LECTURE SCHEDULE

Mon	(Ke3)	12.15 – 14.00
Wed	(Ke2)	10.15 – 12.00
Fri	(Ke5)	10.15 – 12.00

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu
10.	Fri	29.09.	Cu & Magnetism & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

QUESTIONS: Lecture 7

1. Explain shortly the following terms;

   do they involve only inorganics, only organics or both inorganics and organics?

   - Perovskite

   - POM

   - MOF

   - MLD

2. Name the following metal complexes:

   $K_3[Fe(CN)_6]$

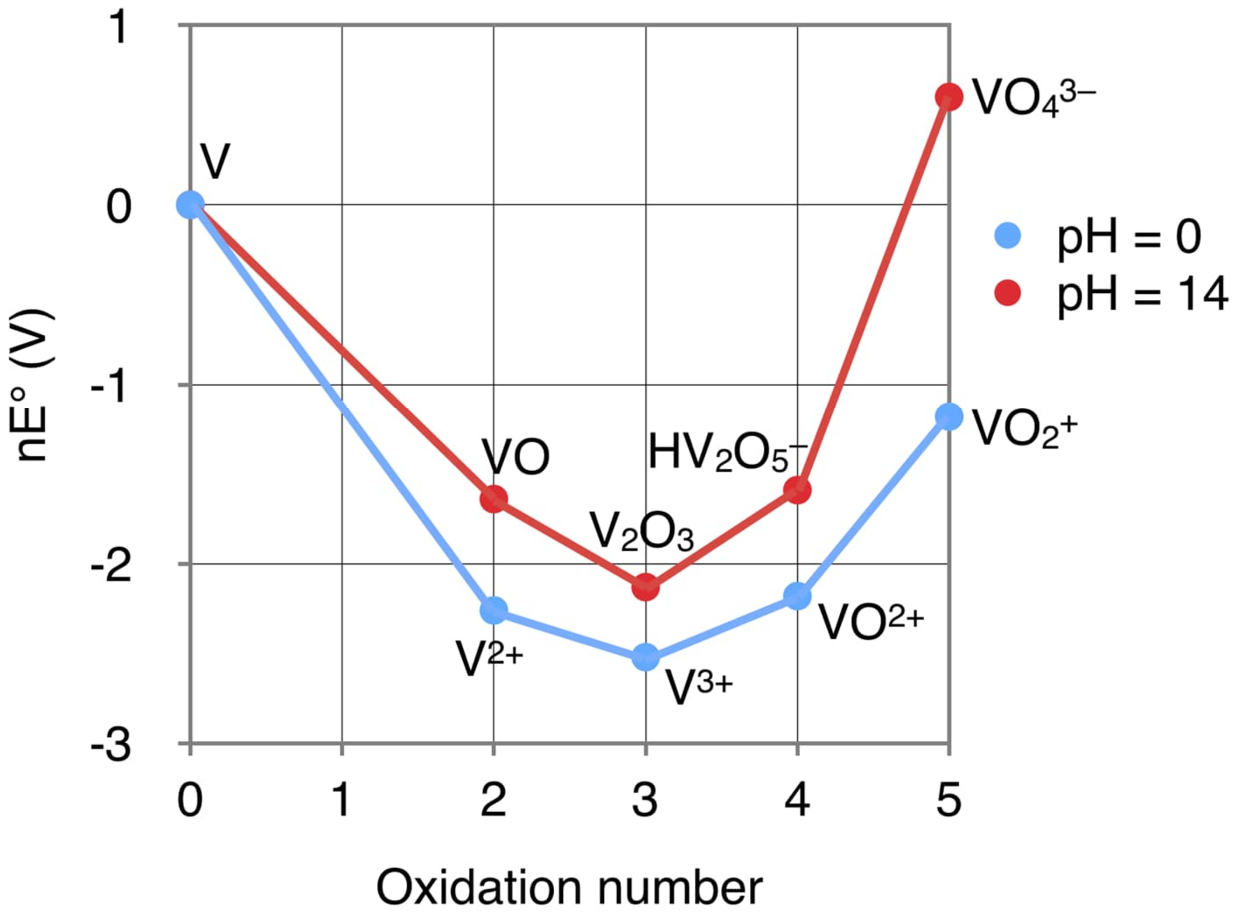
   $[CoN_3(NH_3)_5]SO_4$

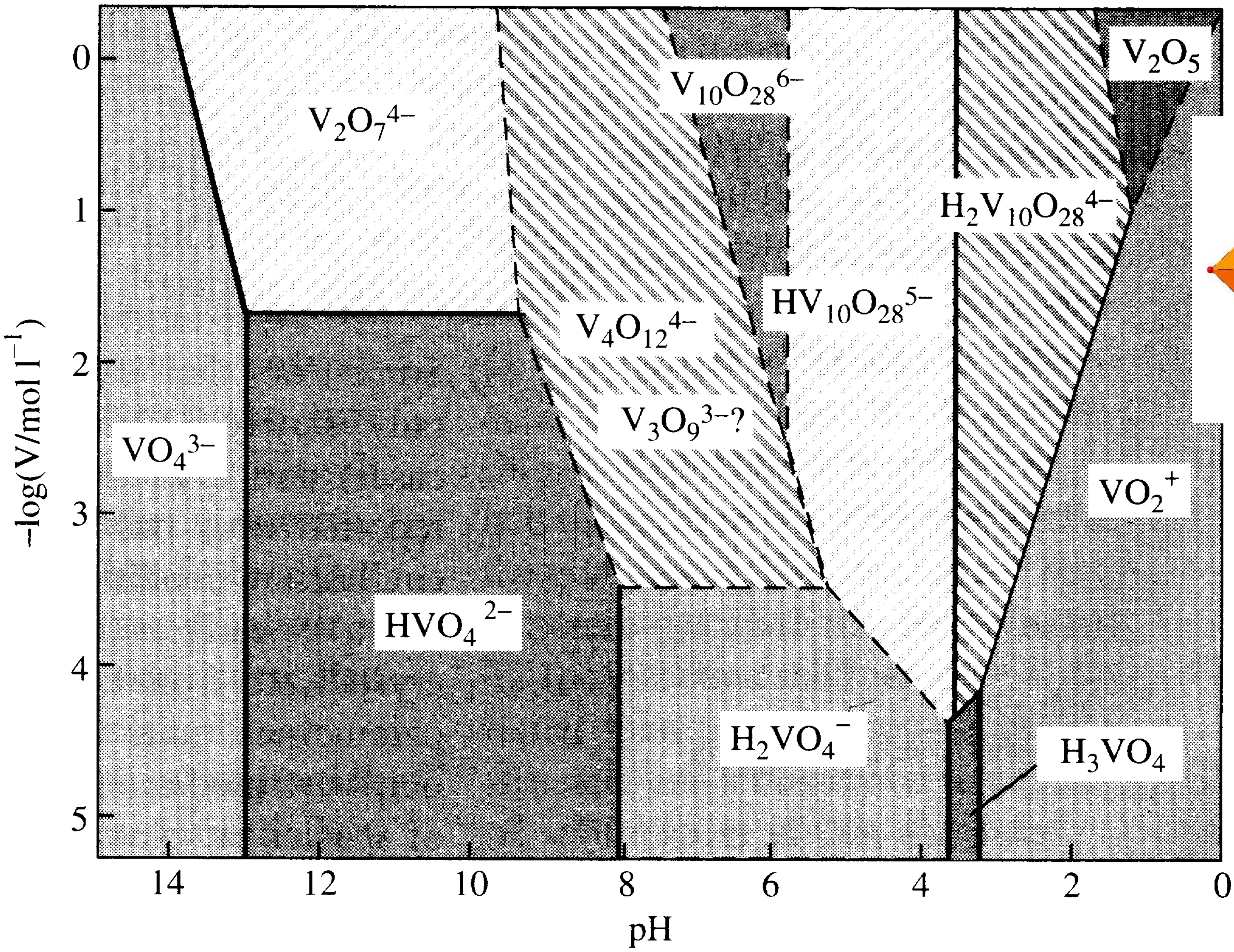
   $NH_4[Cr(NCS)_4(NH_3)_2]$

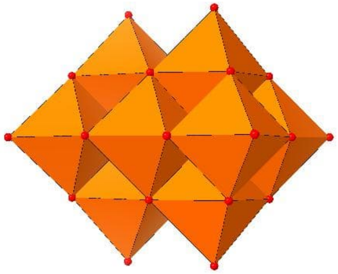
   $[Cr(H_2O)_6]Cl_3$

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

Frost diagram for vanadium







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

PolyOxoMetalate (POM)

- Anionic metal-oxygen clusters; metal at its highest oxidation state
- Basic structure unit: MO_6
- Typical for: V, Nb, Ta, Mo, W
- 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)
  - energy conversion/storage

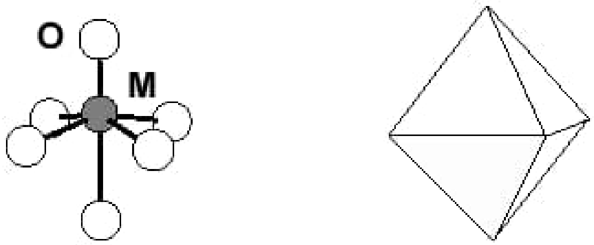


Figure 1.1. Ball-and-stick and polyhedral representations of the fundamental unit MO_6. Note that the M atom is displaced off the geometrical centre of the octahedron towards one of the oxygens, thus giving rise to a distorted C_{4v} unit.

