



# Coordination Chemistry and Ligand Exchange reactions in the Synthesis of New Functional Inorganic Compounds

S. Natarajan

Framework Solids Laboratory, Solid State and Structural Chemistry Unit, IISc, Bangalore 560012

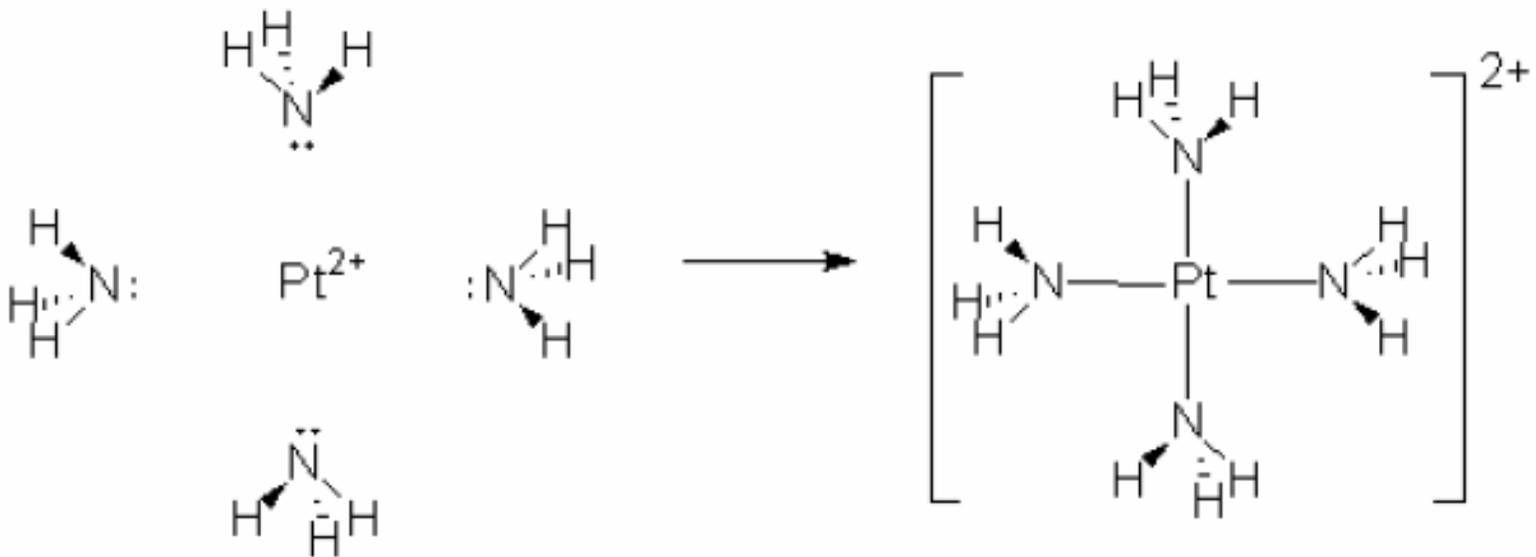
E-mail: [snatarajan@sscu.iisc.ernet.in](mailto:snatarajan@sscu.iisc.ernet.in)





## What is a Coordination Complex/Compound?

One of a number of complex compounds in which an atom or group of atoms is bound to the central atom by a shared pair of electrons supplied by the coordinated group and not by the central atom





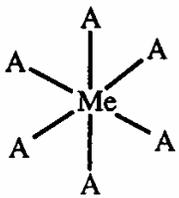
The Founder/Father of Coordination Chemistry

# Werner's Coordination Theory

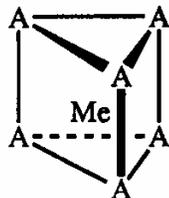


1913 Nobel Prize in Chemistry

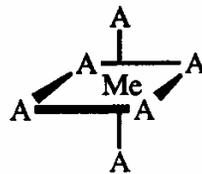
Theory of the structure of coordination compounds



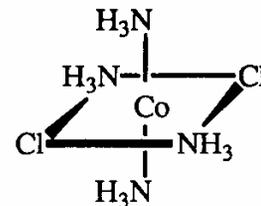
1  
planar



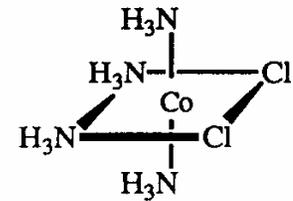
2  
prismatic



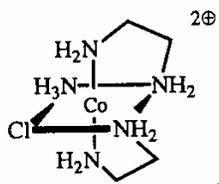
3  
octahedral



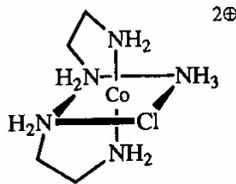
4



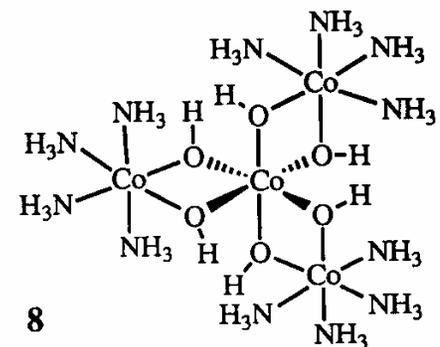
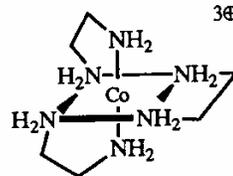
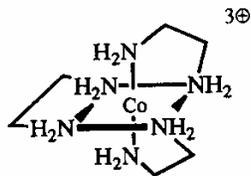
5



6



7



6+

8



# Werner's Theory

According to Wener, in co-ordination compounds, the central metal atoms exhibit primary and secondary valencies.

1. The primary valency is ionizable. Secondary valency is not ionizable.
  - The primary valency corresponds to the oxidation state
  - The secondary valency corresponds to the coordination number
2. Every metal atom has a fixed number of secondary valencies (coordination number).
3. Primary valency is satisfied by negative ions. - The secondary valency is satisfied either by negative ions or by neutral molecules.
4. The secondary valencies are always directed towards the fixed positions in space and this leads to definite geometry of the coordination compound.



Quiz: What's the date (year) of Werner's last published paper?



