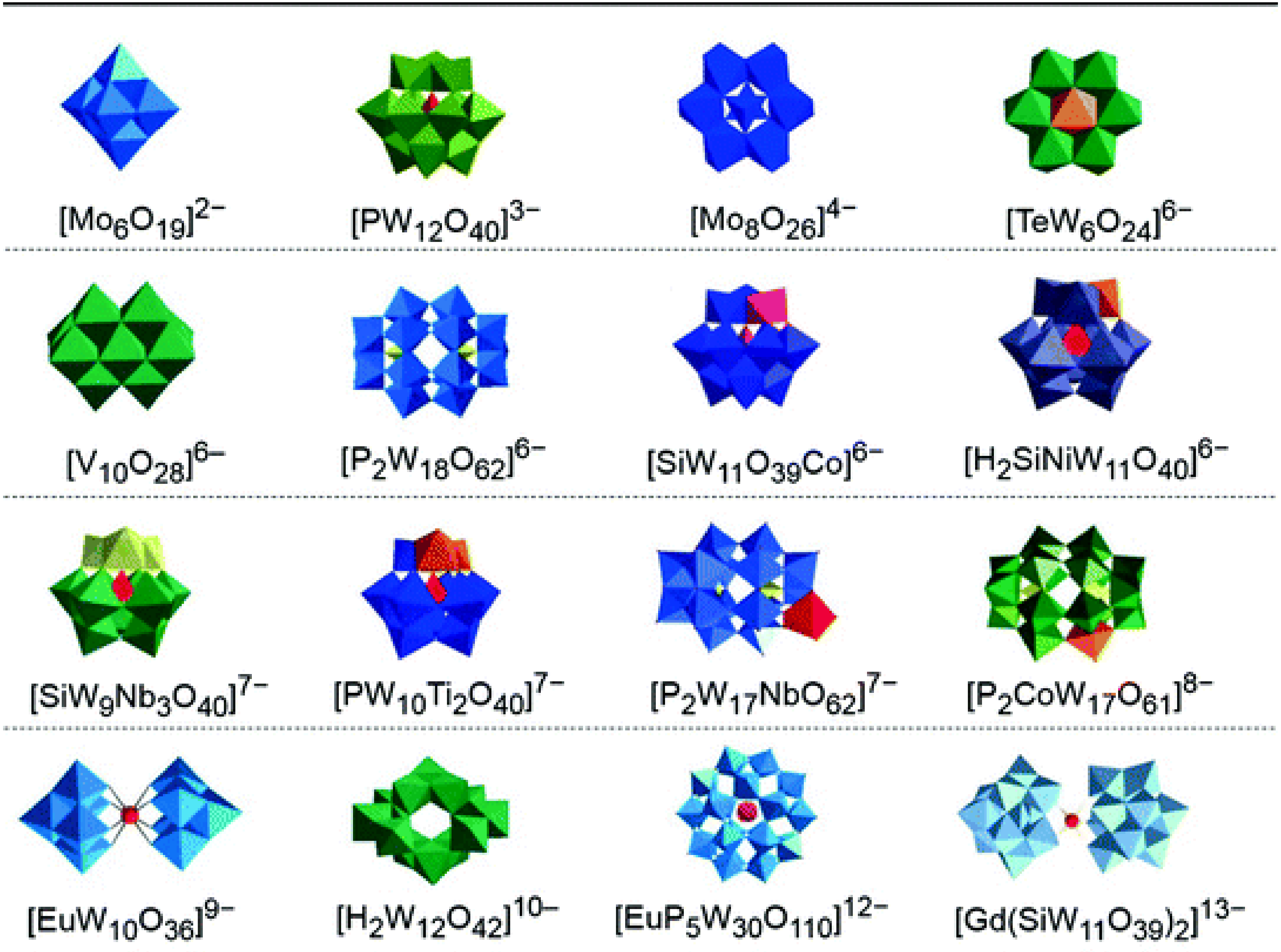
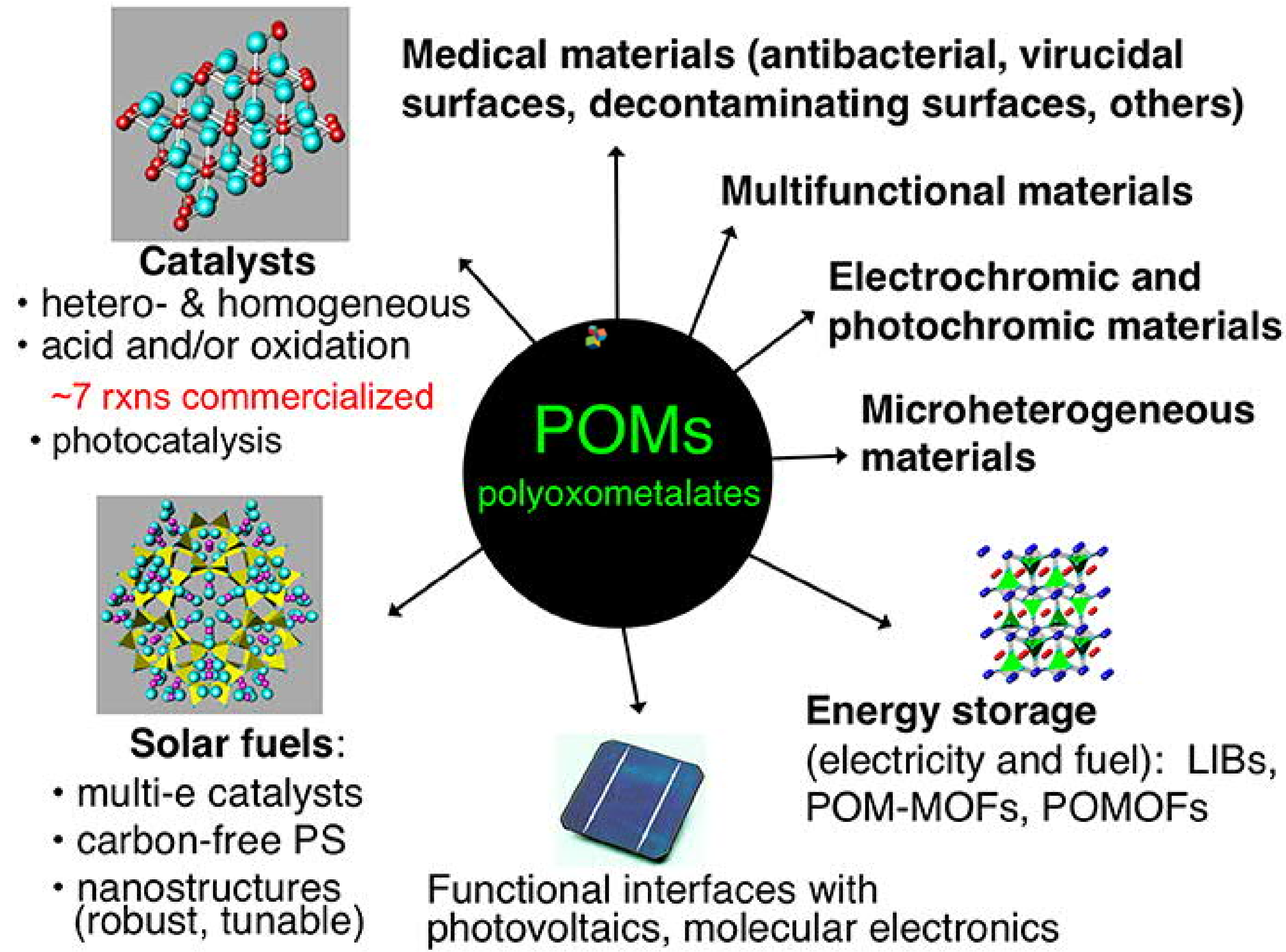


Figure 1.2. The polyhedral models represent the three possible unions between two MO_6 octahedral units. A) corner-sharing, B) edge-sharing and C) face-sharing. Each corner represents an oxygen position.



$[Mo_6O_{19}]^{2-}$
$[PW_{12}O_{40}]^{3-}$
$[Mo_8O_{26}]^{4-}$
$[TeW_6O_{24}]^{6-}$
$[V_{10}O_{28}]^{6-}$
$[P_2W_{18}O_{62}]^{6-}$
$[SiW_{11}O_{39}Co]^{6-}$
$[H_2SiNiW_{11}O_{40}]^{6-}$
$[SiW_9Nb_3O_{40}]^{7-}$
$[PW_{10}Ti_2O_{40}]^{7-}$
$[P_2W_{17}NbO_{62}]^{7-}$
$[P_2CoW_{17}O_{61}]^{8-}$
$[EuW_{10}O_{36}]^{9-}$
$[H_2W_{12}O_{42}]^{10-}$
$[EuP_5W_{30}O_{110}]^{12-}$
$[Gd(SiW_{11}O_{39})_2]^{13-}$


Medical materials (antibacterial, virucidal surfaces, decontaminating surfaces, others)
Multifunctional materials
Electrochromic and photochromic materials
Microheterogeneous materials
Catalysts
• hetero- & homogeneous
• acid and/or oxidation
~7 rxns commercialized
• photocatalysis
POMs
polyoxometalates
Solar fuels:
• multi-e catalysts
• carbon-free PS
• nanostructures (robust, tunable)
Energy storage
(electricity and fuel): LIBs, POM-MOFs, POMOFs
Functional interfaces with photovoltaics, molecular electronics

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

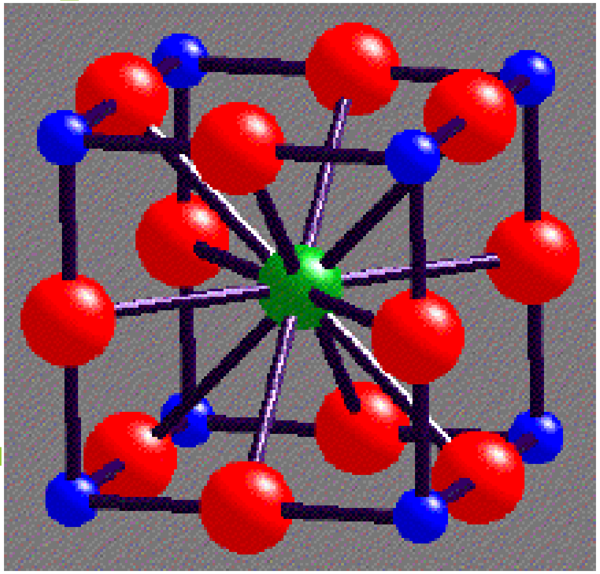
- $LiNbO_3$ and $LiTaO_3$:
  - distorted perovskite structure
  - ferroelectric
    (electrical dipole moment without external electric field)

- 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)