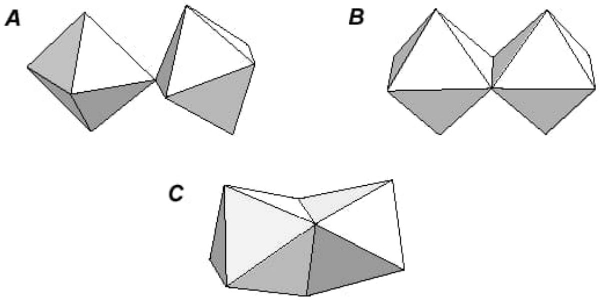
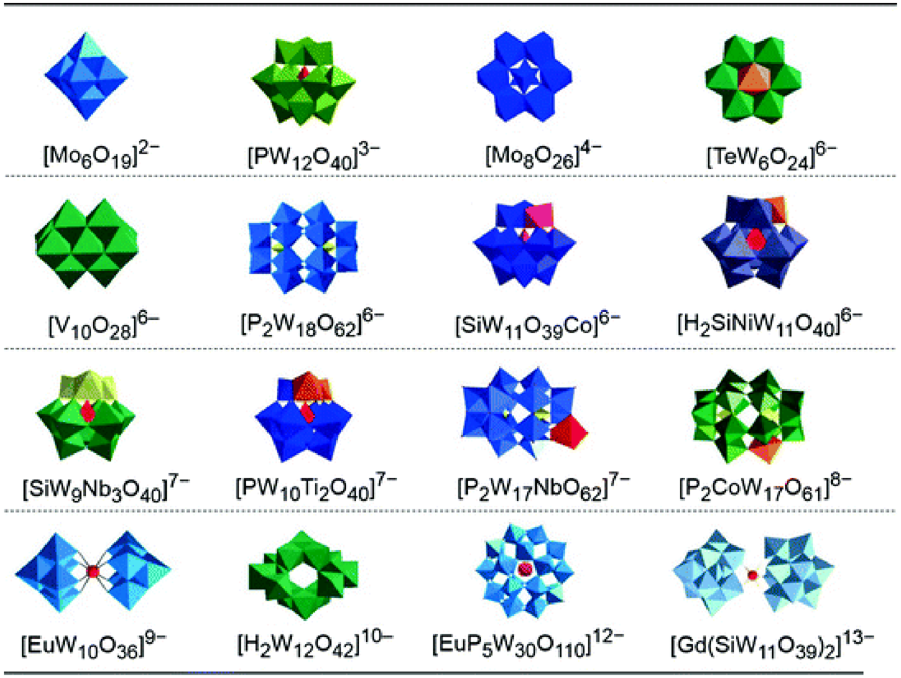
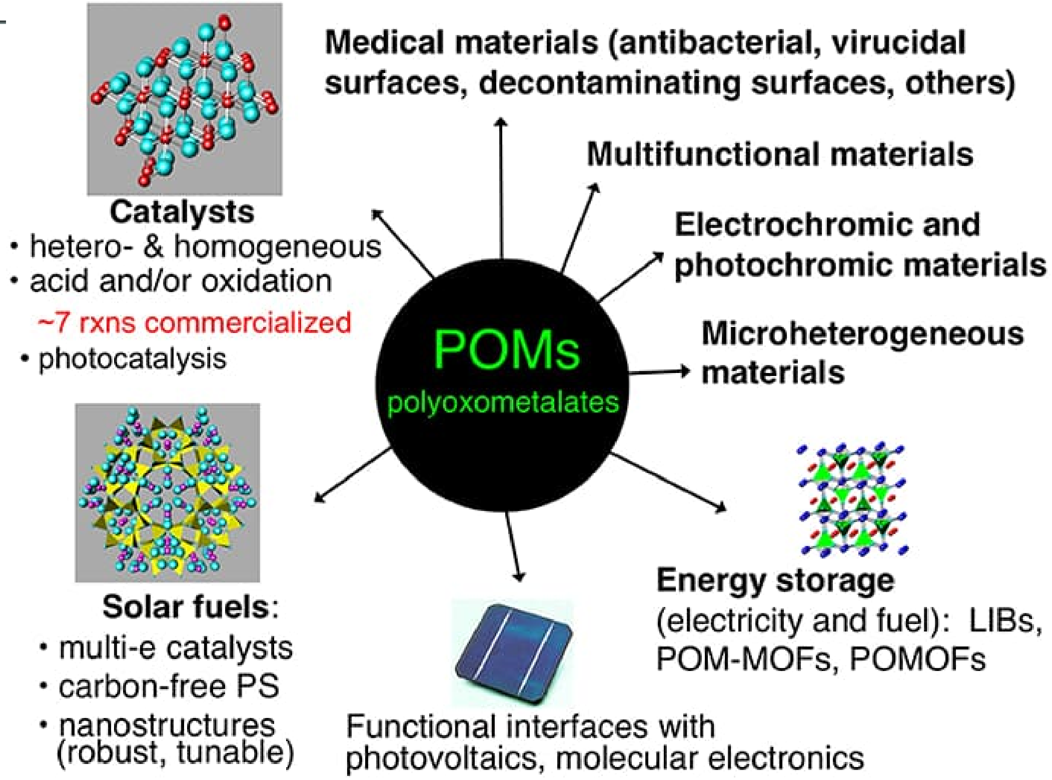


Figure 1.2. The polyhedral models represent the three possible unions between two MO_6 octahedral units. A) corner-sharing, B) edge-sharing and C) face-sharing. Each corner represents an oxygen position.


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


POMs
polyoxometalates
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
Solar fuels:
• multi-e catalysts
• carbon-free PS
• nanostructures (robust, tunable)
Functional interfaces with photovoltaics, molecular electronics
Energy storage (electricity and fuel): LIBs, POM-MOFs, POMOFs

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

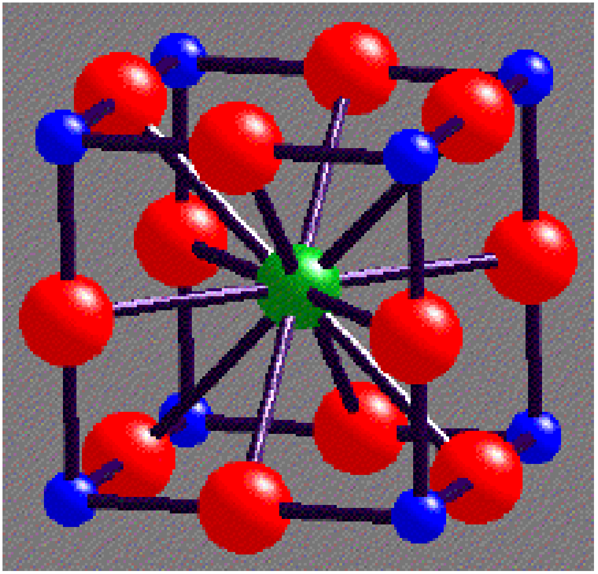
    (electrical dipole moment without external electric field)

- **Bronzes: e.g. Sr_xNbO_3 (x = 0.7 - 0.95)**
  - good electrical conductivity (mixed valency)
  - A-cation deficient ABO_3 perovskite structure
  - ref. Na_xWO_3

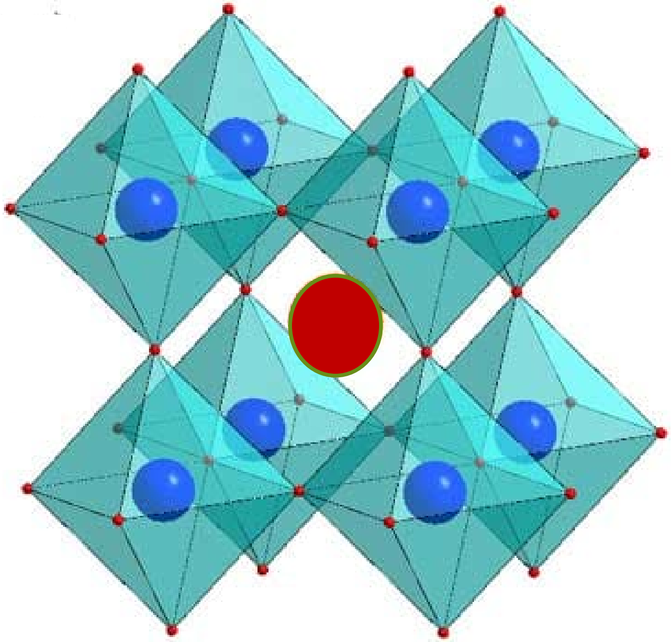
- **Additive in steels and metal alloys**

- **Low neutron absorption (ref. Zr)**

ABO_3



PERოVSKITE STRUCTURE



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

A: large cation

B: small cation (transition metal)

O: oxygen (sometimes halogen)

δ: oxygen deficiency !!!

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 – 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

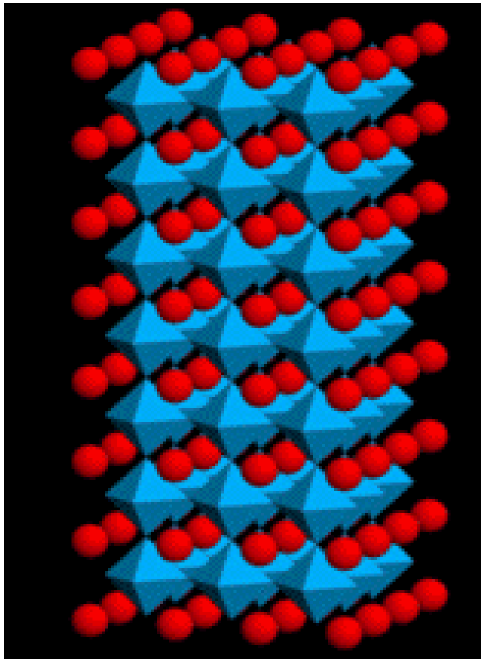
Metallic conductor
$LaCrO_3$

Piezoelectric material
Pb(Zr,Ti)O_3

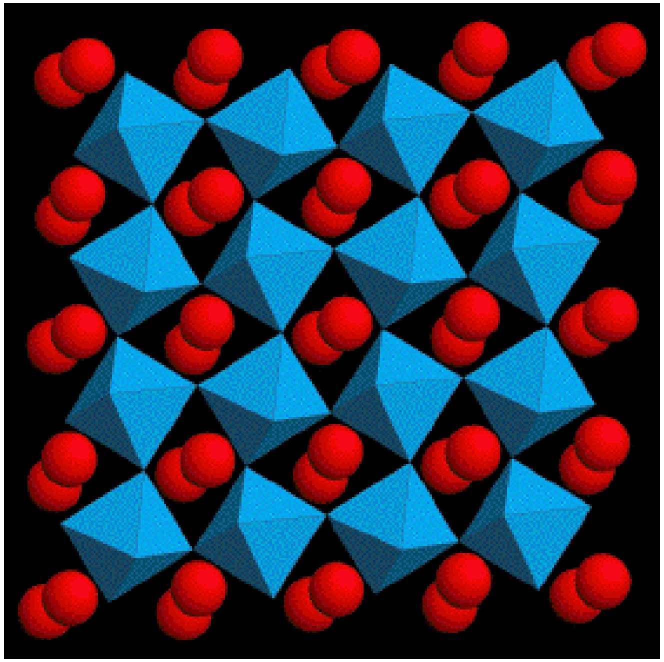
Capasitor
(high dielectric constant)
$BaTiO_3$