# Last published paper of Werner

*Inorg. Chem.* **2001**, 40, 1065–1066

## Crystal Structure Determination of a ( $\mu$ -Amido)( $\mu$ -hydroxo)( $\mu$ -superoxo)dicobalt(III) Complex from the Werner Collection

Bernhard Spingler,<sup>†</sup> Marie Scanavy-Grigorieff,<sup>‡,§</sup>  
**Alfred Werner,<sup>||,§</sup>** Heinz Berke,<sup>\*,§</sup> and  
Stephen J. Lippard<sup>\*,†</sup>

Department of Chemistry, Massachusetts Institute of  
Technology, Cambridge, Massachusetts 02139, and the  
Anorganisch-Chemisches Institut der Universität Zürich,  
CH-8057 Zürich, Switzerland

*Received October 16, 2000*

---

\* To whom correspondence should be addressed. E-mail: berke@aci.unizh.ch  
or lippard@lippard.mit.edu.

<sup>†</sup> Massachusetts Institute of Technology.

<sup>‡</sup> Student of Alfred Werner, Ph.D. 1911.

<sup>§</sup> Anorganisch-Chemisches Institut der Universität Zürich.

**<sup>||</sup> Deceased November 15, 1919.**



# Some important concepts on coordination compounds

## Ligands

Defined as - The neutral molecule or ions which are directly attached to the central metal ion or atom through coordinate bonds in the complex ion is called Ligand.

- Ligands should have lone pair of electrons
- Ligands donate the lone pair to the central metal atom or ion forming coordinate covalent bond
- The Ligand is Lewis base and central metal ion is a Lewis acid.



## Types of ligands:

1. monodentate ligands : ligand having only one donor atom.
2. bidentate ligand : ligand having two donor atoms
3. polydentate ligand : ligand having more than two donor atoms.  
(tridentate, tetradentate, pentadentate, hexadentate, etc)



## Chelating ligands:

A bidentate or a polydentate ligand bonded with the same central metal ion or atom forming a ring structure.

Chelating ligands generally forms a ring structure around the central metal ion.

## Ambident ligand:

A ligand (monodentate) which binds with the metal ion through more than one site.

M-CN (cyanide)

M-NC (isocyanide)



## Coordination number:

The total number of ligands attached to the central metal ion

## Coordination sphere:

The central metal ion along with the ligands are collectively called the coordination sphere

## Charge of a complex:

The total charge of a complex is the algebraic sum of the charges carried by the central ion and the ligands bound to it.

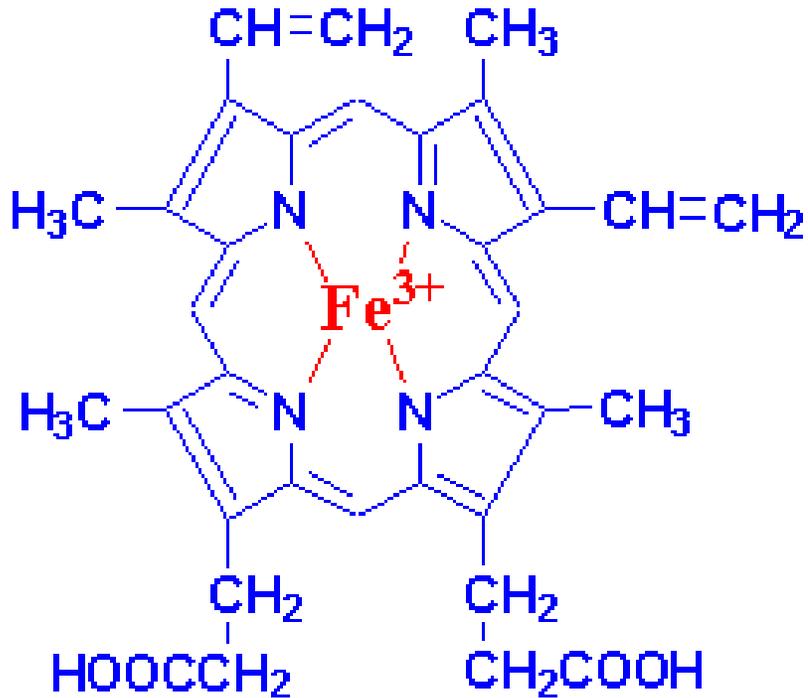


# Examples of the use of coordination complexes/compounds



## Hemoglobin and coordination chemistry

Max Ferdinand Perutz

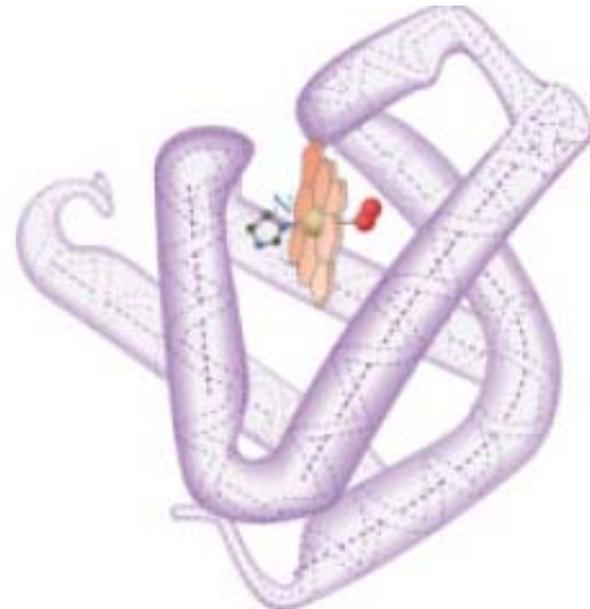
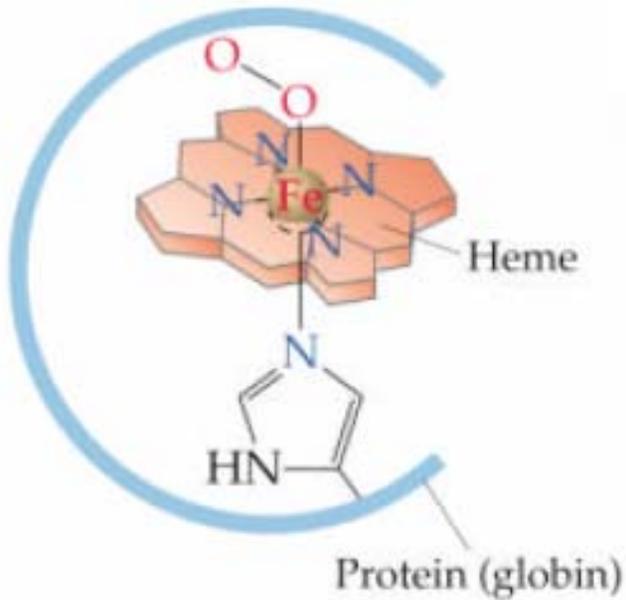
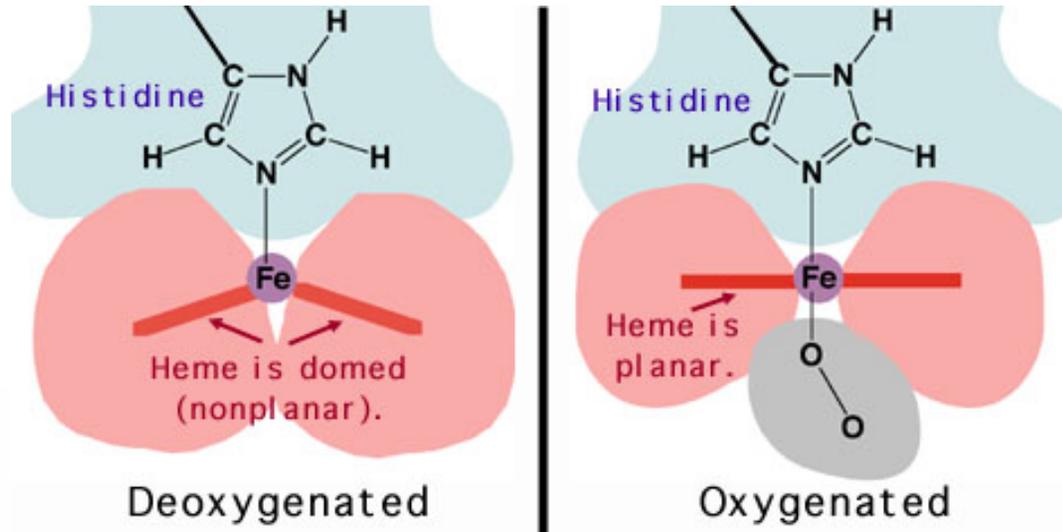