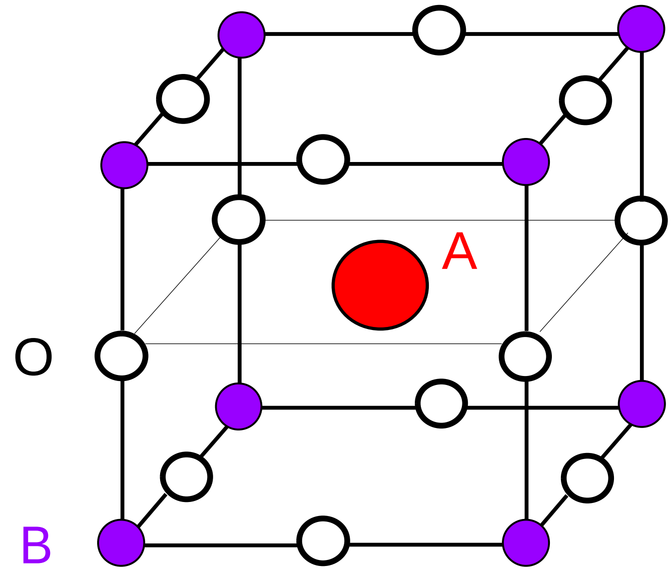
ABO_3



PEROVSKITE STRUCTURE

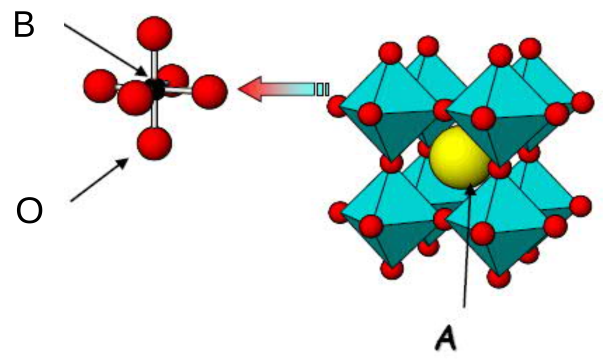
General formula: $ABO_{3-\delta}$

A: large cation
B: small cation (transition metal)
O: oxygen (sometimes halogen)



V(A) + V(B) = 6

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

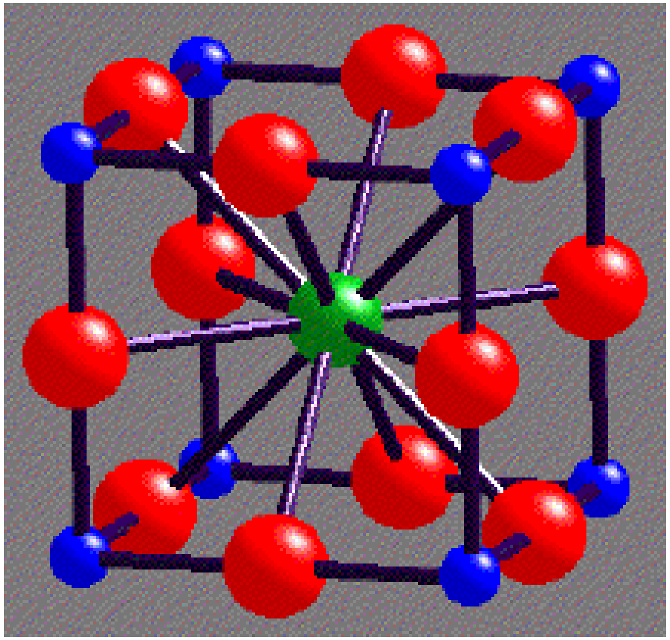


CN(A)=12, CN(B)=6, CN(O)=6

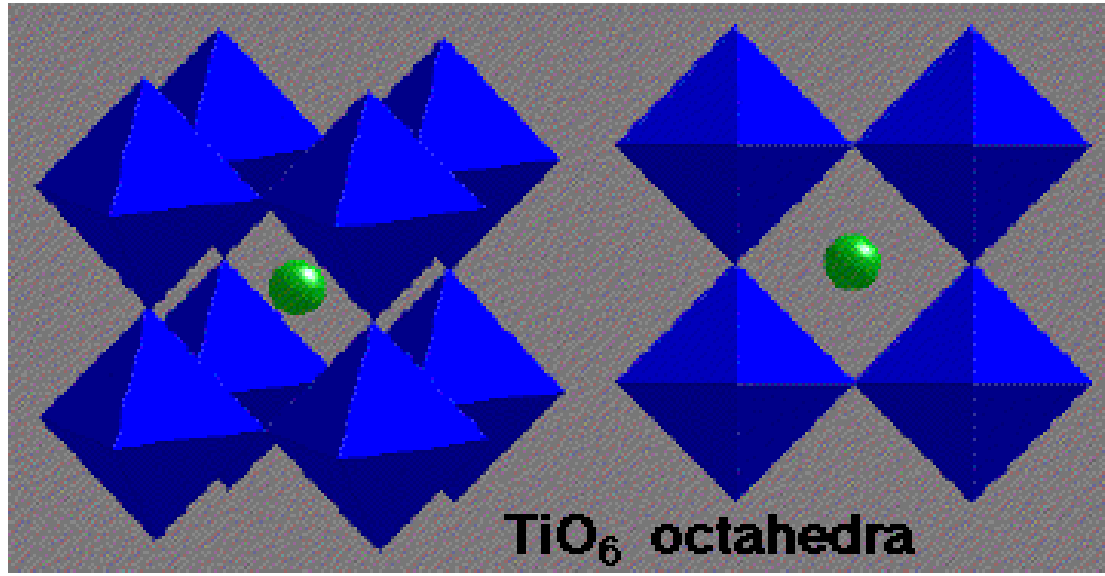
Mineral Perovskite: $CaTiO_3$

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

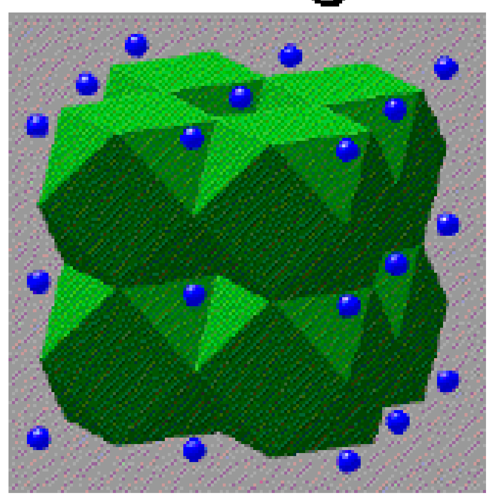
Perovskite $CaTiO_3$



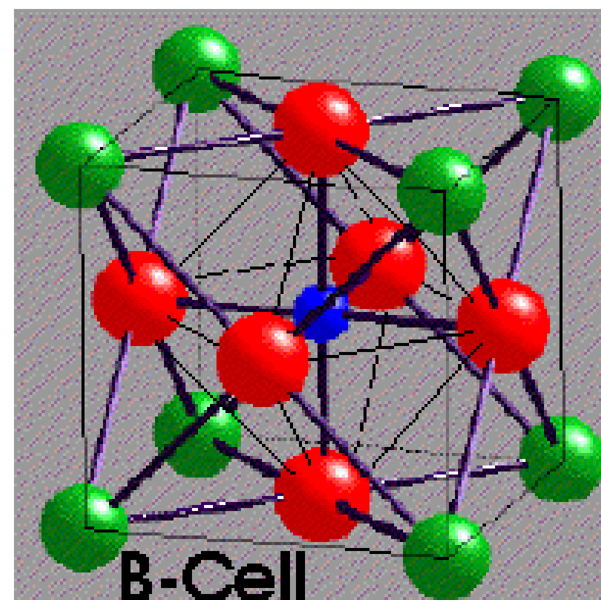
A-Cell



Ca Ti O



CaO_{12} cuboctahedra



Perovskite – Multifunctional structure

Perovskite
***AB*O$_3$**

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

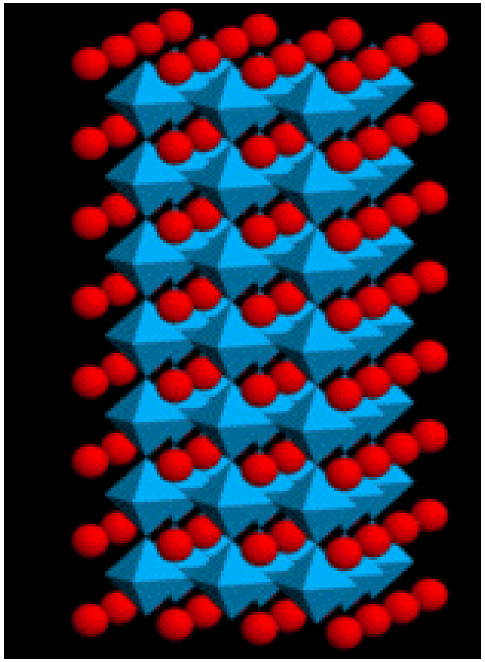
Metallic conductor
$LaCrO_3$

Piezoelectric material
Pb(Zr,Ti)O_3

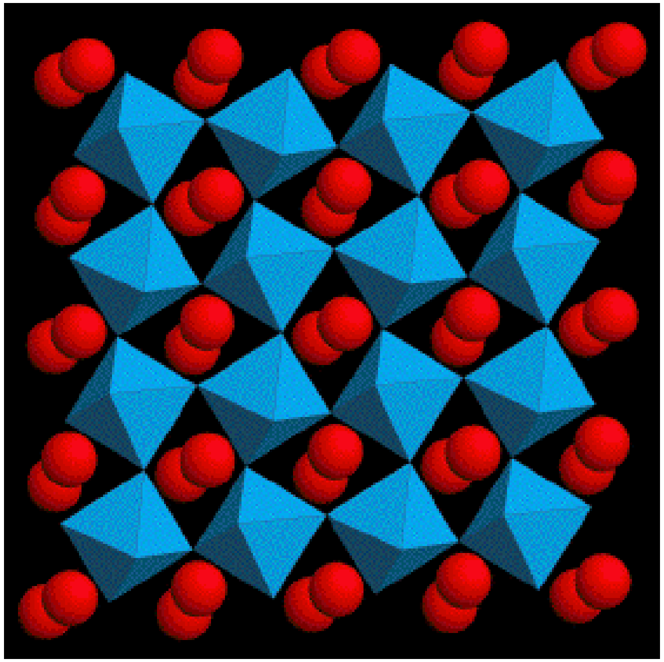
Capasitor
(high dielectric constant)
$BaTiO_3$

“Distortions and Imperfections” in Perovskite Structure

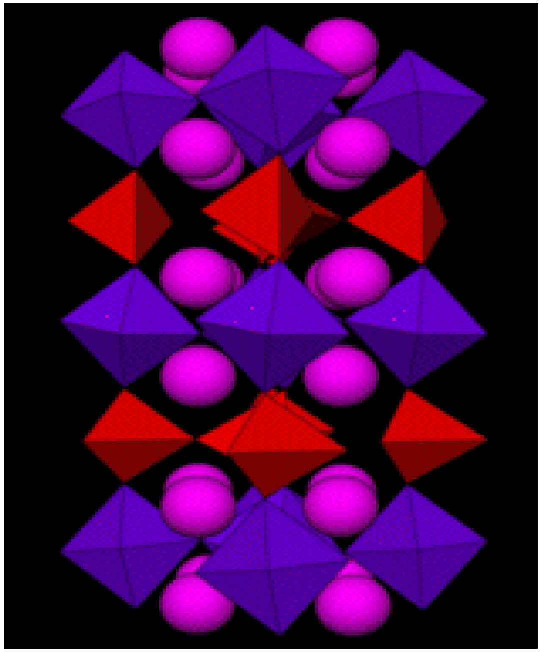
- often the source of the desired properties