“Distortions and Imperfections” in Perovskite Structure

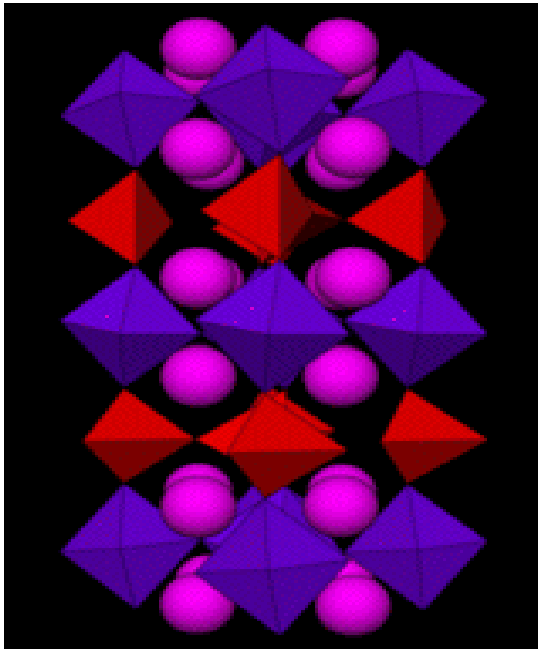
- often the source of the desired properties



IDEAL

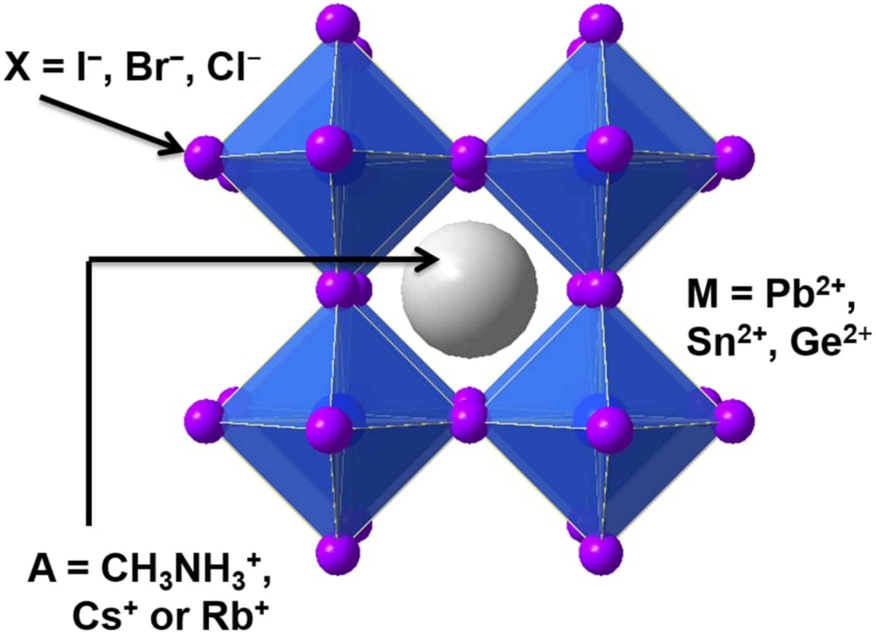


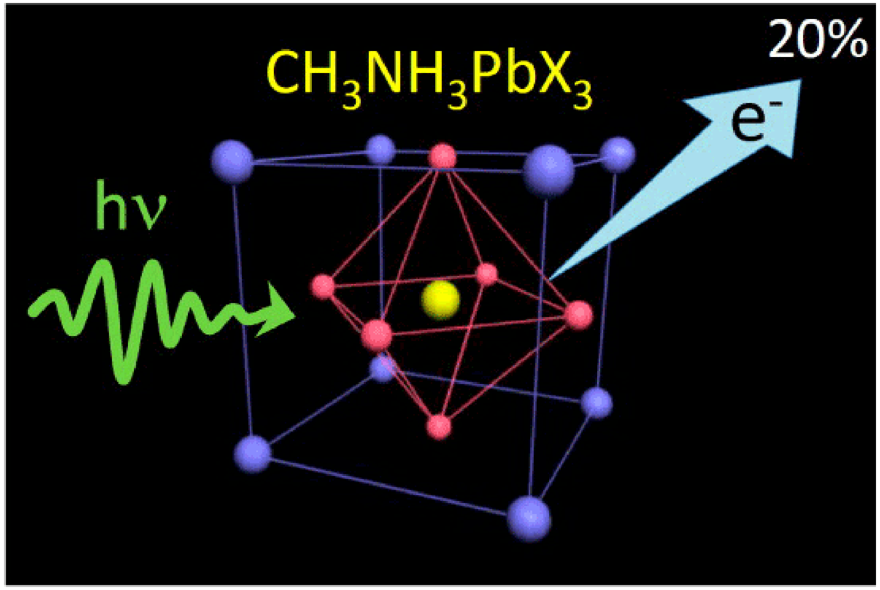
Changes in atomic positions

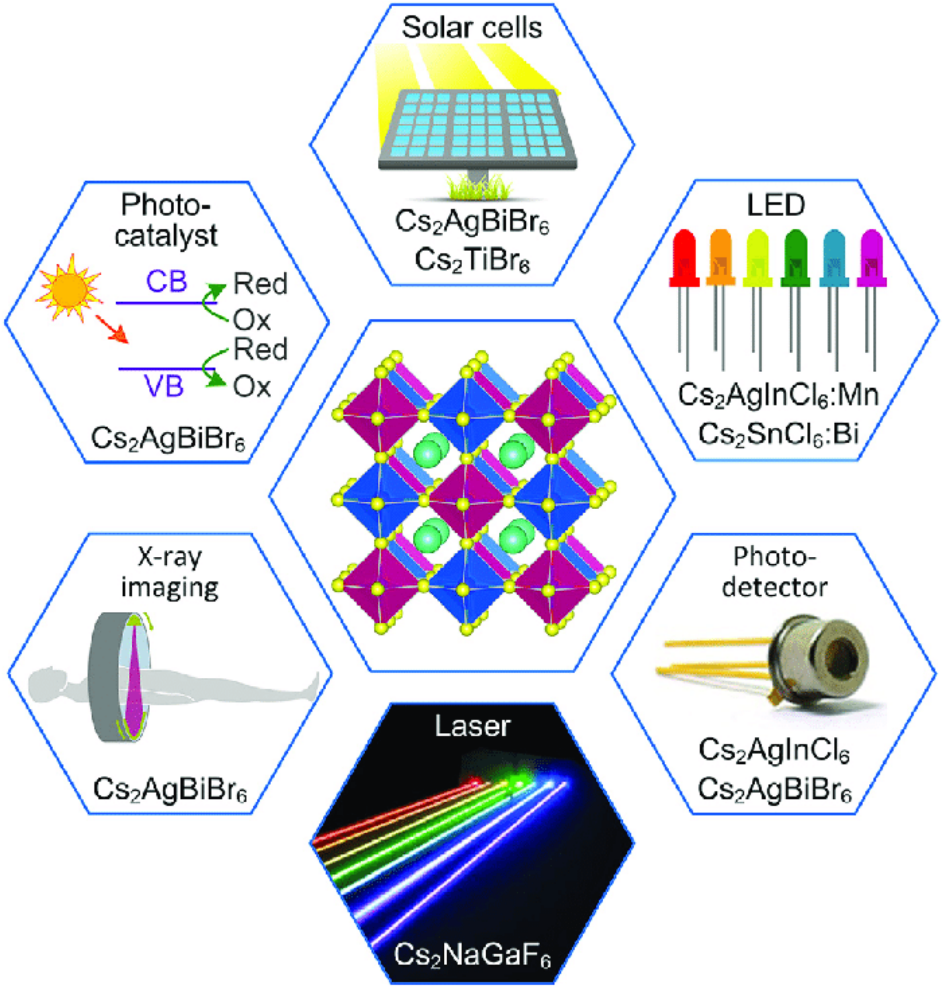


Oxygen deficiency

“Perovskite Solar Cell”

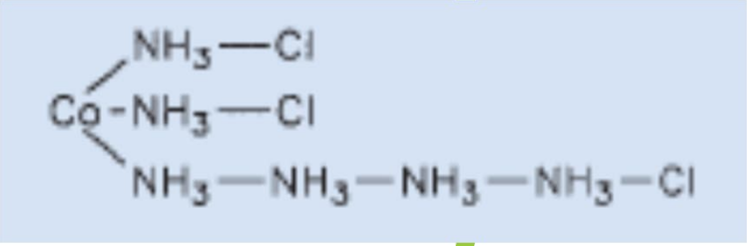






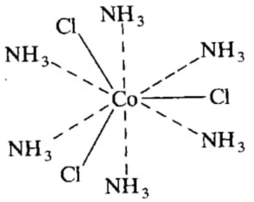
HISTORY of COORDINATION COMPLEXES

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

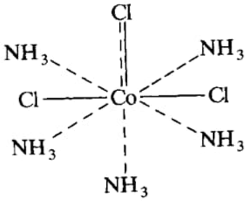


- **Alfred Werner (1866-1919), Nobel 1913:**
  - ”primary valence” ≈ oxidation state
  - “secondary valence” ≈ coordination number

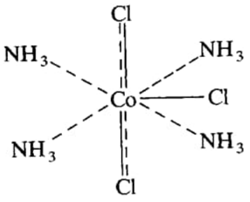
(1) $CoCl_3 \cdot 6NH_3$



(2) $CoCl_3 \cdot 5NH_3$



(3) $CoCl_3 \cdot 4NH_3$



COORDINATION COMPLEXES

- **Central cation**: Co (oxidation state 3+, coordination number 6)
- **Coordinated ligands:** (NH_3 or Cl^-) within the brackets
  - Cl^- ions within brackets belong to the coordination sphere, and also contribute to the oxidation state of Co
- **Counter ions:**
  - Cl^- ions outside of brackets contribute to the oxidation state only
  - Outside-of-brackets Cl^- ions are removed in water solutions

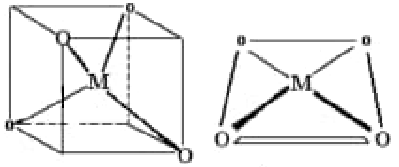
(1) $CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$
(2) $CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$
(3) $CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4]Cl_2]Cl$
(4) $CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$

These complexes differ in colour and electrical conductivity

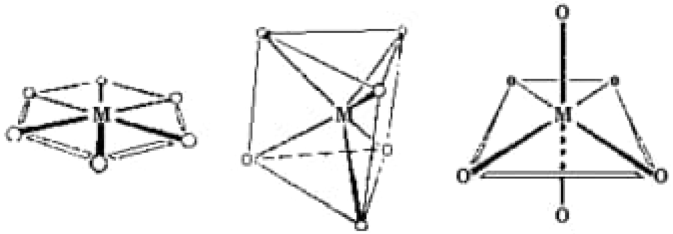
- $[Pt(NH_3)_6]Cl_4$ has relatively high conductivity (more ions)
- $[Pt(NH_3)_5Cl]Cl_3$ has decreasing conductivity
- $[Pt(NH_3)_4Cl_2]Cl_2$ has decreasing conductivity
- $[Pt(NH_3)_3Cl_3]Cl$ has decreasing conductivity
- $[Pt(NH_3)_2Cl_4]$ has zero conductivity