Nobel Prize 1962

Hemoglobin, contains a molecule of *heme*, which serves as the active site of oxygen transport ( $\text{Fe}^{2+}/\text{Fe}^{3+}$  couple) from the lungs to the tissues in which it is used to oxidize glucose, this oxidation serving as the source of energy required for cellular metabolic processes.



# The schematic of the oxygen binding in Heme



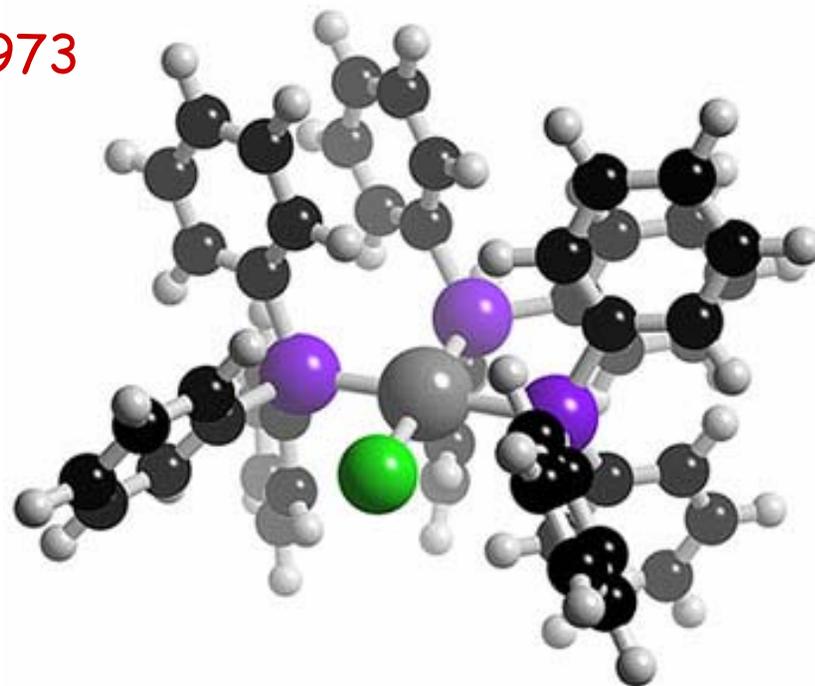


# Wilkinson's Catalyst

chlorotris(triphenylphosphine)rhodium(I),



Nobel Prize, 1973

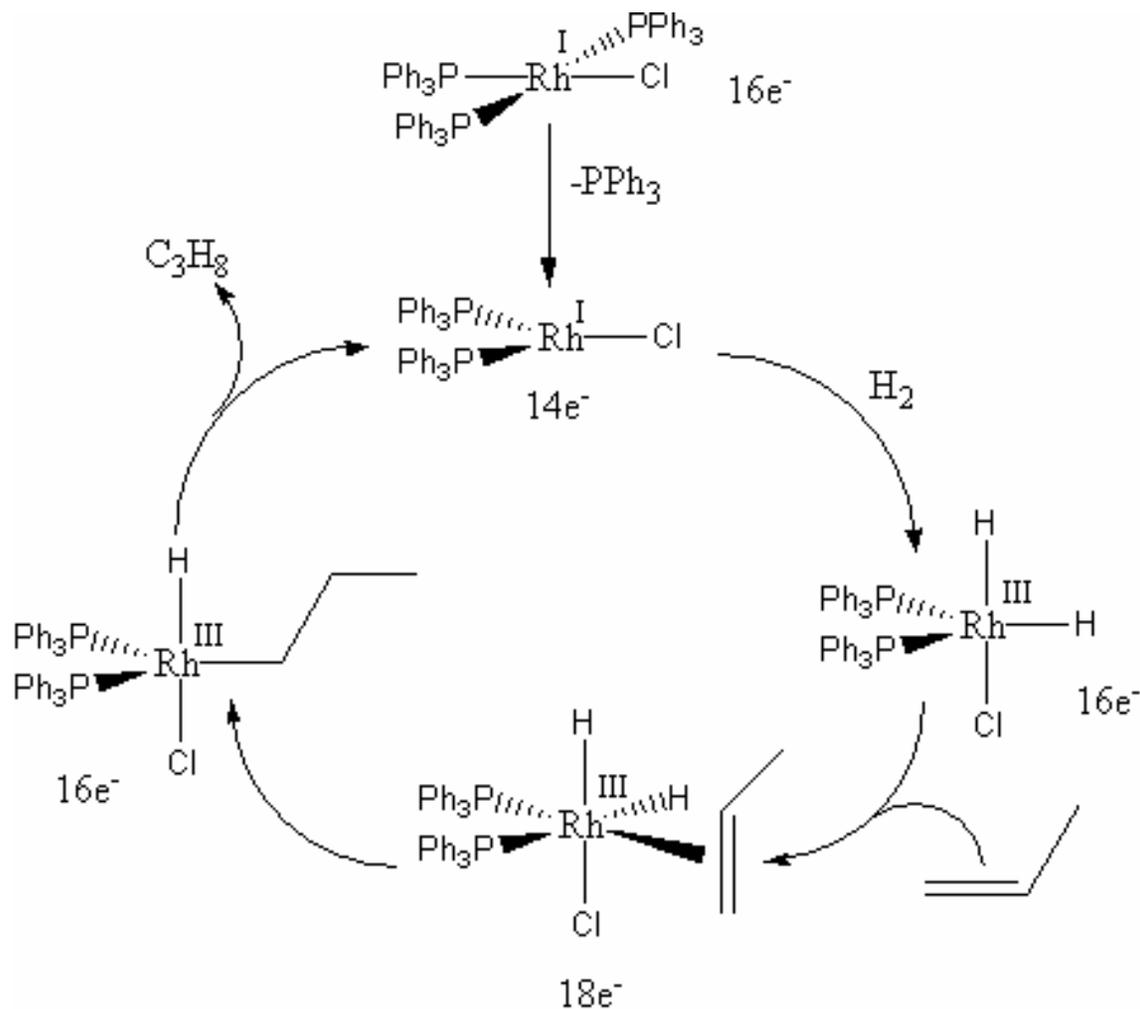


Imperial College, London



## Mechanism of hydrogenation using Wilkinson's catalyst

Wilkinson's catalyst is used for catalyzing the hydrogenation of alkenes. The mechanism involves the initial dissociation of one or two triphenylphosphine ligands to give 14 or 12-electron complex followed by oxidative addition of  $H_2$  to the metal. Subsequent  $\pi$ -complexation of alkene, intramolecular hydride transfer (olefin insertion), and reductive elimination forming the alkane.



Catalytic hydrogenation of propylene



# Coordination Chemistry in 21<sup>st</sup> Century



## Coordination chemistry in new materials

1. Combine different coordination preferences of metals and binding modes on the ligands
2. The ligands can be of many different types - simple carboxylates, nitrogen containing ones or combinations of these
3. The ligands can also have functional groups as well - which can be selectively reactive!!