IDEAL

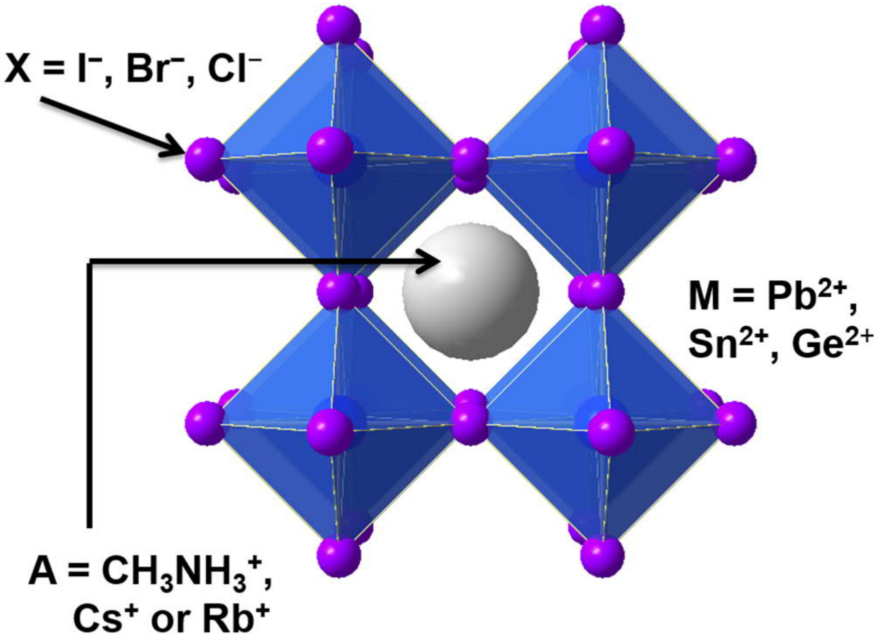


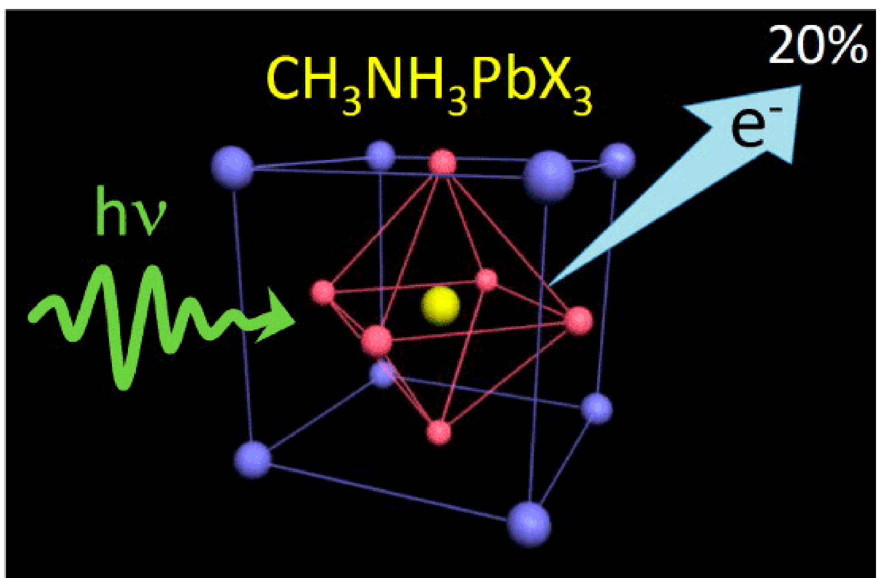
Changes in atomic positions

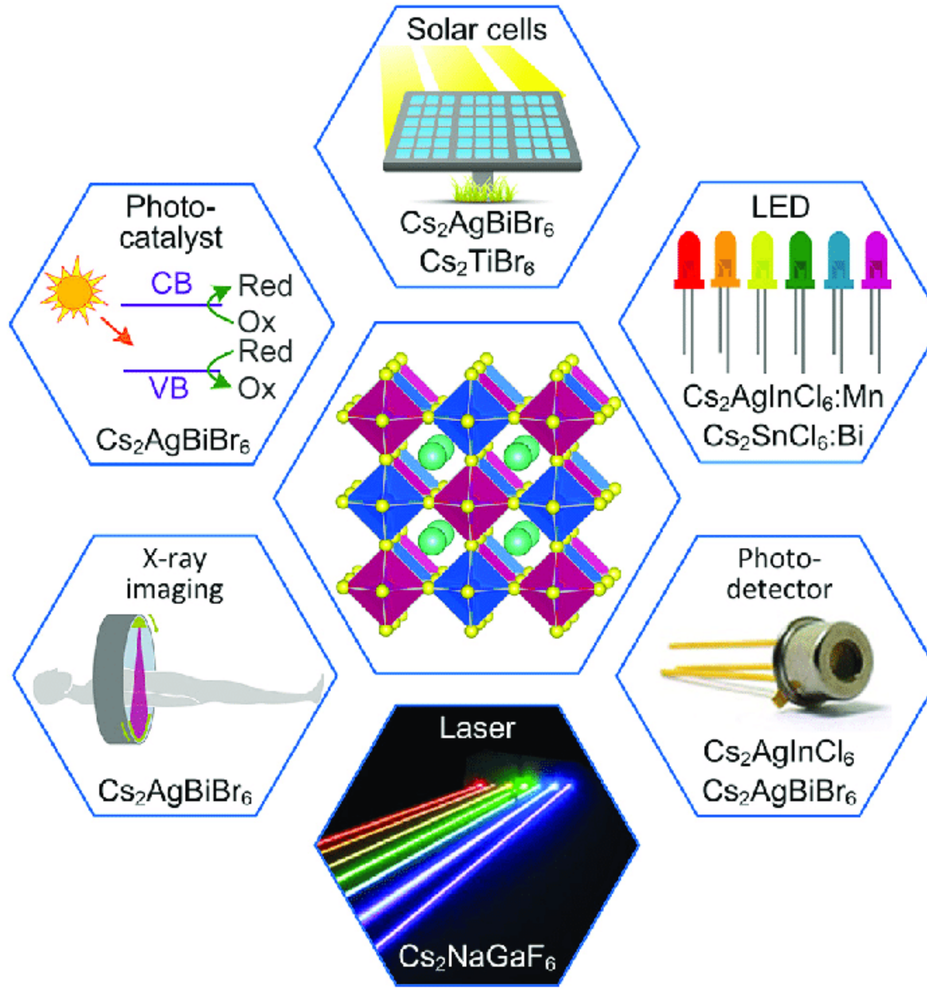


Oxygen deficiency

"Perovskite Solar Cell"





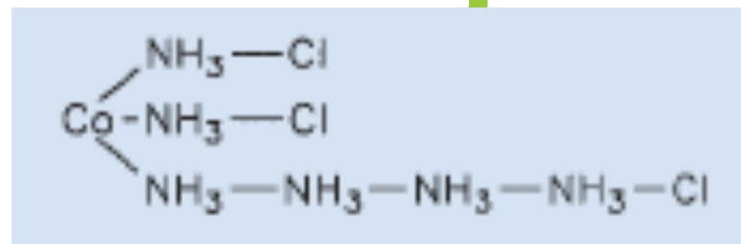


HISTORY of COORDINATION COMPLEXES

- **Prussian blue: $KFe[Fe(CN)_6]$**
  - synthesized in 1704 in Berlin
  - used as a pigment in Prussian army uniform

- **Tassaert 1798: $CoCl_3 \times 6\ NH_3 \rightarrow$ brownish red product**

- **Blomstrand-Jörgensen chain theory:**
  - derived from organic chemistry: ammine-chains + chlorine at the ends

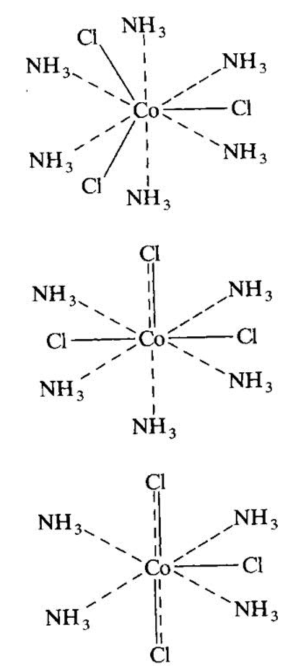


- **Alfred Werner (1866-1919), Nobel 1913:**
  - "primary valence" ≈ oxidation state
  - "secondary valence" ≈ coordination number

(1) $CoCl_3 \cdot 6NH_3$

(2) $CoCl_3 \cdot 5NH_3$

(3) $CoCl_3 \cdot 4NH_3$



COORDINATION COMPLEXES

- central cation: Co
- coordinated ligands (e.g. NH_3 or Cl^{-}) within the brackets
- Cl^- ions within the brackets belong to the coordination sphere
- Cl^- ions outside of the brackets (= counter ions) contribute to the oxidation state only (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]Xy tai Ab[MLn]**
- **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**

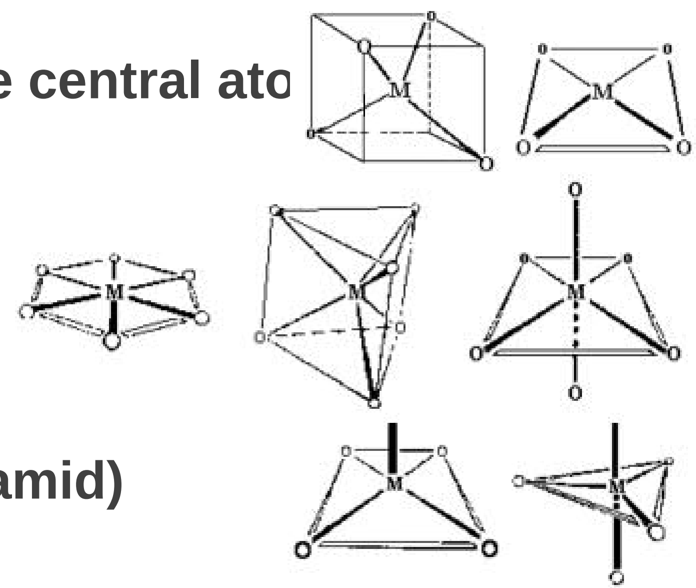
  - each ligand gives an electron pair to the central ato

  - COVALENT COORDINATION BOND
- **Coordination number (CN = n):**

  - typically 4 (tetrahedron or square-plane

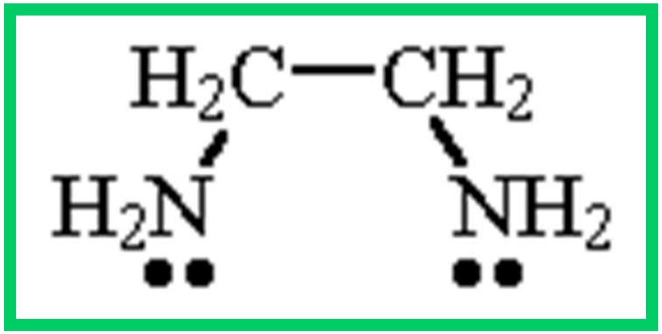
  or 6 (octahedron)

  - sometimes 5 (pyramid or trigonal bipyramid)
- **Counter ion: anion (X) or cation (A)**
- **Typical for metal complexes: bright colours & magnetism**