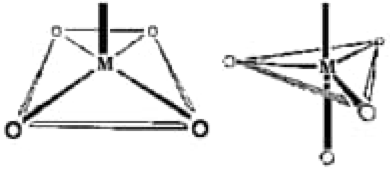
COORDINATION CHEMISTRY

- **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):**
  - **(inorganic or organic) molecules or ions around the central atom**
  - **infinite/integer number (n)**
  - **ligands form the coordination sphere of the central atom**
- **Metal-ligand bond: M ← :L**
  - **each ligand gives an electron pair to central atom**
  - **COVALENT COORDINATION BOND**



- **Coordination number (CN = n):**
  - **typically 4 (tetrahedron or square-plane
    or 6 (octahedron)**
  - **sometimes 5 (pyramid or trigonal bipyramid)**

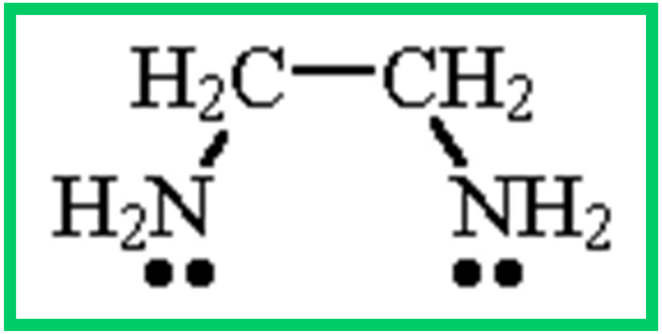




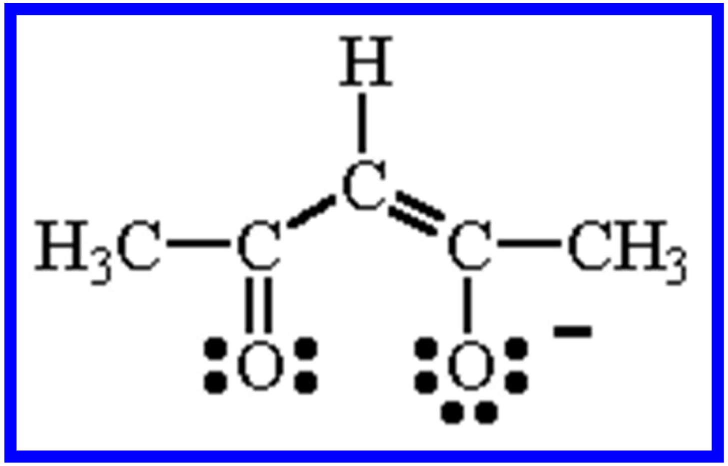
- **Counter ion: anion (X) or cation (A)**
- **Typical for metal complexes: bright colours & magnetism**

MULTIDENTATE 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)**

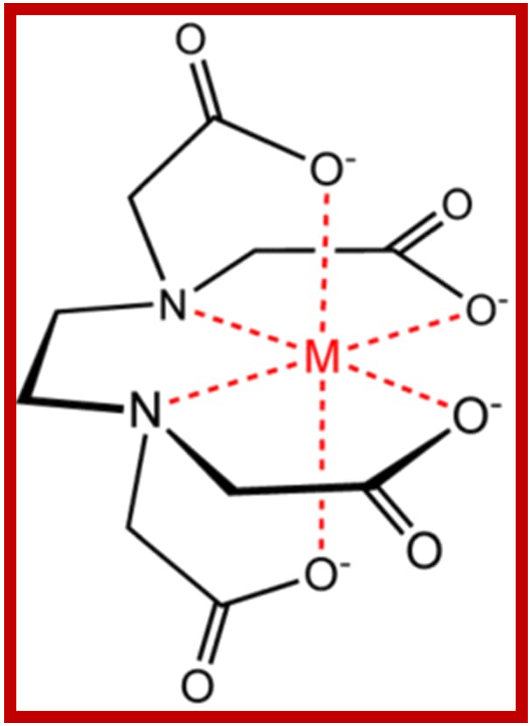


Ethylenediamine (en):2



Asetyleneacetonato (acac): 2

EDTA: 6



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 names
- 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

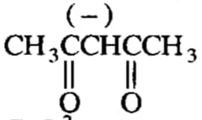
negative ligand: o-ending (F^- fluoro, O^{2-} oxo, OH^- hydroxo, NO^{2-} nitro, CN^- cyano)

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

ambidentate: 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	
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)	
 $CH_3\underset{\underset{O}{\Vert}}{C}\overset{(-)}{CH}\underset{\underset{O}{\Vert}}{C}CH_3$	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 EXAMPLES

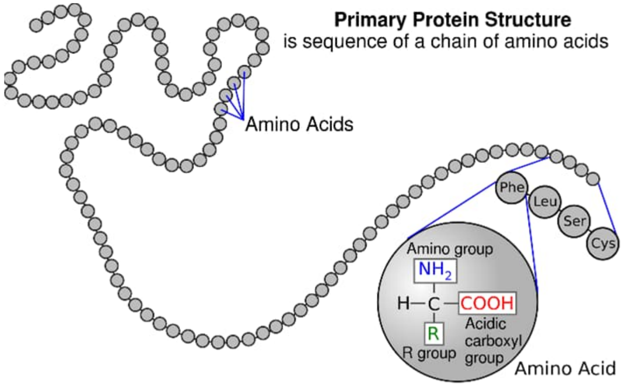
- **$[Co(NH_3)_4Cl_2]Cl$ → cobalt(III) tetraamminedichlorocobalt(III)chloride**
  - ligands in alphabetical order: NH_3 neutral (trivial) → ammine
    Cl negative → chloro
  - 4 ammine ligands and 2 chloro ligands → tetraamminedichloro
  - Cl is anion (Cl^-), complex is cation, cobalt oxidation state +3

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

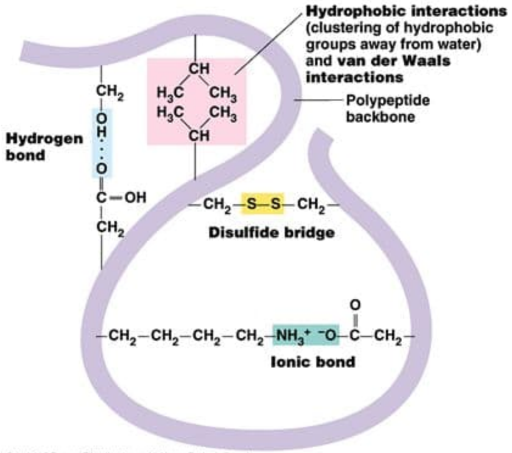
- **$[Cu(NH_2CH_2CH_2NH_2)_2]SO_4$ → bis(ethylenediamine)copper(II)sulphate**

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

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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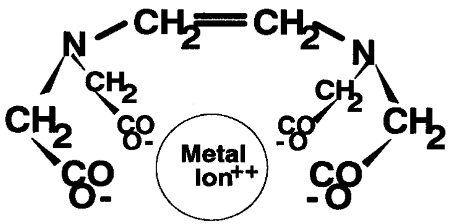
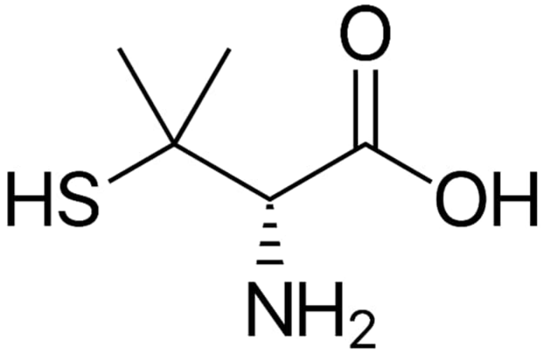
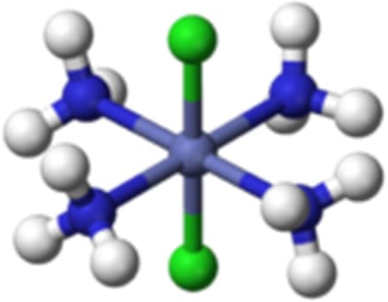


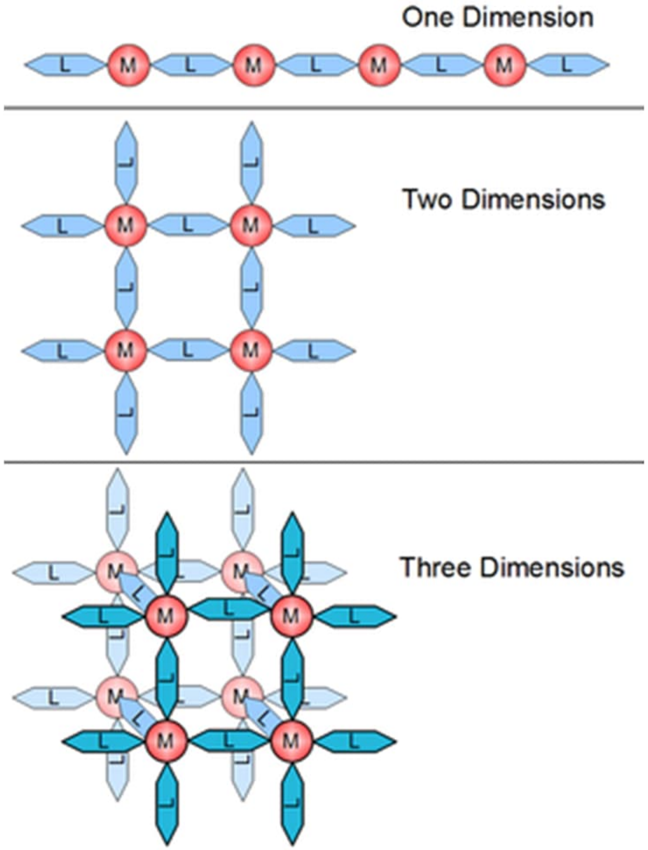
Ethylenediaminetetraacetic acid (EDTA) chelates a metal ion