4. The compounds/complexes can be prepared at elevated temperatures - what are the effects of such reactions
5. Using this to form large channel structures



# Basic Building Units

- Geometrical Considerations ...



# Metals Coordination Requirement

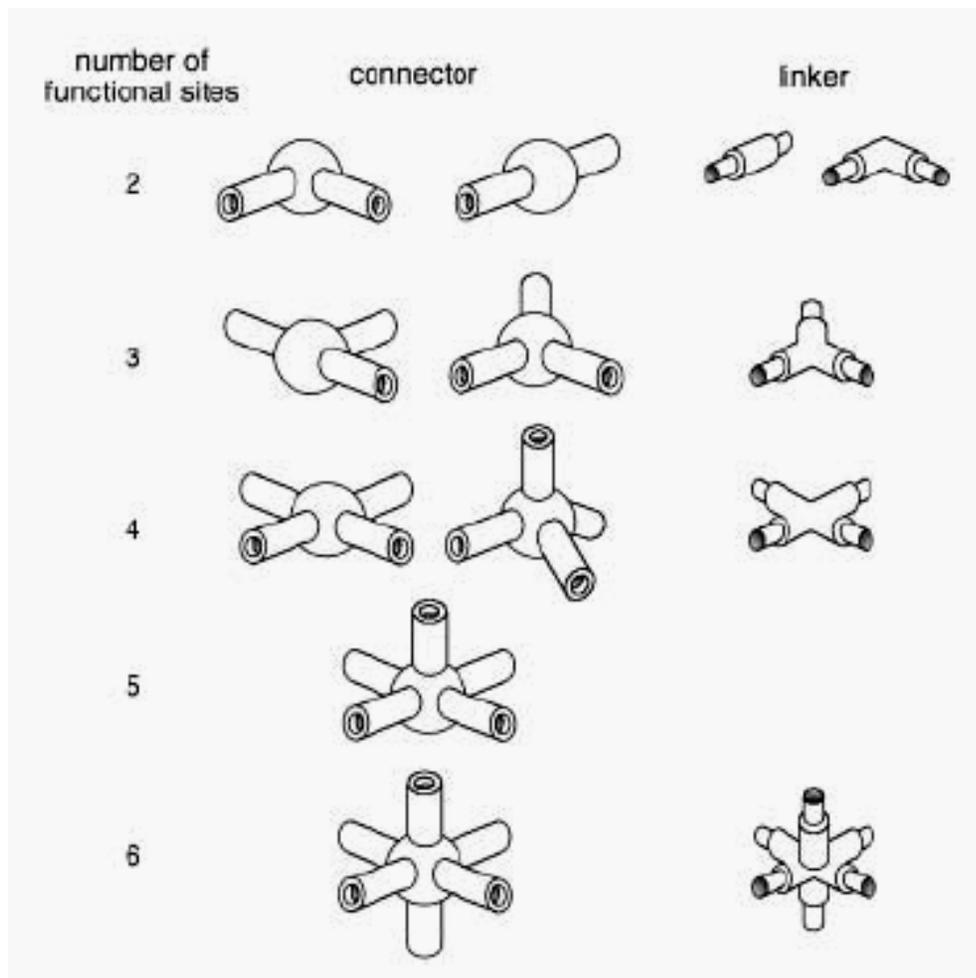
- Coordination of 2 linear
- Coordination of 2 Bent
- Coordination of 3 Trigonal planar
- Coordination of 3 T-shaped
- Coordination of 3 Pyramidal
- Coordination of 4 Tetrahedral
- Coordination of 4 Trigonal pyramidal
- Coordination of 4 Square Planar
- Coordination of 5 Pentagonal
- Coordination of 5 Trigonal bipyramidal
- Coordination of 5 Square pyramidal
- Coordination of 6 Octahedral
- Coordination of 6 Trigonal Prism

		Coordination		Comments
Number	Geometry	Polyhedron		
1		—	Unimportant	
2	Linear		—	Uncommon: found mainly with d <sup>10</sup> metal ions
3	Trigonal plane			Rare; can be induced by use of sterically bulky ligands
4	Square plane			Common for d <sup>8</sup> metal ions otherwise unusual;
4	Tetrahedron			Fairly common, especially for d <sup>10</sup> and some d <sup>5</sup> ions
5	Trigonal bipyramid			Rare } Examples are often similar in structure and energy so may easily interconvert
5	Square pyramid			
6	Octahedron			Very common; usually the most favoured energetically and gives the lowest ligand–ligand repulsions
(Octahedron = trigonal antiprism)				An alternative view of an octahedron down a three-fold rotation axis
6	Trigonal prismatic			Rare, and requires some extra steric or electronic benefit to be favoured over octahedral