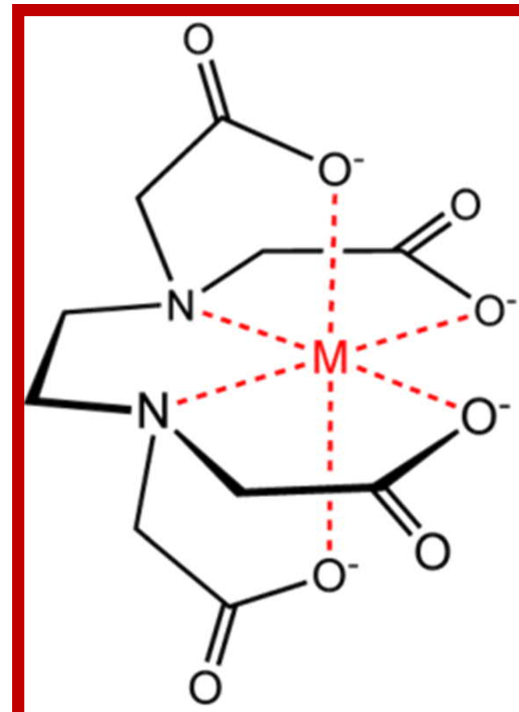
MULTIDENTANTE LIGANDS

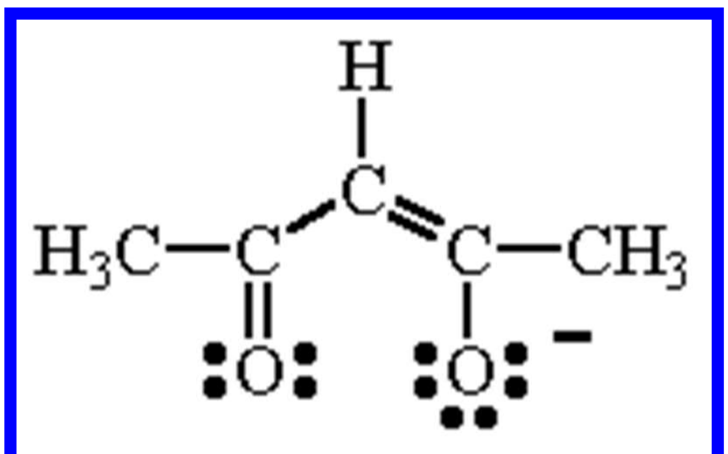
- **Stabilize the complex:** $[Ni(en)_3]^{2+}$ 10 times more stable than $[Ni(NH_3)_6]^2$
- NOTE: Ambidentate CN (cyano) & NC (isocyano), NO_2 (nitro) & ONO (nitrito)



Ethylenediamine (en):2

EDTA: 6





Asetyleneacetonato (acac): 2

NAMING of COMPLEXES

(1) Cation first, then anion

(2) Ligands in alphabetical order (prefix NOT counted) 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

negative ligand: o-ending (F^- fluoro, O^{2-} oxo, OH^- hydroxo, NO^{2-} nitro, CN^- cyano)

neutral ligand: name of the molecule without changes

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

trivial names: aqua H_2O, ammine NH_3, carbonyl CO, nitrosyl NO

ambidentante: nitro NO^{2-} & nitrito ONO^-, thiocyanato SCN^- & isothiocyanato NCS^-

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 (sulfato through nitro)	
CO	carbonyl		
Cl^-	chloro		
O^{2-}	oxo		
O_2^{2-}	peroxo		
OH^-	hydroxo		
NH_2^-	amido		
CN^-	cyano		Ambiden ligands (cyano through nitro)
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)
$CH_3\underset{O}{\underset{\|}{C}}\overset{(-)}{C}H\underset{O}{\underset{\|}{C}}CH_3$	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)
$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$	ethylenediamine-tetraacetato (EDTA)	(6)

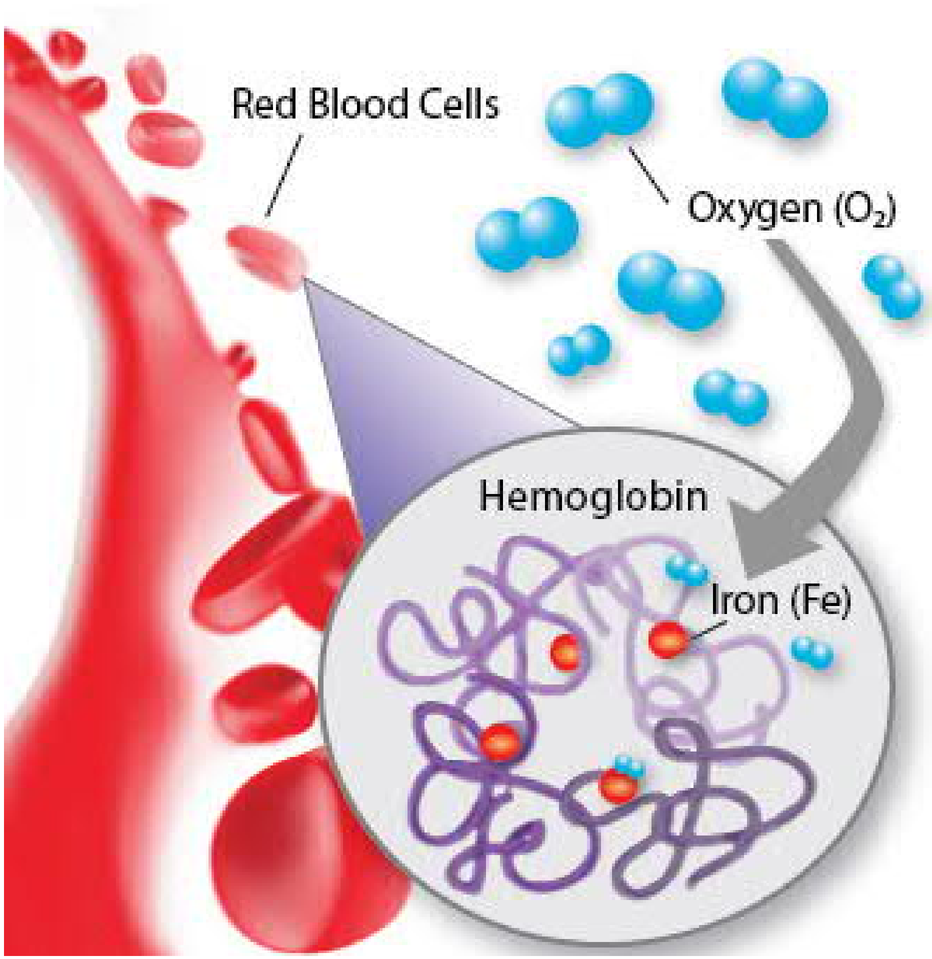
NAMING EXAMPLES

- **$[Co(NH_3)_4Cl_2]Cl$ → cobalt(III) tetraamminedichlorocobalt(III)chloride**
  - 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

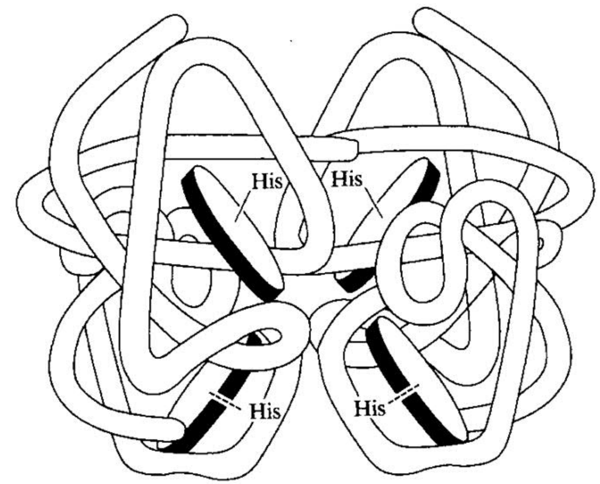
- **$(NH_4)_2[Pt(NCS)_6]$ → platinate(IV) ammoniumhexaisothiocyanatoplatinate(IV)**
  - 6 negative NCS ligands (bonding via N) → hexaisothiocyanato
  - NH_4 cation → ammonium
  - complex is anion, platinum oxidation state +4

- **$[Cu(NH_2CH_2CH_2NH_2)_2]SO_4$ → bis(ethylenediamine)copper(II)sulphate**

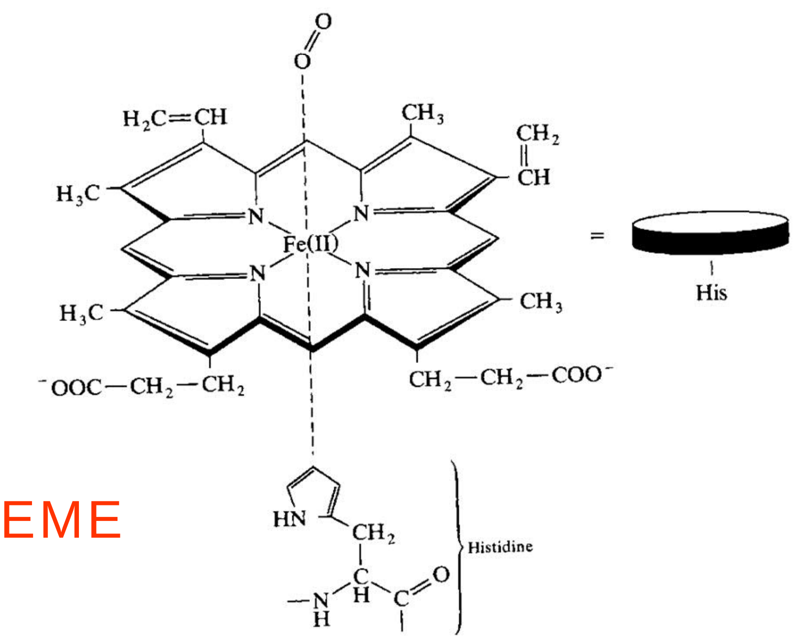
- **$[Ag(CH_3NH_2)_2]$ $[Mn(H_2O)_2(C_2O_4)_2]$ →
  bis(methylamine)silver(I) diaquadioxalatomanganate(III)**



GLOBIN



(a)

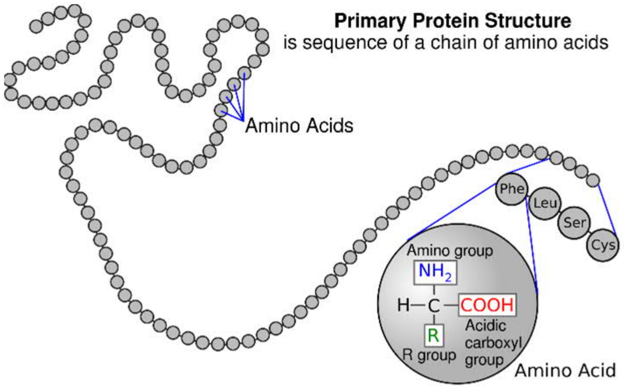


HEME

(b)

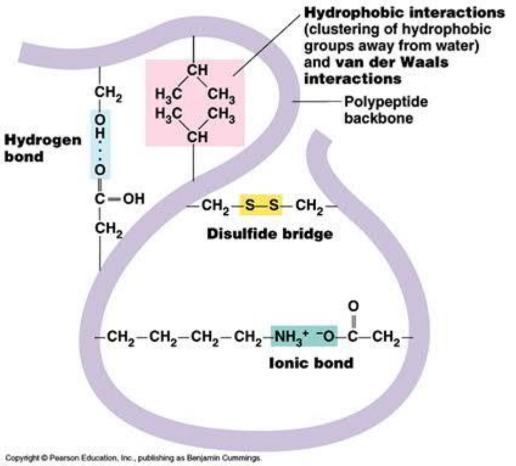
LEAD POISONING

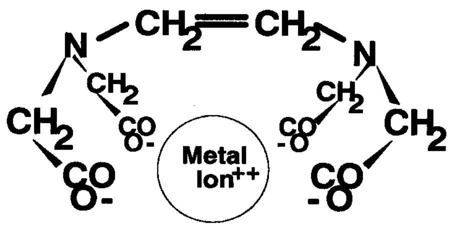
- **Lead (and other heavy metals):**
  - **readily binds to aminoacids (of proteins)**