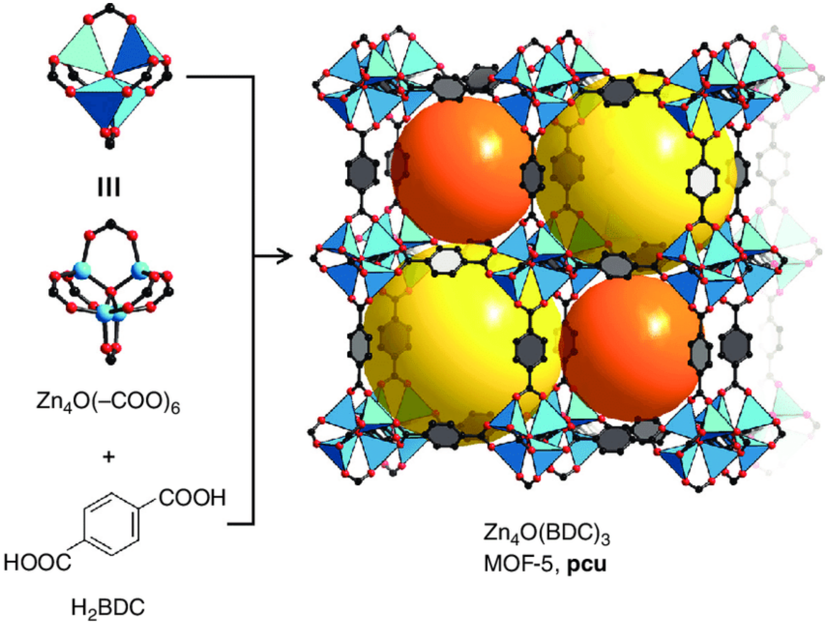


Metal-Organic Materials

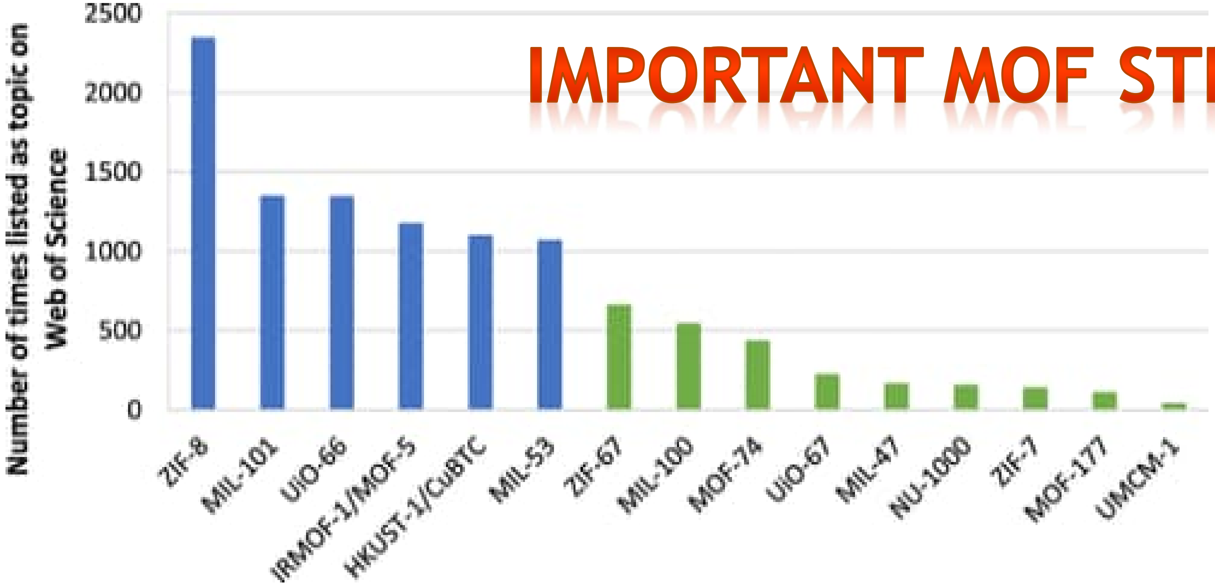
- **Coordination complex: central metal ion + (organic) ligands**
- **Coordination Polymer: ligands act as bridges → 1D, 2D, 3D**
- **Metal-Organic Framework (MOF): crystalline and highly porous**