# Characteristics of connecting units (transition-metal ions): Number and orientation of binding sites

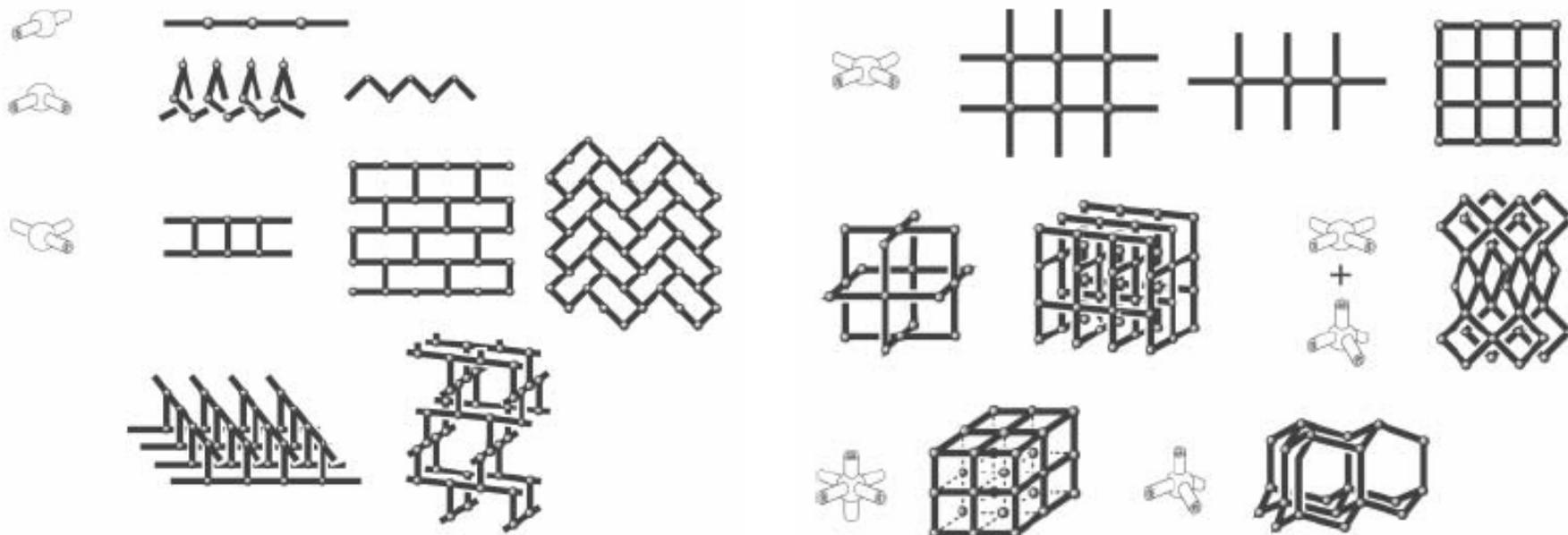
- Coordination of 2 linear
- Coordination of 2 Bent
- Coordination of 3 Trigonal planar
- Coordination of 3 T-shaped
- Coordination of 3 Pyramidal
- Coordination of 4 Tetrahedral
- Coordination of 4 Trigonal pyramidal
- Coordination of 4 Square Planar
- Coordination of 5 Pentagonal
- Coordination of 5 Trigonal bipyramidal
- Coordination of 5 Square pyramidal
- Coordination of 6 Octahedral
- Coordination of 6 Trigonal Prism





# Theoretical Arrangements

Combinations of different connector(s), auxiliary ligand(s)



Some of these structures have been observed - note that by clever manipulation of the coordinating ability of the central metal and the ligand, one can make a large variety of structures

R. Robson et al., *Angew. Chem. Int. Ed.* 1998, 37, 1460



What are the different types  
of bonding one can consider?

Bonding Considerations ...



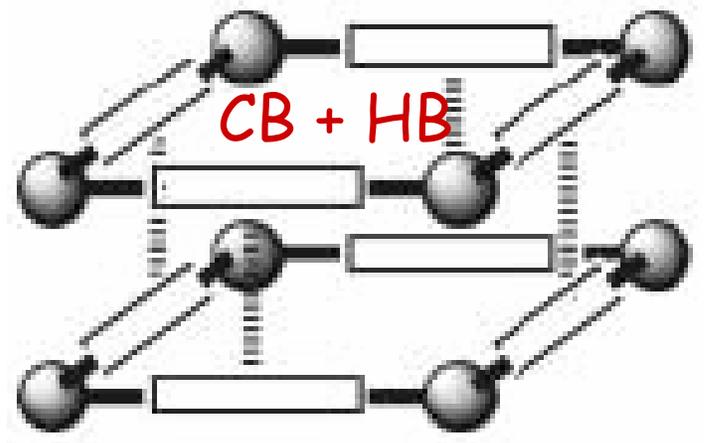
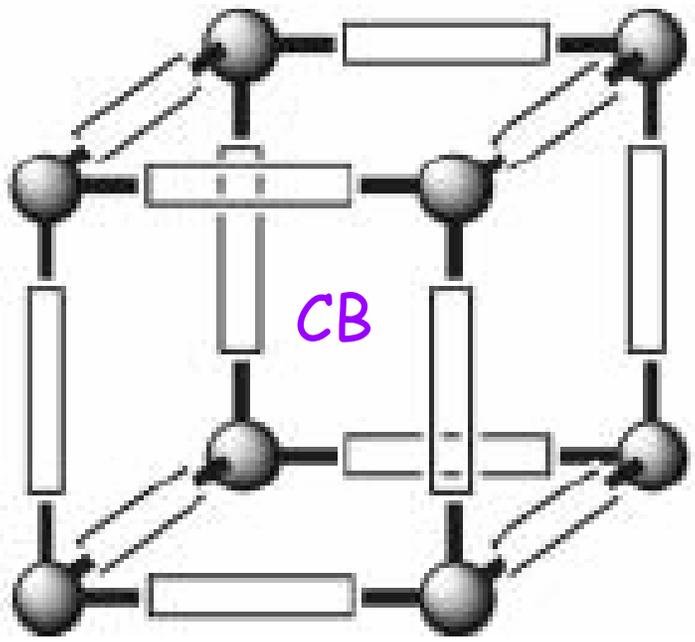
# The Bonding Interactions

The following bond interactions are important when considering the network self-assembly:

Coordination Bond (CB), Hydrogen Bonds (HB)

• Other Interactions (MMB,  $\pi\cdots\pi$ , CH $\cdots\pi$ , etc.)