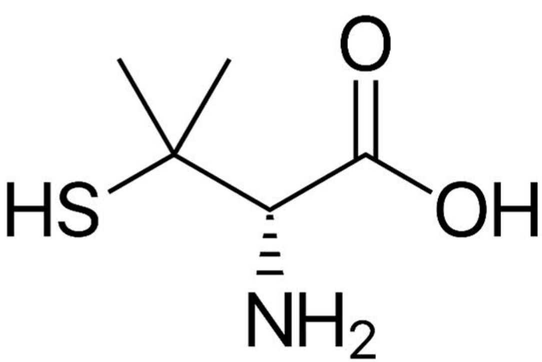
- **EDTA first aid:**
  - **binds effectively Pb, but also other metals (e.g. Ca)**

- **Penicillamine treatment:**
  - **binds via S more selectively to Pb**



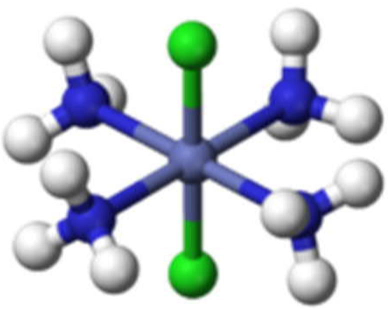


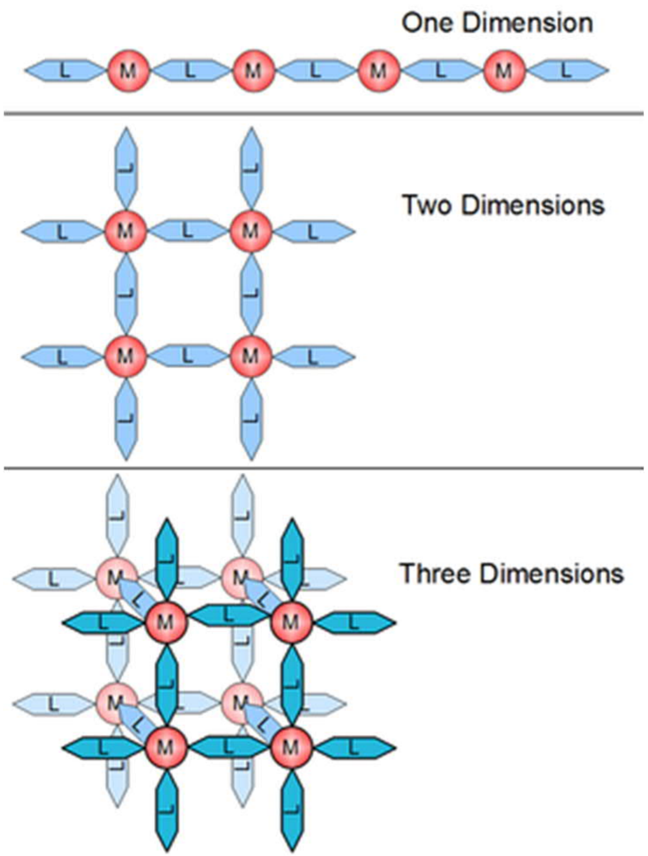
Ethylenediaminetetraacetic acid (EDTA) chelates a metal ion

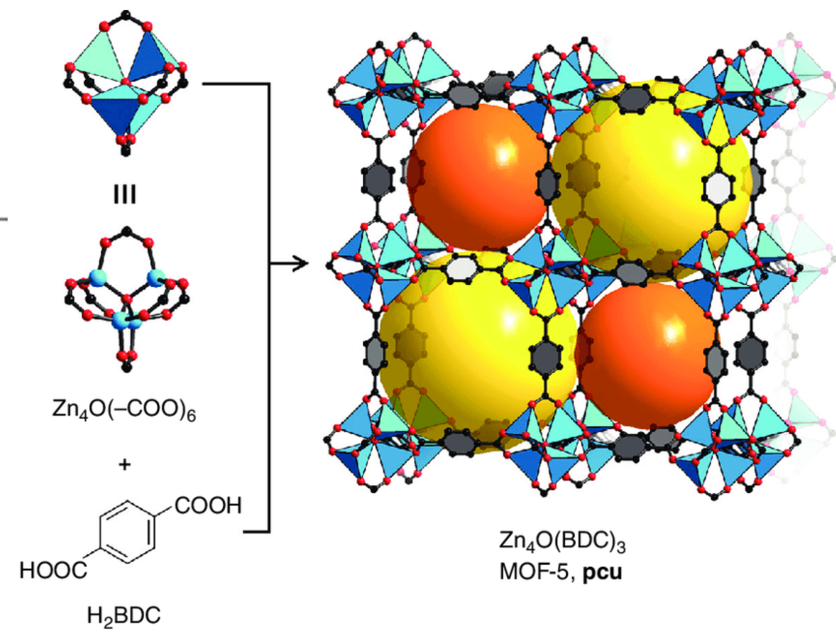


Inorganic-Organic Materials

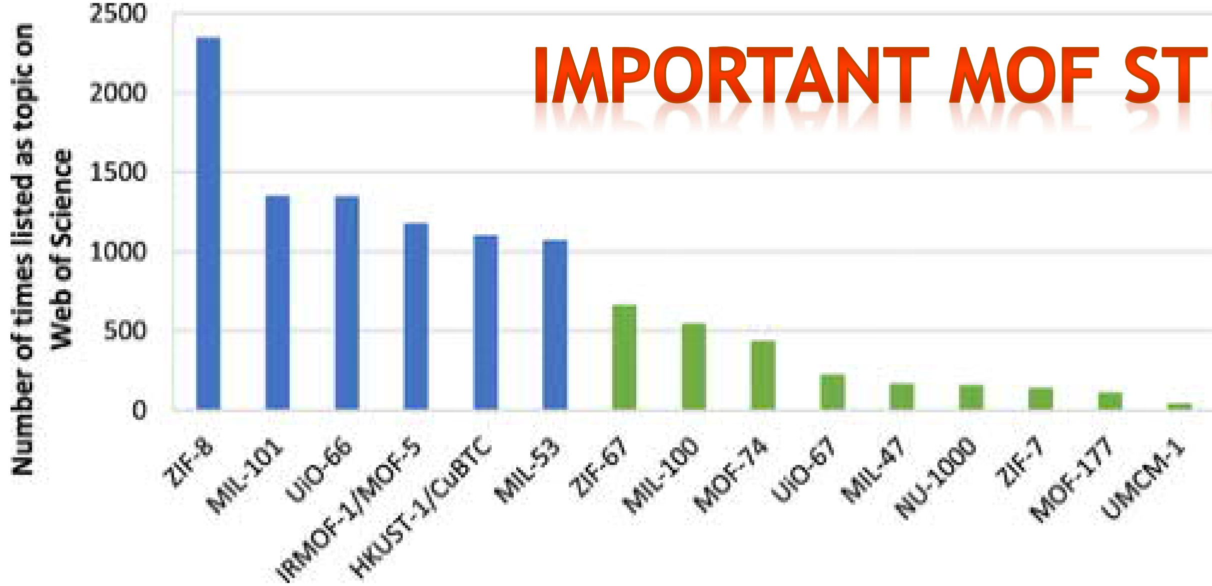
- **Compound NOT Composite**
- **Coordination Complex: central metal ion + (organic) ligands**
- **Coordination Polymer/Network: ligands act as bridges**
- **Metal-Organic Framework (MOF): crystalline and highly porous**