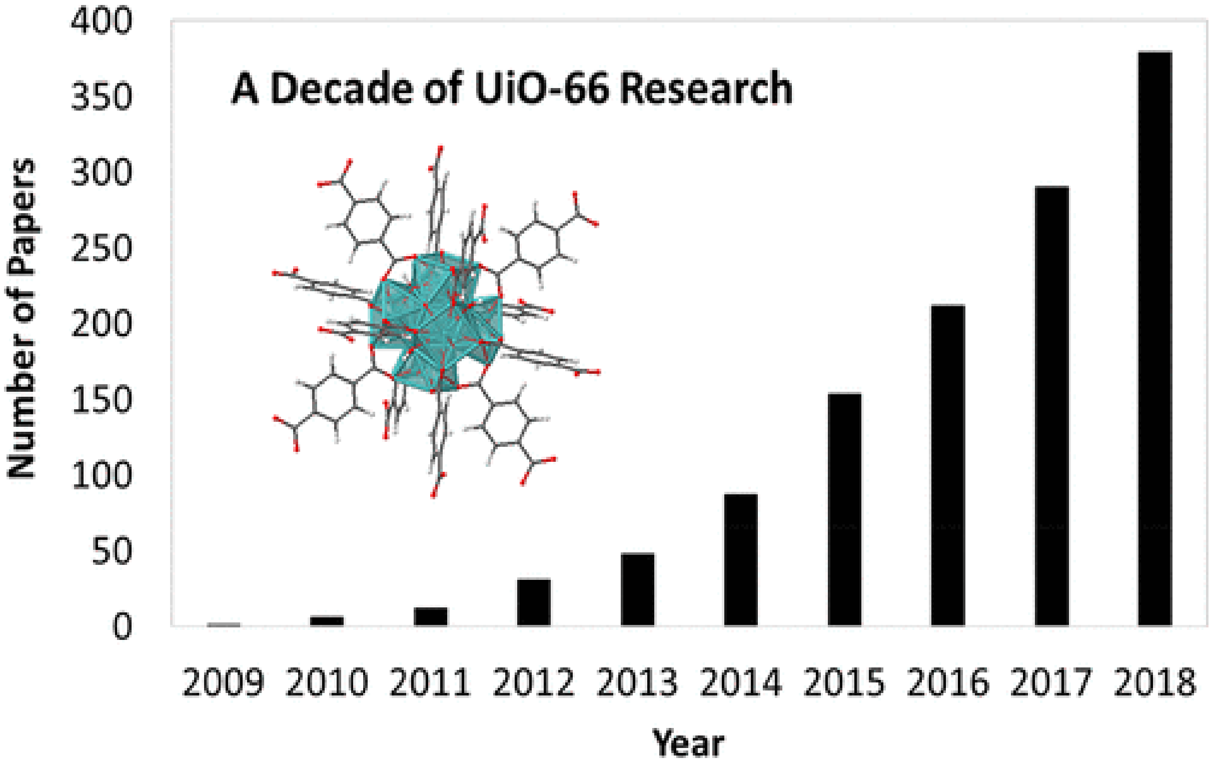






IMPORTANT MOF STRUCTURES





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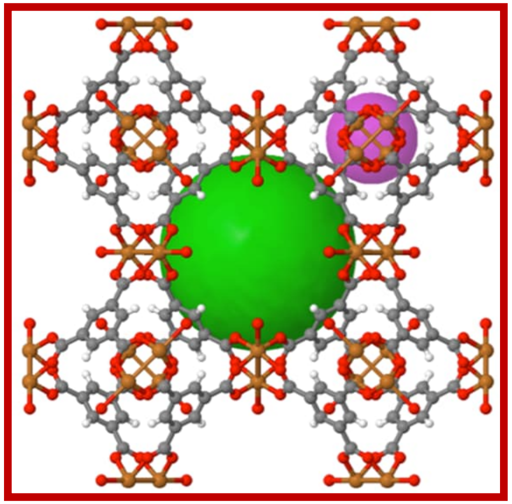
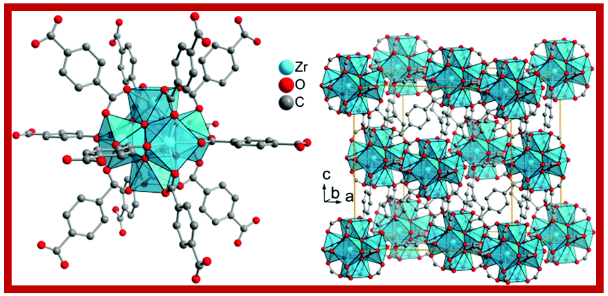
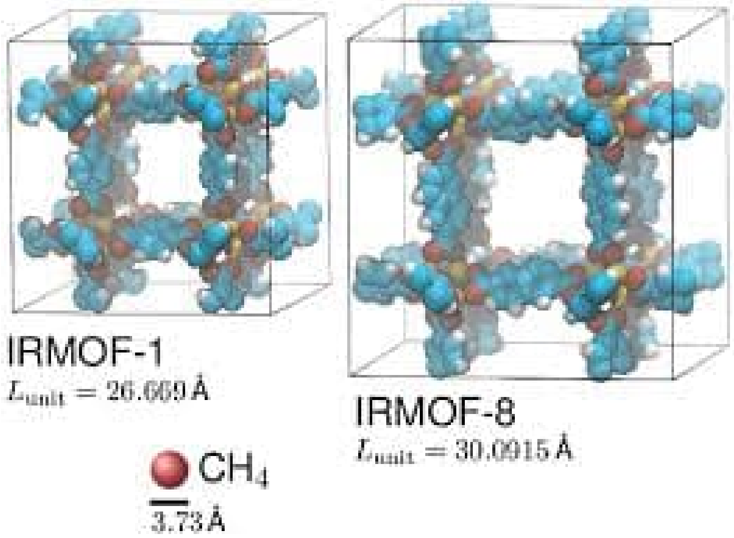
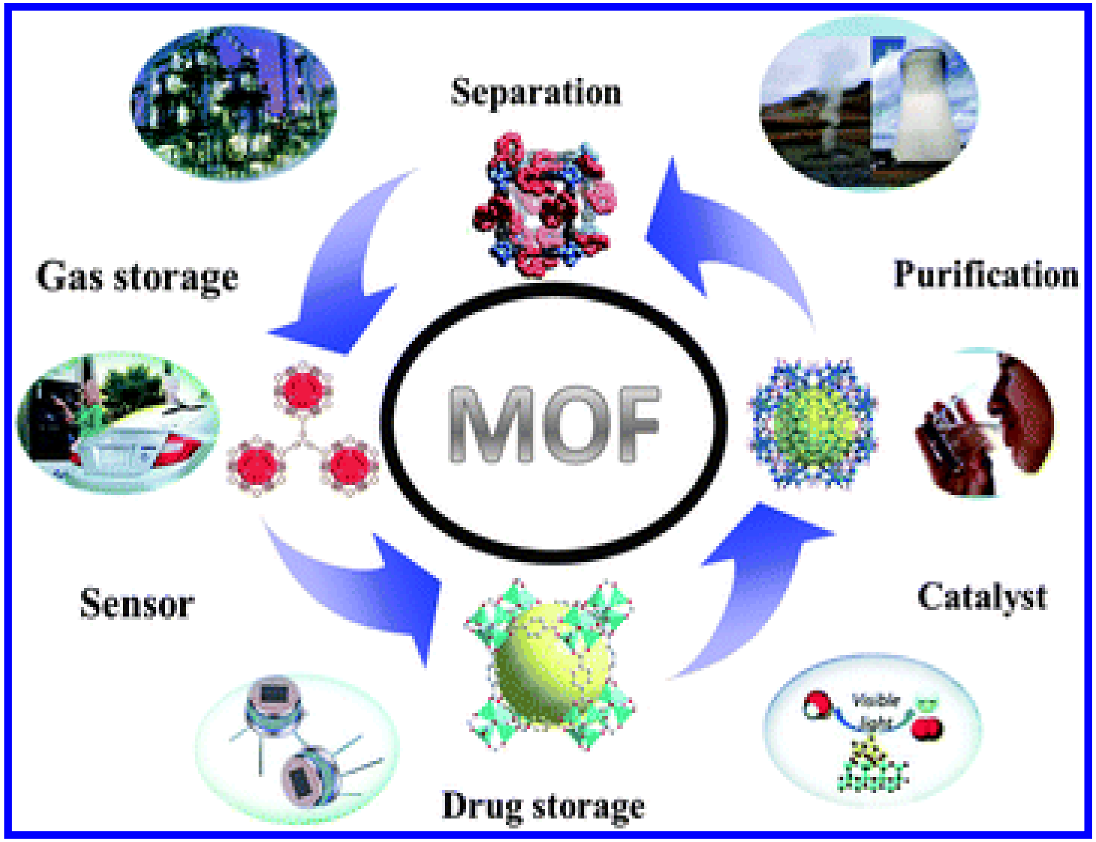
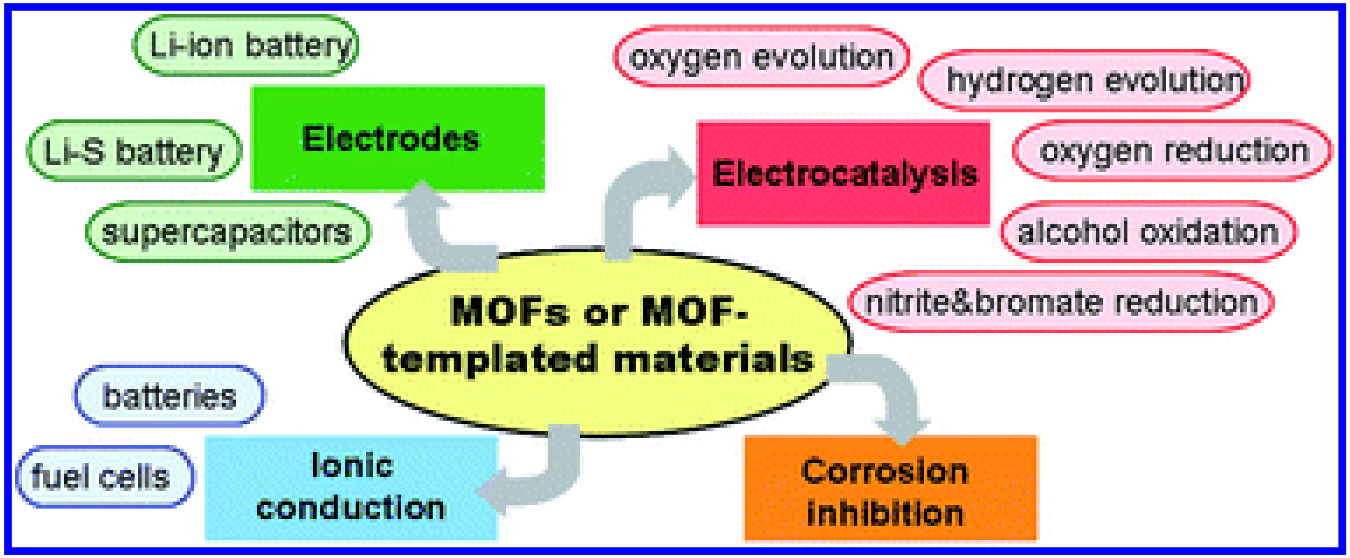


UiO-66



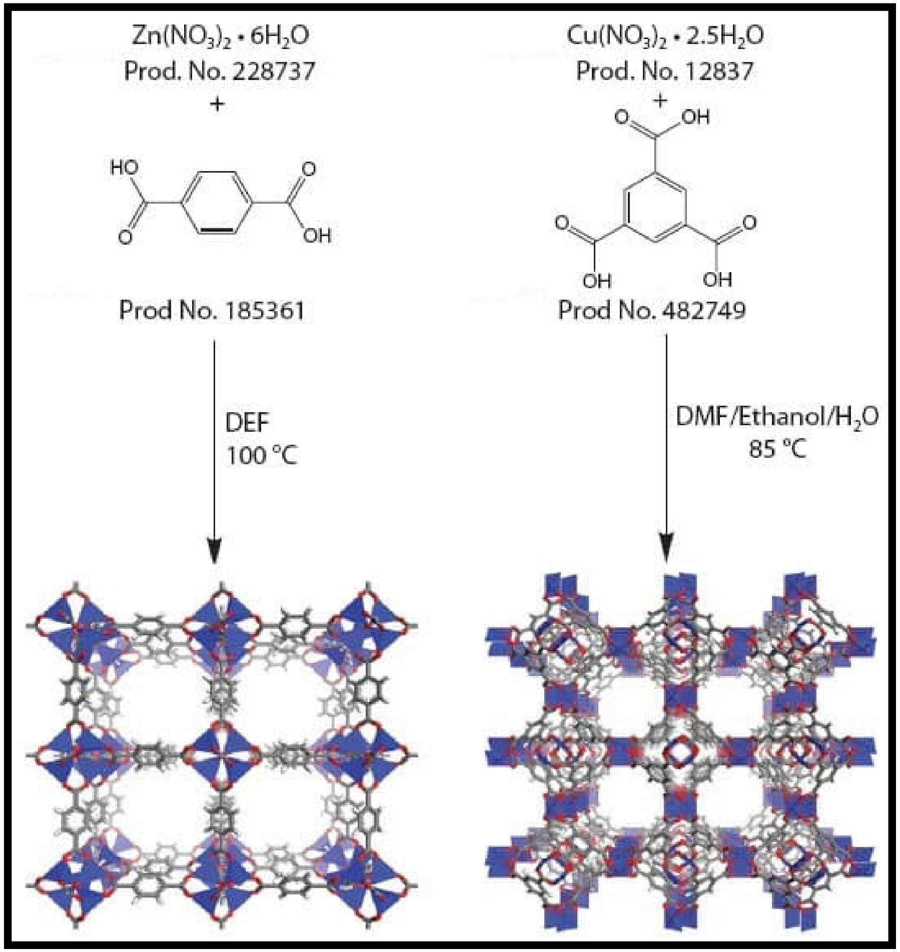

IRMOF-1
$L_{\text{unit}} = 26.669\,\text{Å}$
IRMOF-8
$L_{\text{unit}} = 30.0915\,\text{Å}$
CH_4
3.73 Å

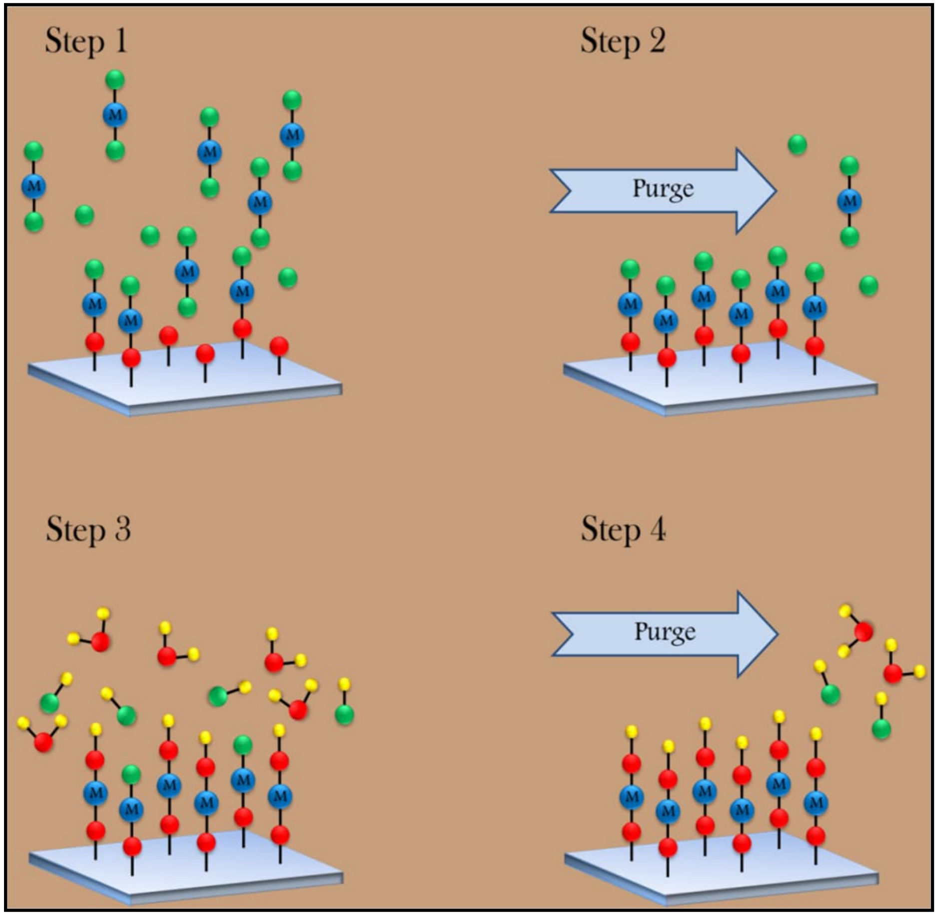

Separation
Gas storage
Purification
MOF
Sensor
Catalyst
Drug storage
Visible light


Li-ion battery
Electrodes
Li-S battery
supercapacitors
oxygen evolution
hydrogen evolution
Electrocatalysis
oxygen reduction
alcohol oxidation
nitrite&bromate reduction
MOFs or MOF-templated materials
batteries
fuel cells
Ionic conduction
Corrosion inhibition