- 1) 1-D and 2-D motifs often aggregates through additional weak bonds
- 2) Stability of 3-D motifs increases with increasing CB contributions
- 3) Combinations of strong and weak interactions provide flexibility to the molecular open-frameworks



— = CB

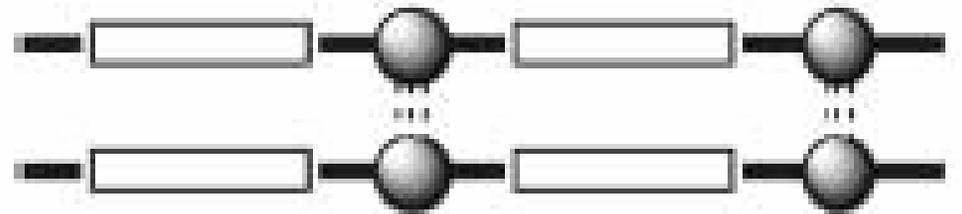
----- = HB

⋮ = other interaction (MB, π-π, CH-π, etc.)

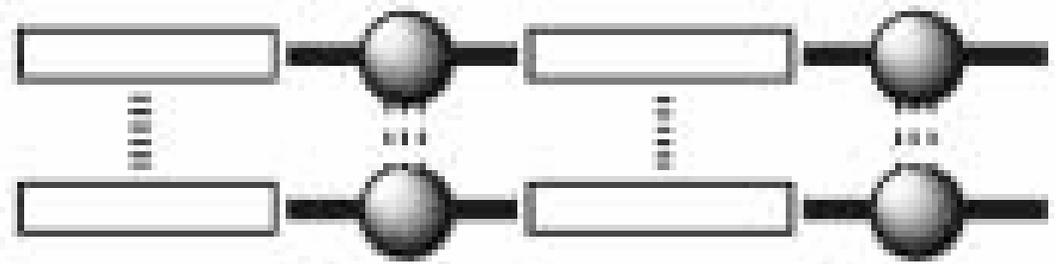
● = connector

▭ = linker

CB + others



CB + multiple





# Basic Building Units

- Ligand Considerations ...

# Important Coordination ligands in New Materials

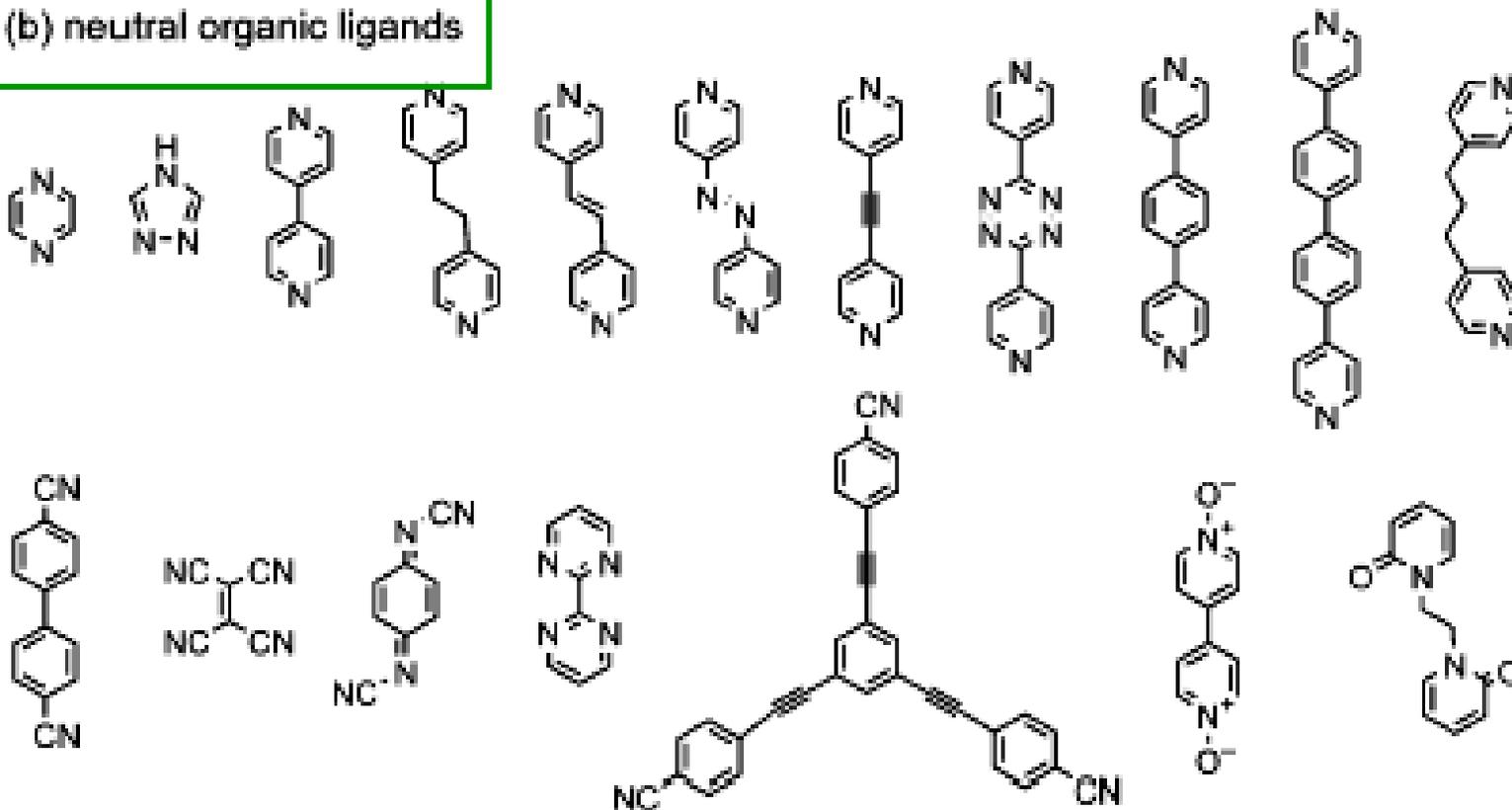
## (a) inorganic ligands

Halides (F, Cl, Br, and I)