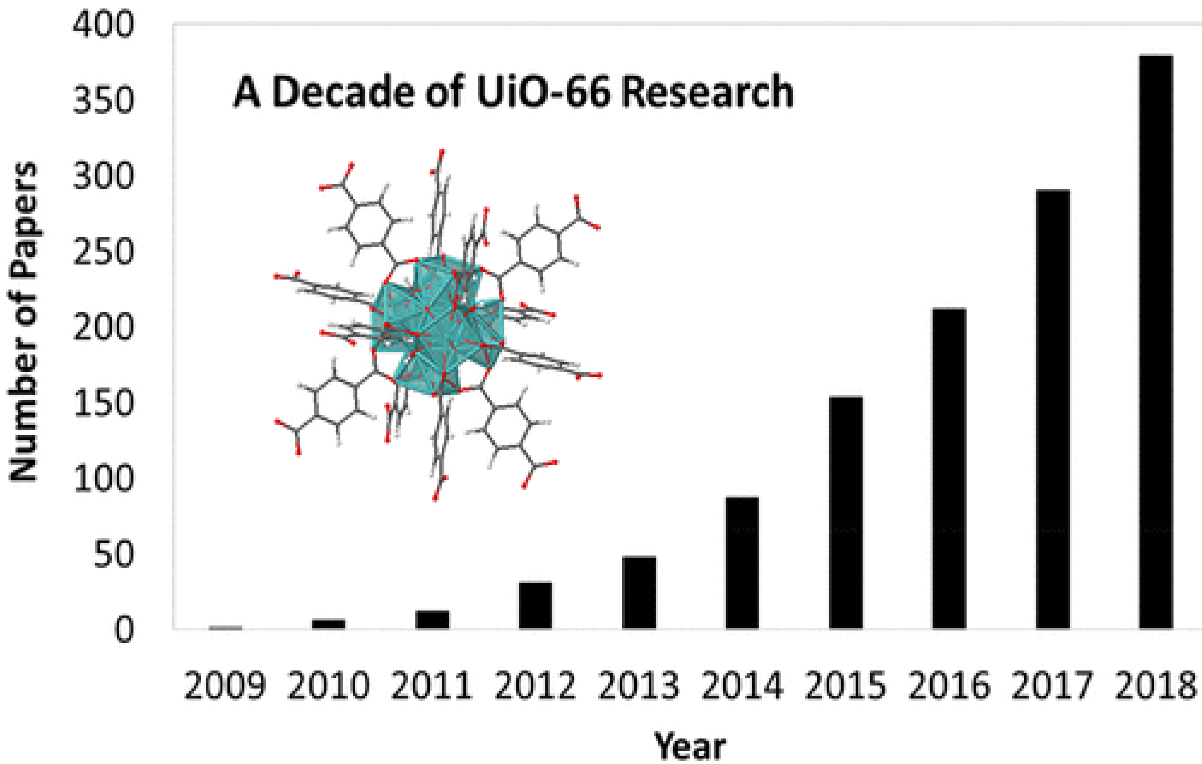




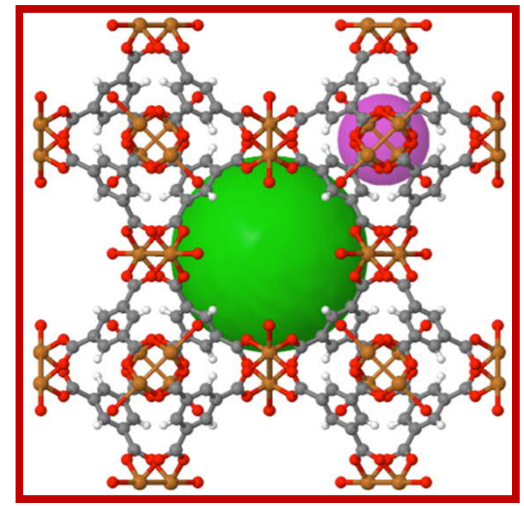


IMPORTANT MOF STRUCTURES

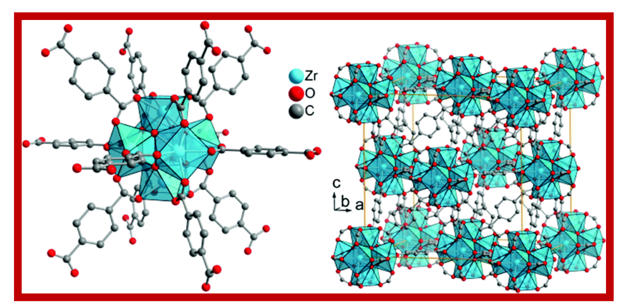


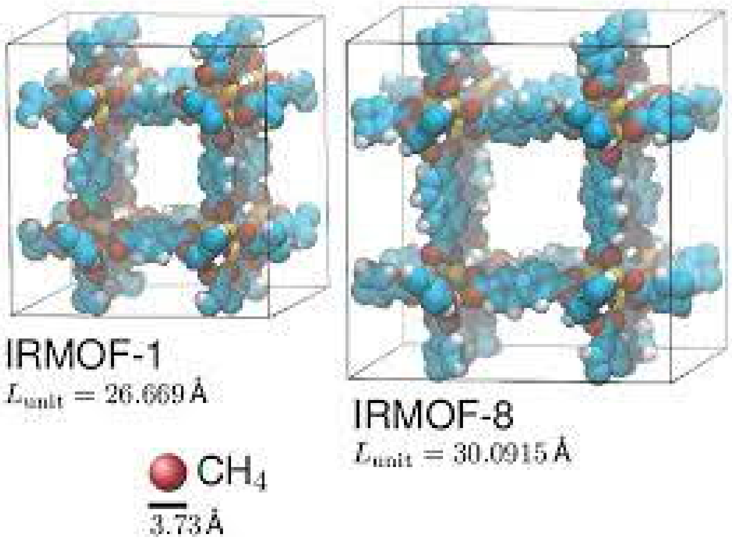


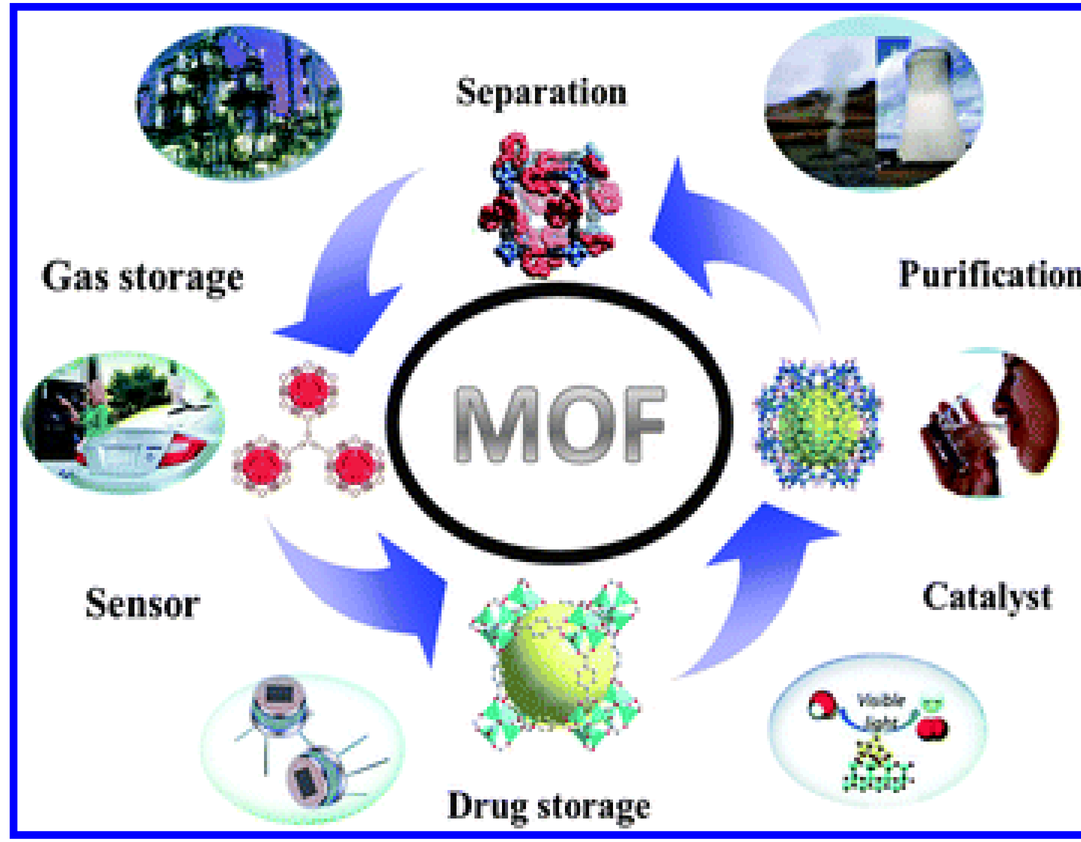
HKUST-1



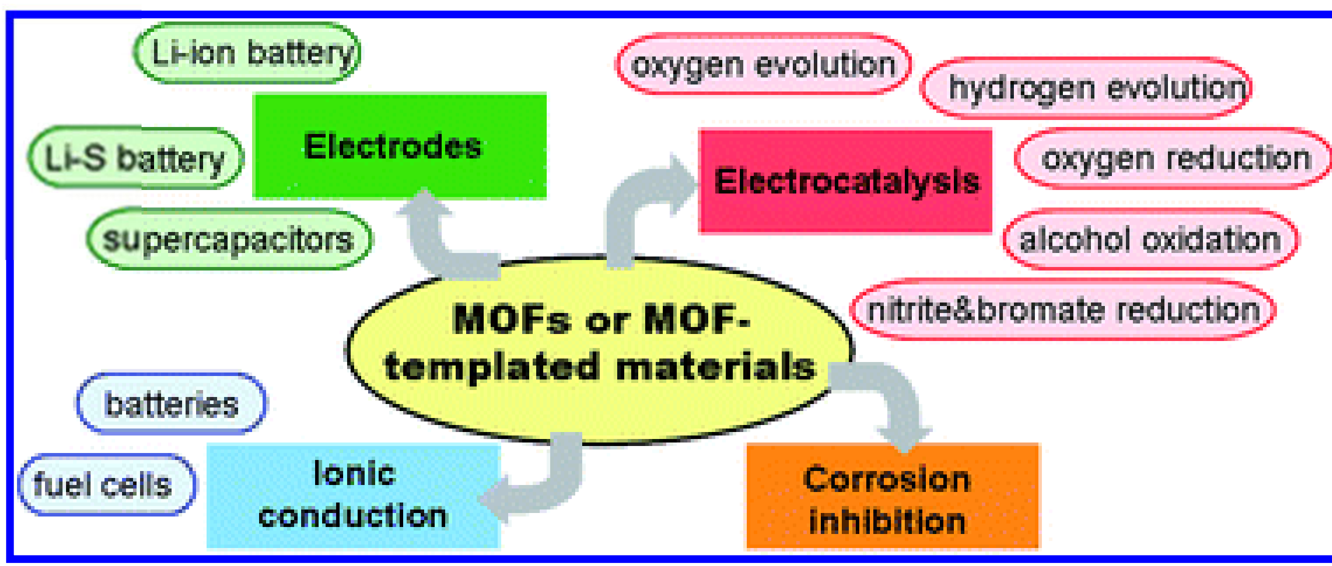
UiO-66

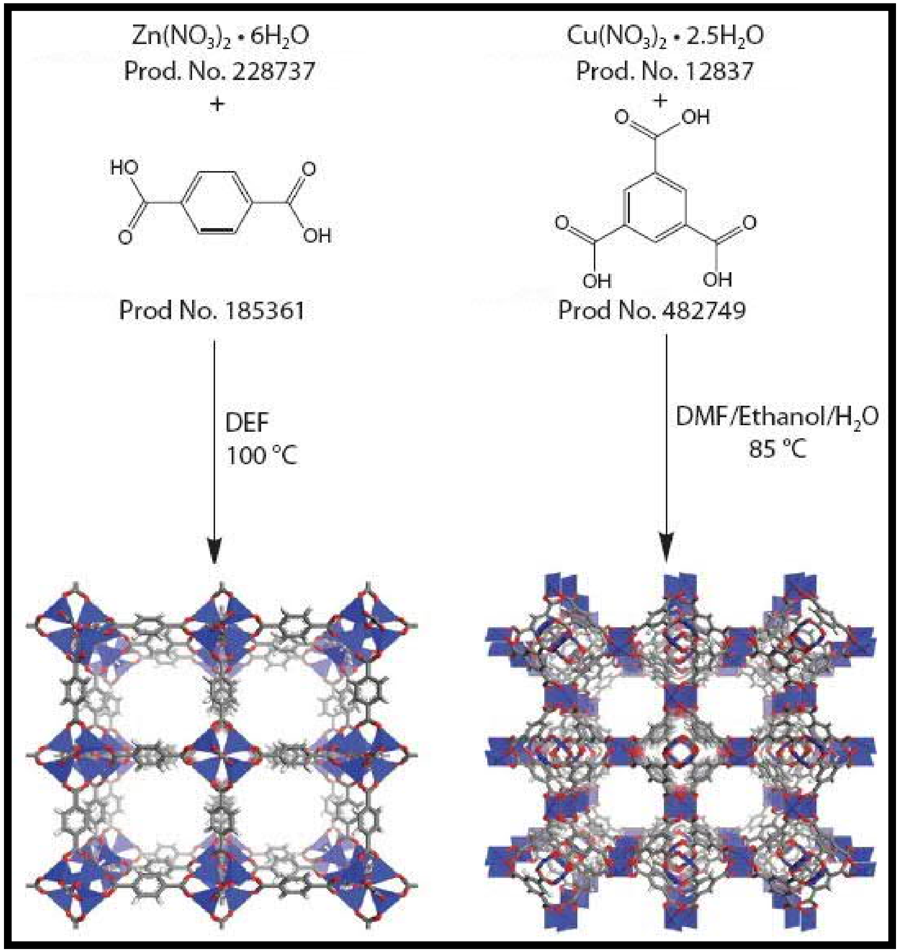






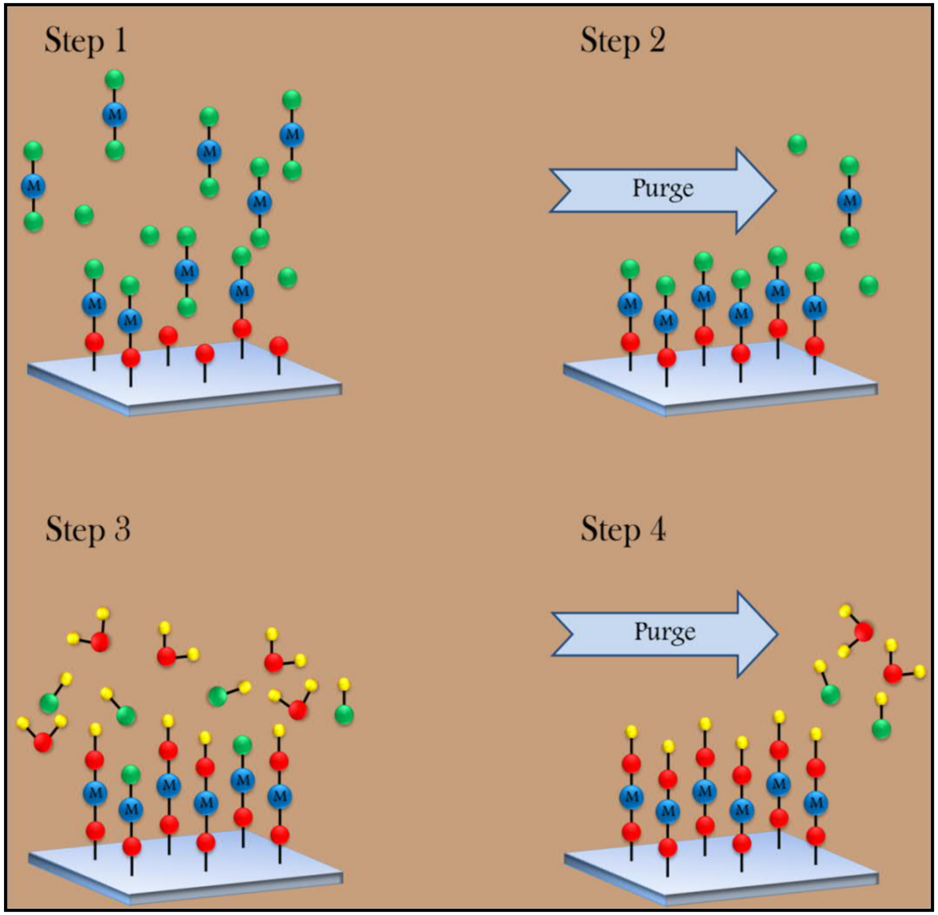
MOF THIN FILMS!