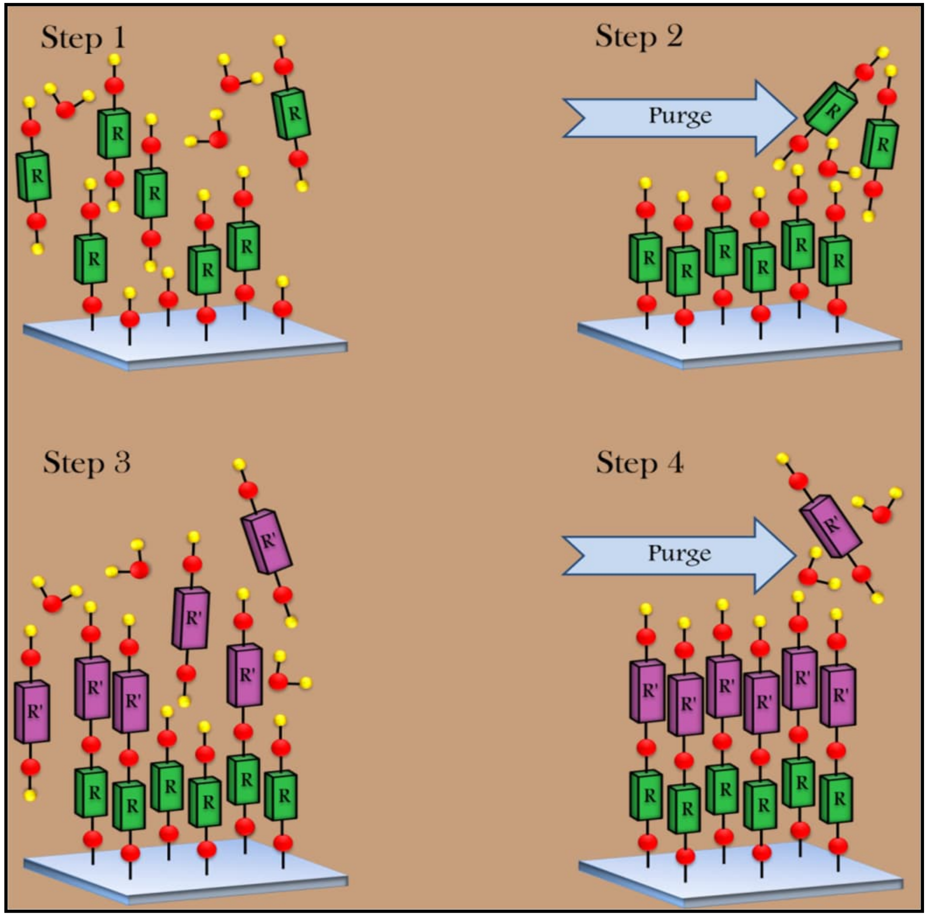
Synthesis of MOFs

- 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)

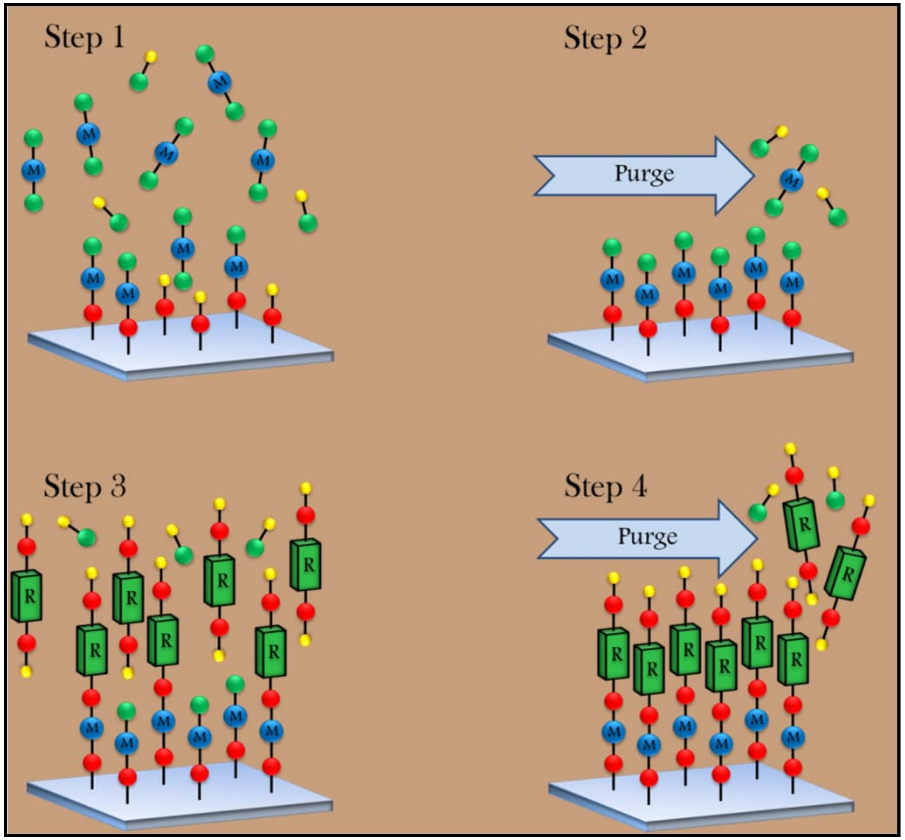


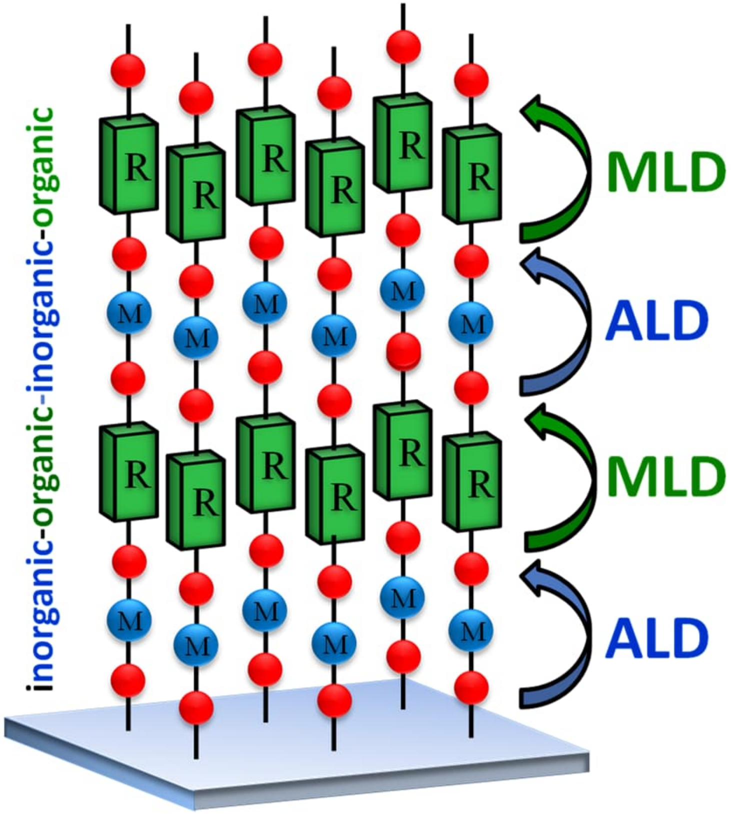
MLD (Molecular Layer Deposition)

High-quality
INORGANIC thin films
with atomic level control

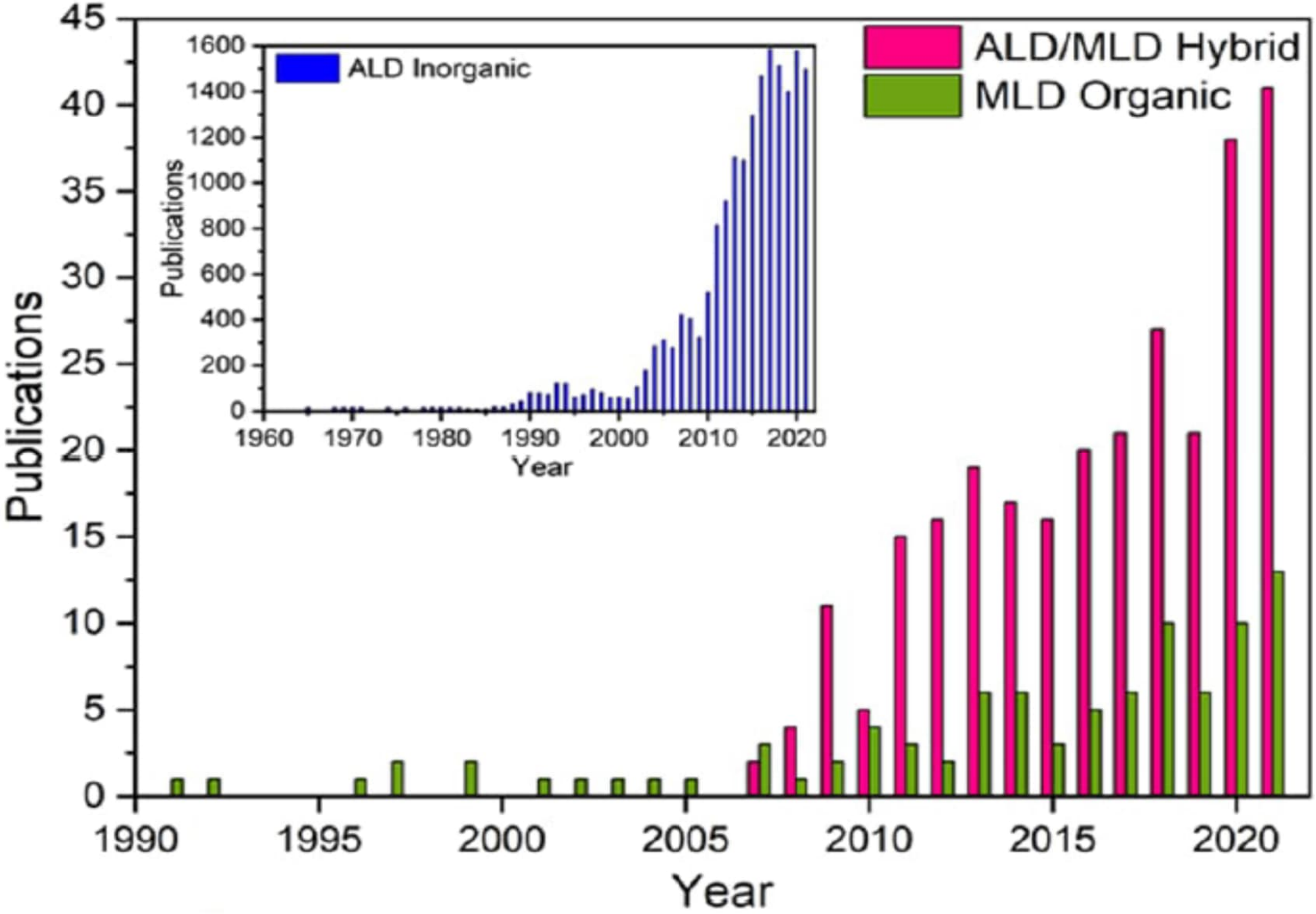
ORGANICS !
(in 1990s)

Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD



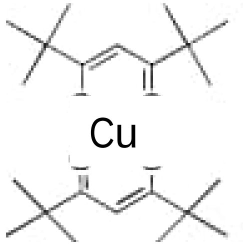


MULTIFUNCTIONAL SINGLE-PHASE HYBRID (compound) MATERIALS !!!