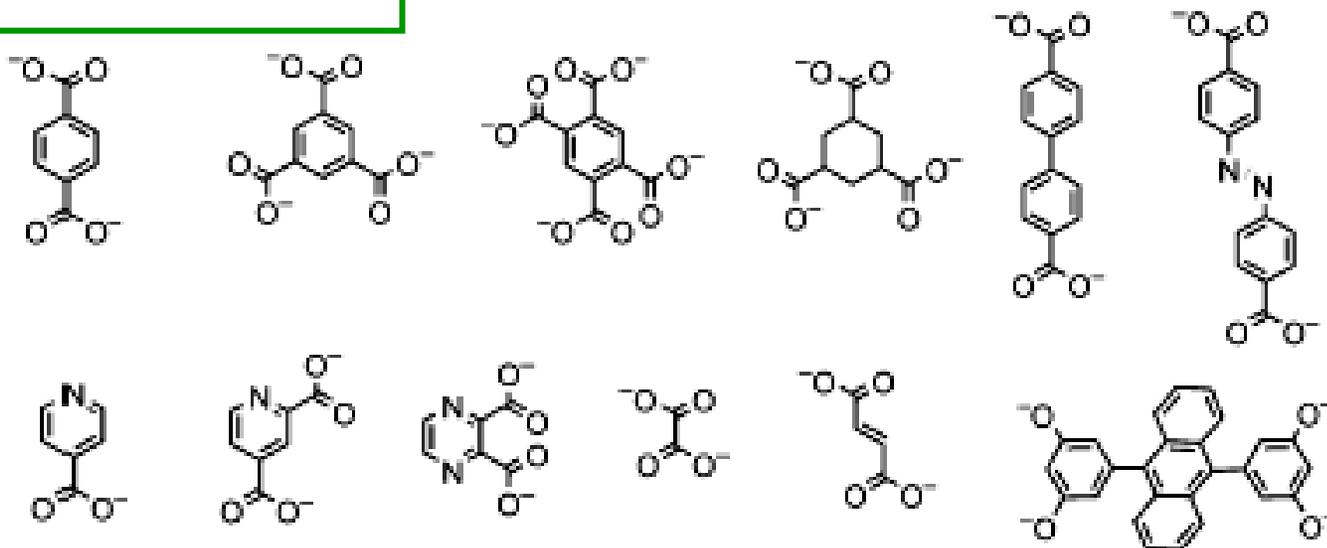
Cyanometallate ( $[M(CN)_x]^{n-}$ )

$CN^-$   $SCN^-$

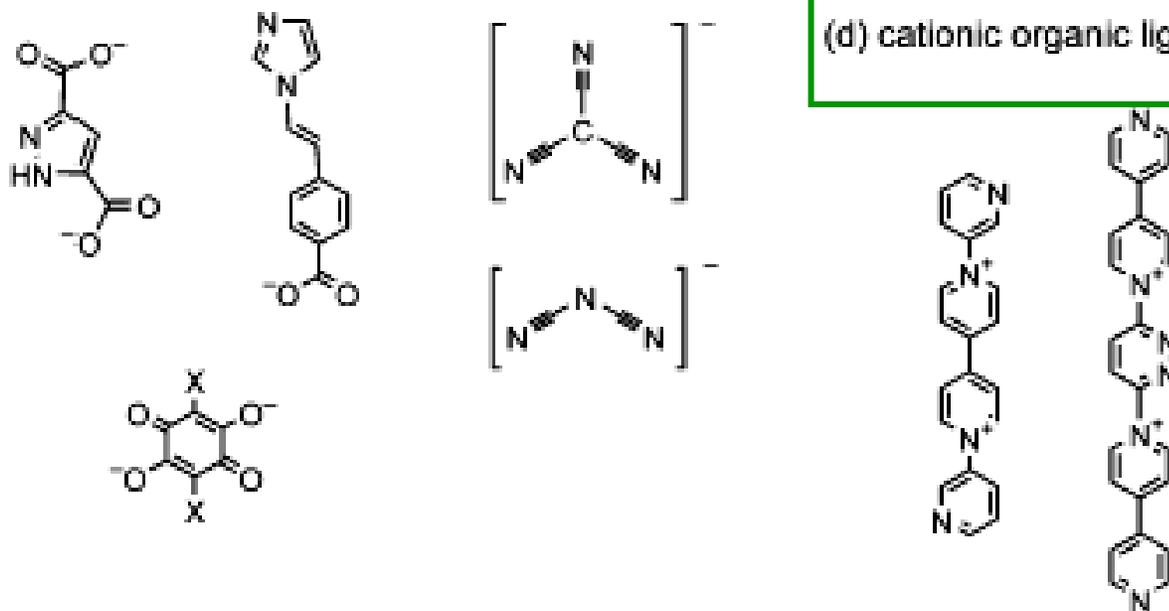
## (b) neutral organic ligands



(c) anionic organic ligands



(d) cationic organic ligands





Assembling the coordination  
geometry of the metal and the  
ligands

What do we get ? ...