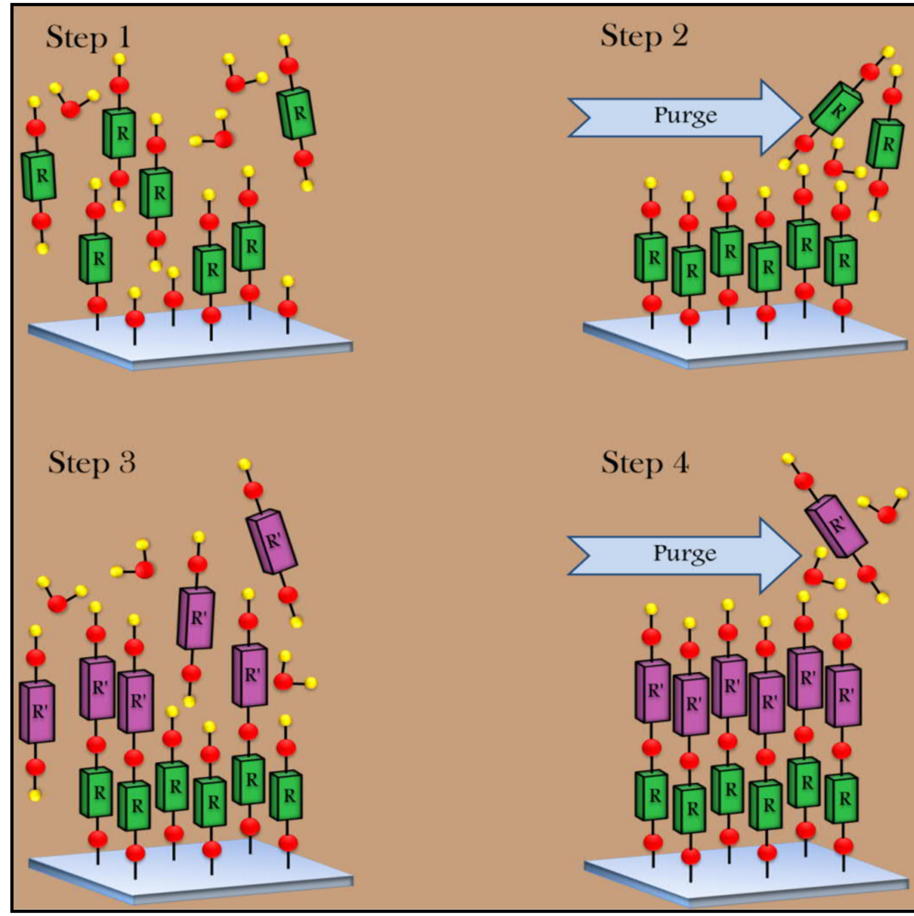


Synthesis of MOFs

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



ALD (Atomic Layer Deposition)



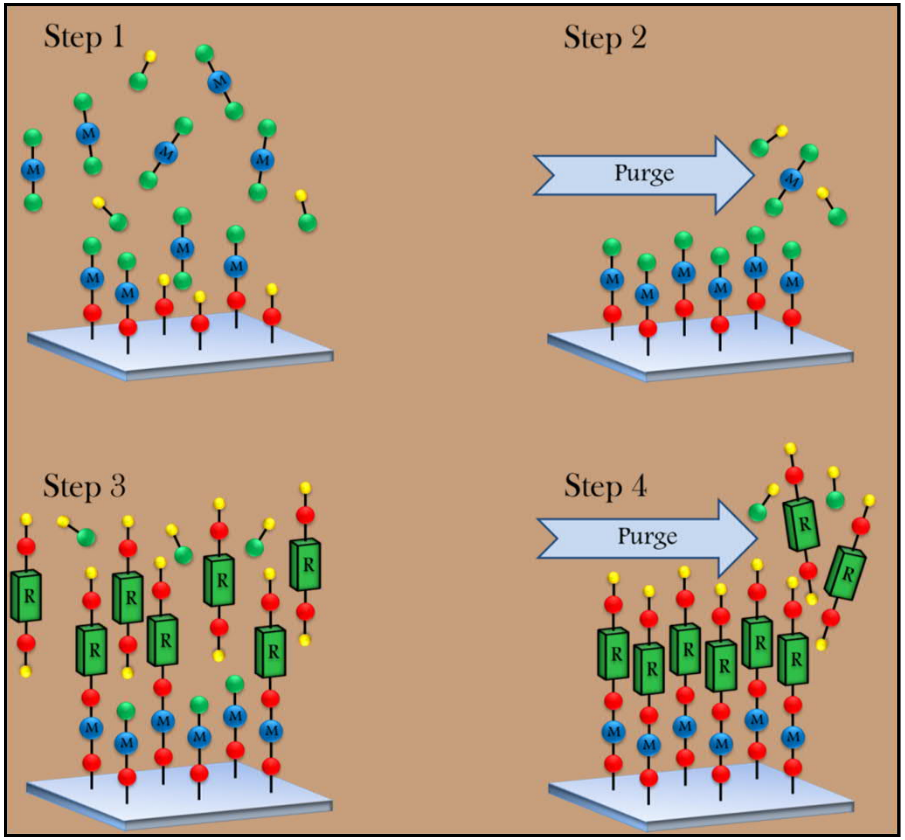
MLD (Molecular Layer Deposition)

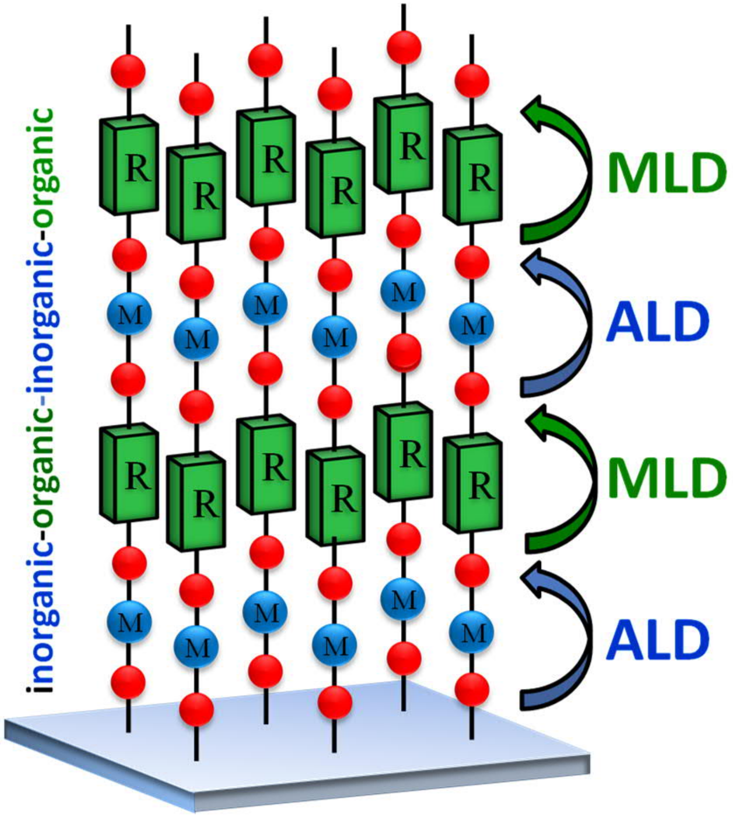
High-quality
INORGANIC thin films
with atomic level control

ORGANICS !

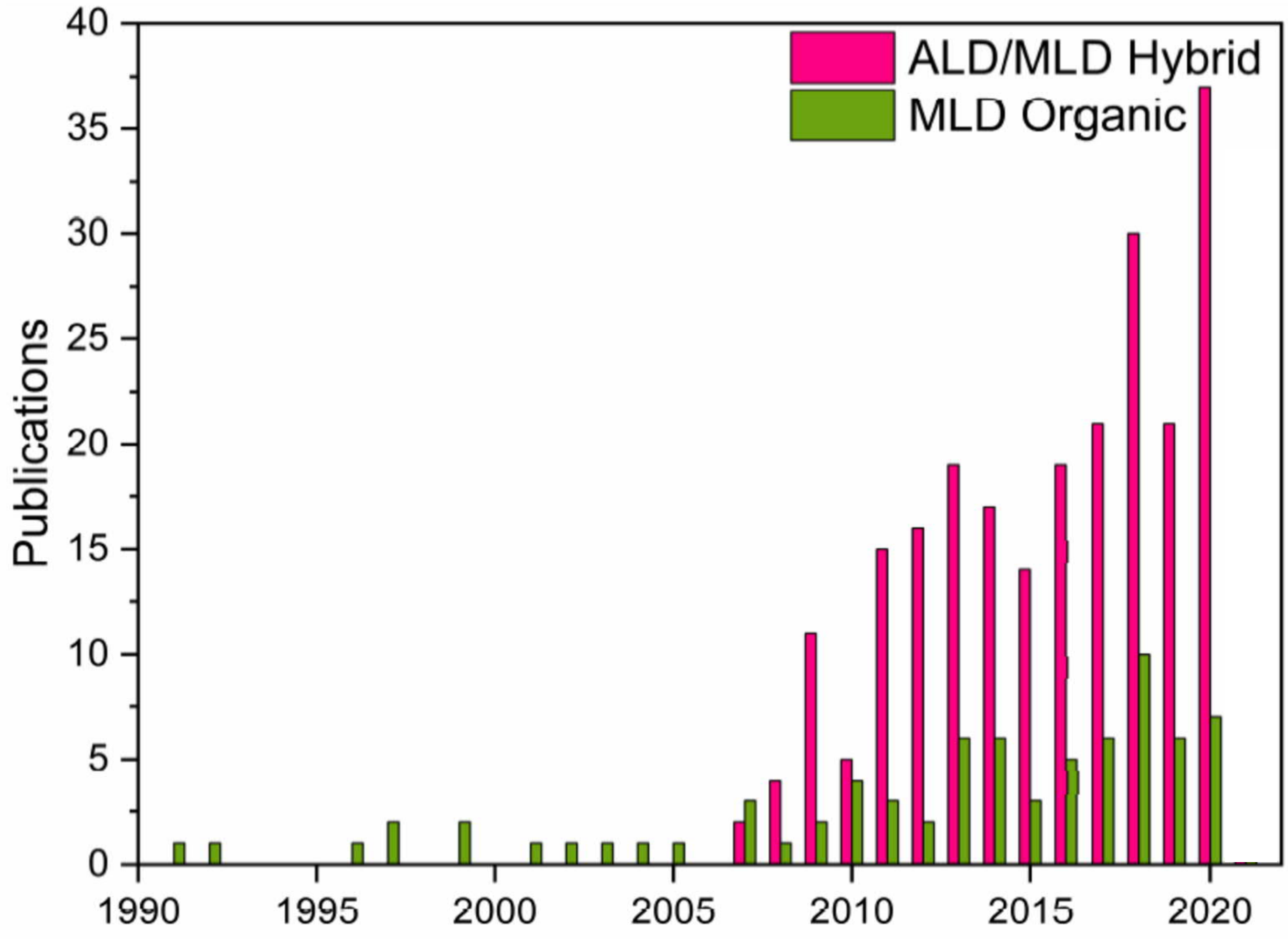
(in 1990s)

Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD





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



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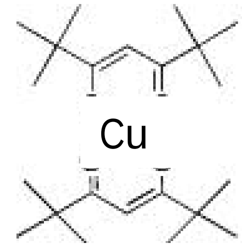
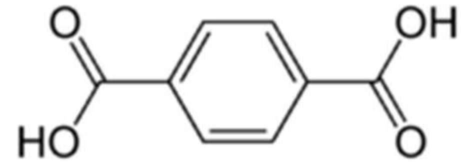
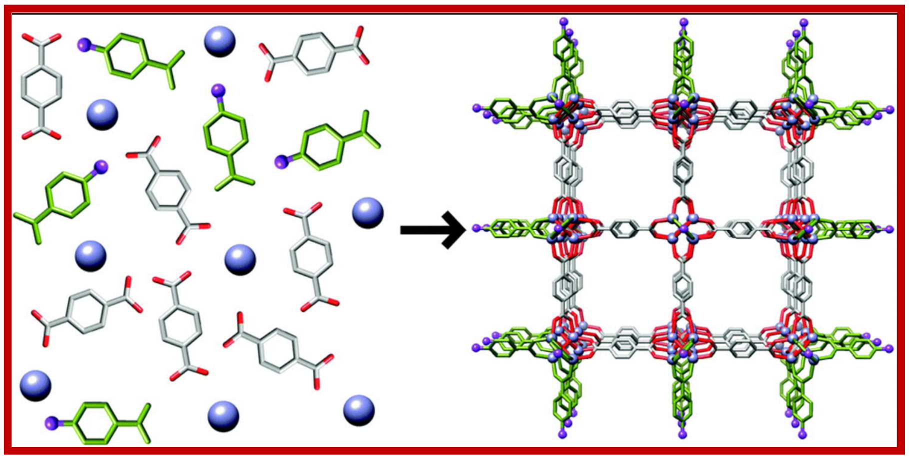
PRECURSORS for ALD/MLD



$Cu(thd)_2$



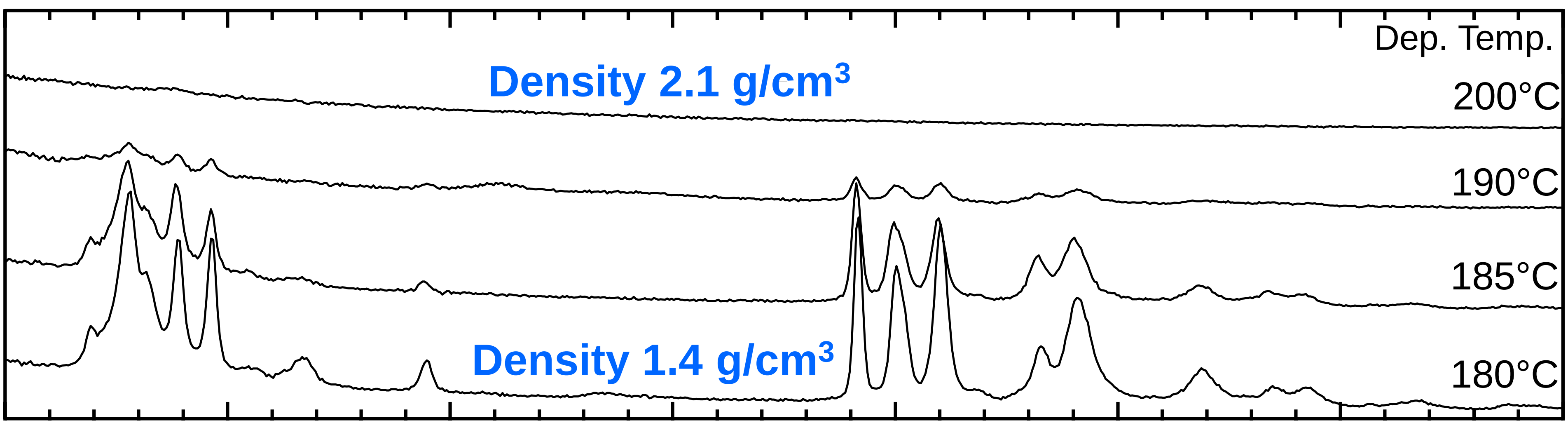
Terephthalic acid (TPA)

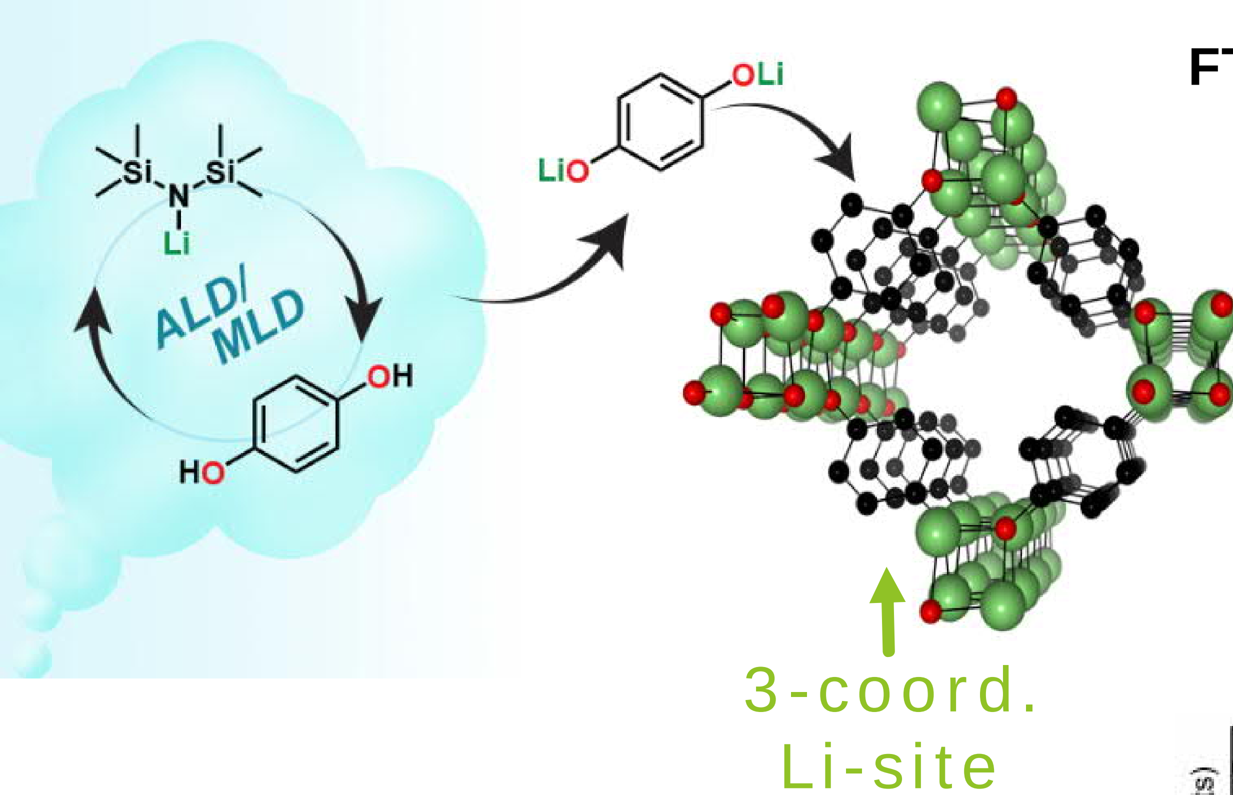


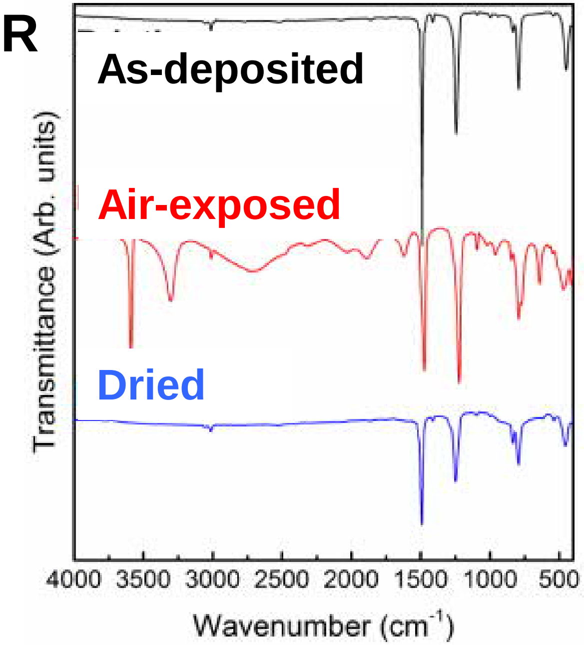
MOF

METAL-ORGANIC FRAMEWORK

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

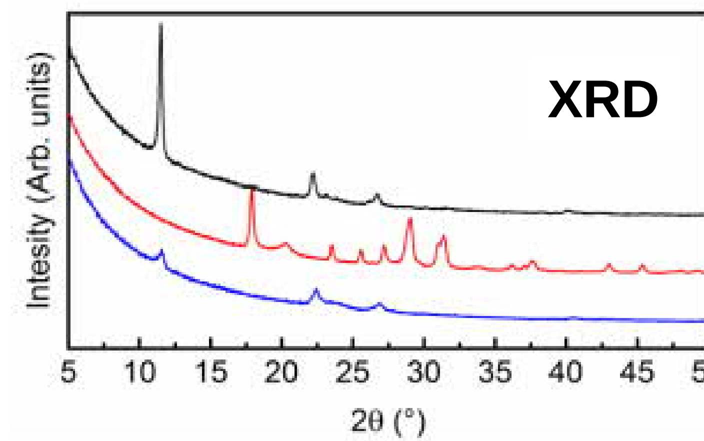






Li + Hydroquinone

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



Structure predicted by DFT

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).