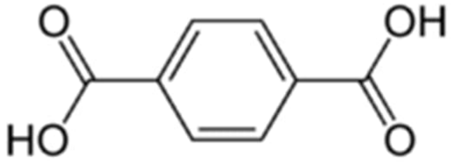


J. Multia & M. Karppinen, Atomic/molecular layer deposition for designer's functional metal-organic materials, ***Applied Materials Interfaces*** 9, 202200210 (**2022**).

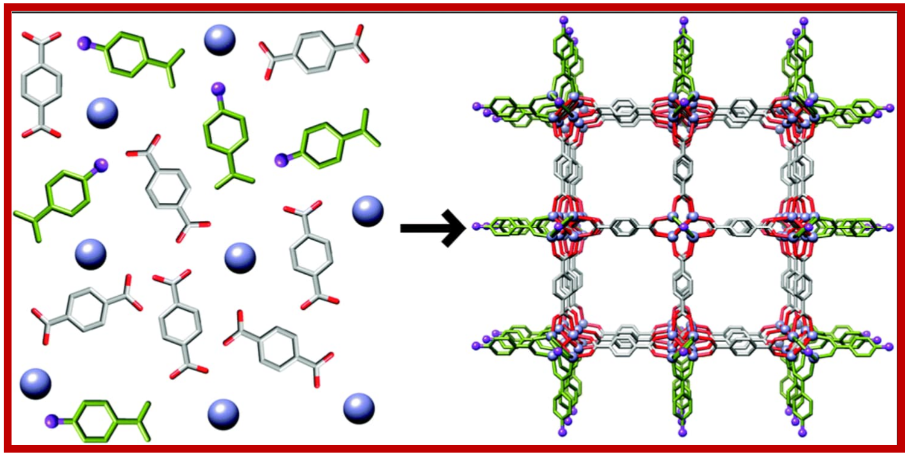
PRECURSORS for ALD/MLD



Cu(thd)$_2$



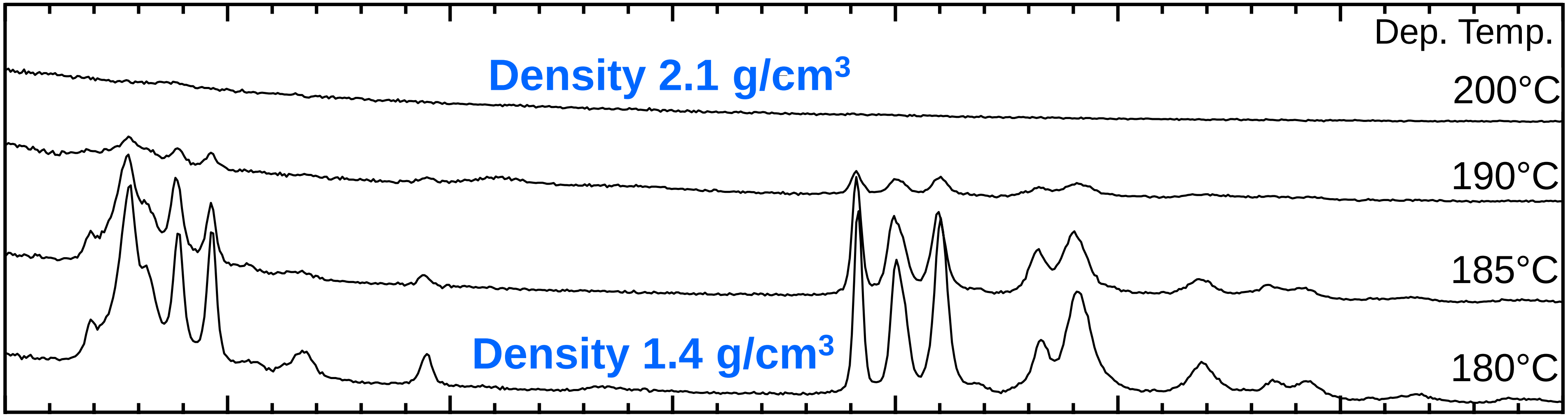
Terephthalic acid (TPA)

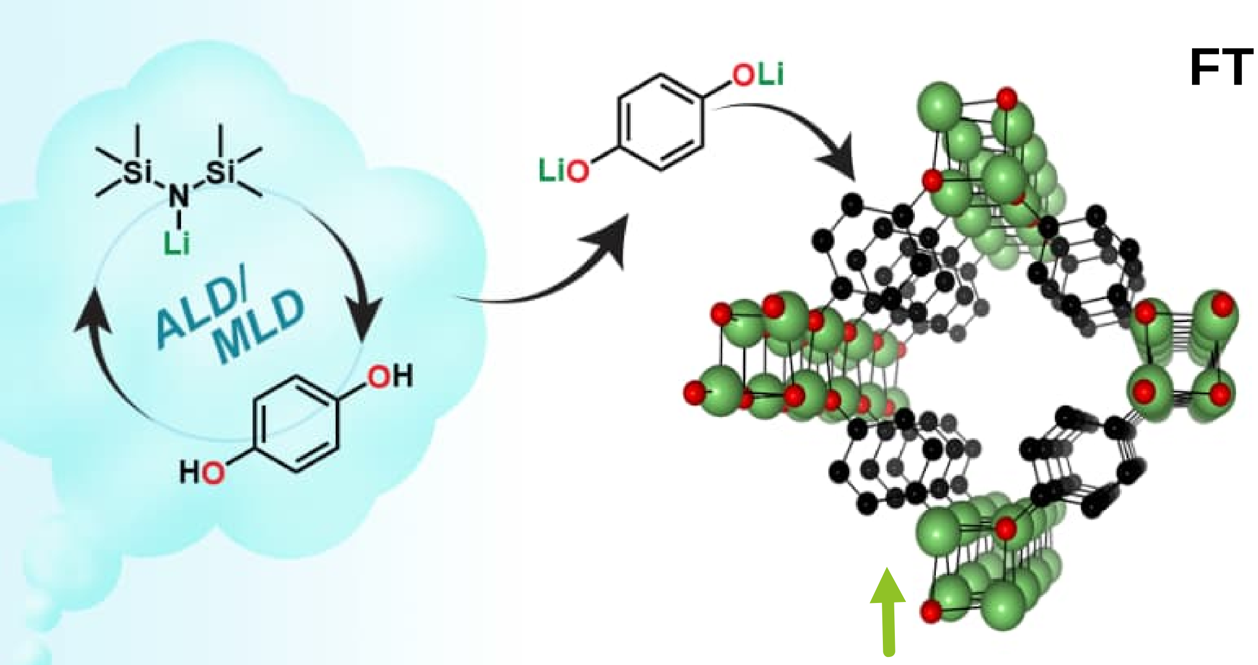


MOF

METAL-ORGANIC FRAMEWORK

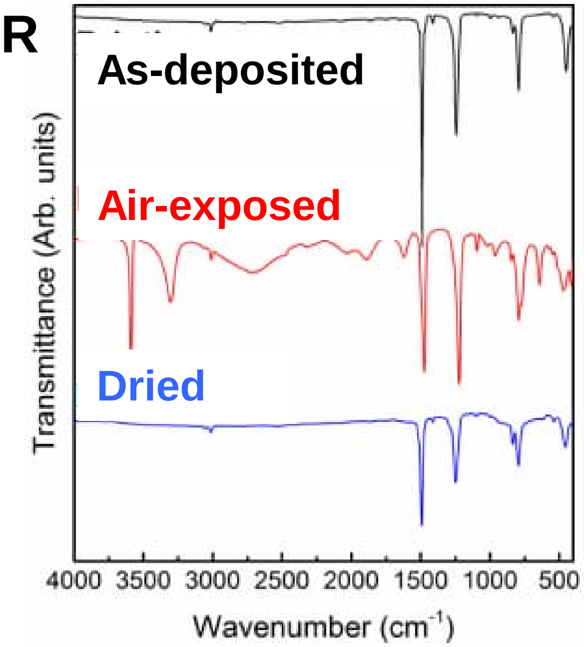
E. Ahvenniemi & M. Karppinen,
Chem. Commun. **52**, 1139 (2016).





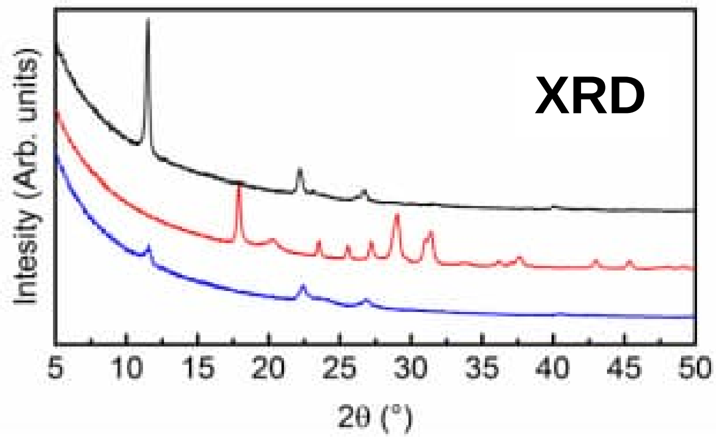
3-coord. Li-site

FTIR



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).

Name the following metal complexes

1.	$K_3[Fe(CN)_6]$	**potassium hexacyanoferrate(III)**
2.	$Na[B(NO_3)_4]$	**sodium tetranitratoborate(III)**
3.	$[CoN_3(NH_3)_5]SO_4$	**penta-ammine atsido cobalt(III)sulphate**
4.	$NH_4[Cr(NCS)_4(NH_3)_2]$	**ammonium diamine tetrakis(isothiocyanato)chromate(III)**
5.	$[Cr(H_2O)_6]Cl_3$	**hexa-aqua chromium(III)chloride**
6.	$[Al(OH)(H_2O)_5]^{2+}$	**penta-aqua hydroxo aluminium(III)ion**
7.	$Na_2[Fe(CN)_5NO]$	**sodium pentacyanonitrosylferrate(III)**
8.	$[Co(ONO)(NH_3)_5]SO_4$	**penta-ammine nitrito cobalt(III)sulphate**