# Structural Components of New Materials

## Central components

- Connectors



- Linkers



## Auxiliary components

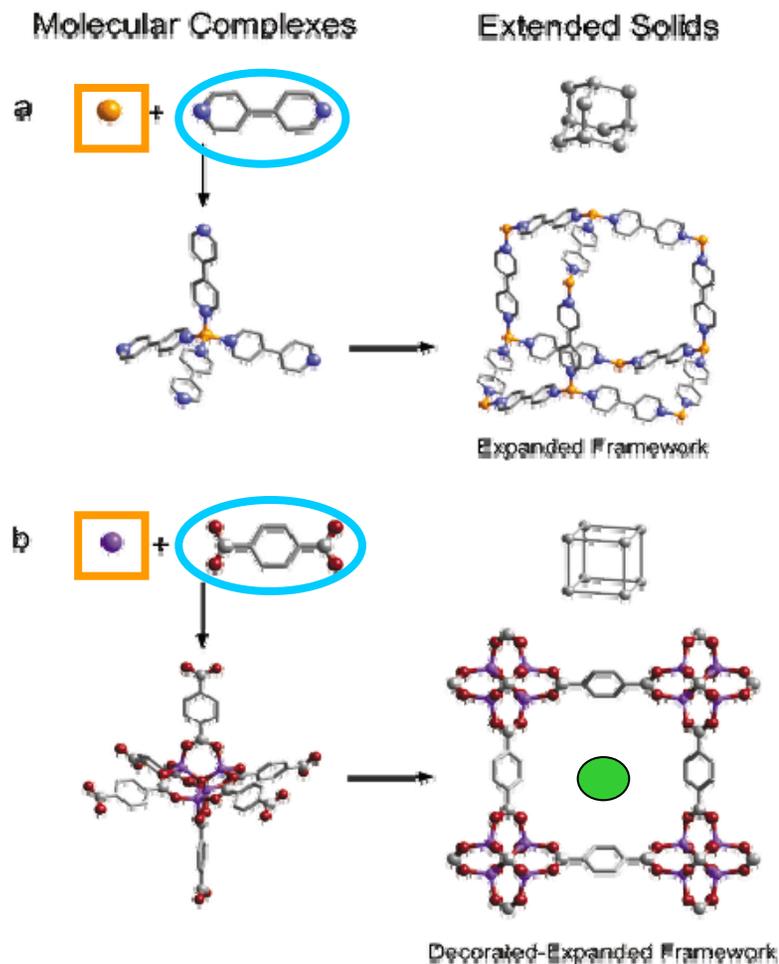
- Counterions

- Blocking ligands

- Guest molecules



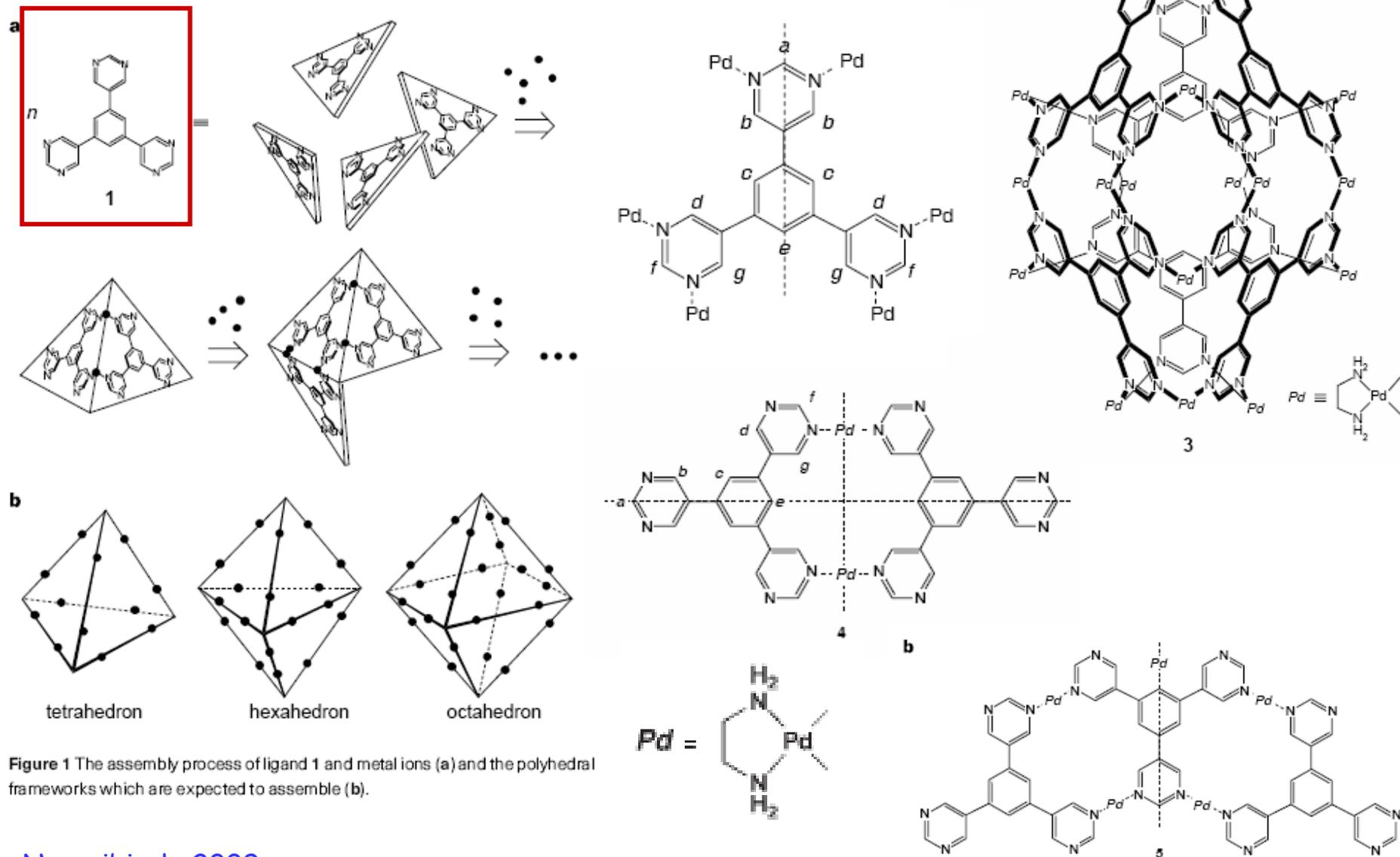
- Template molecules



A.F. Wells, "Three Dimensional Nets and Polyhedra", Wiley, New York, 1977

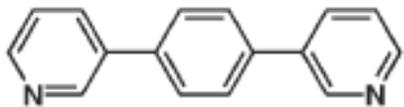
R. Robson et al. *J. Am. Chem. Soc.*, 1991, 113, 3606

# The use of self assembly in forming new types of coordination compounds of immense potential

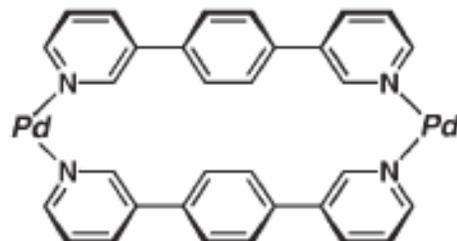




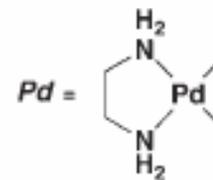
Different types of pyridyl units can be assembled to give rise to a variety of structures



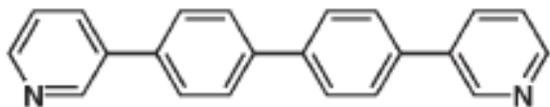
1



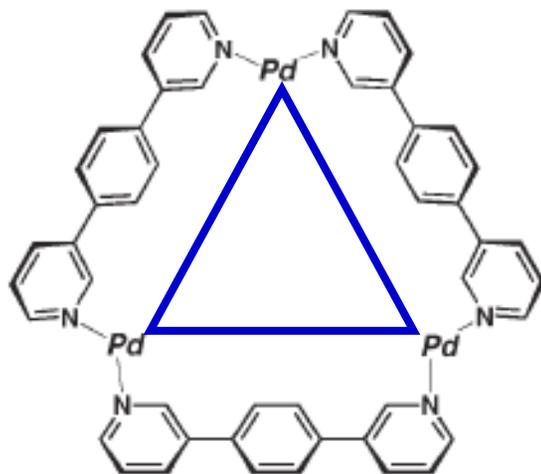
3



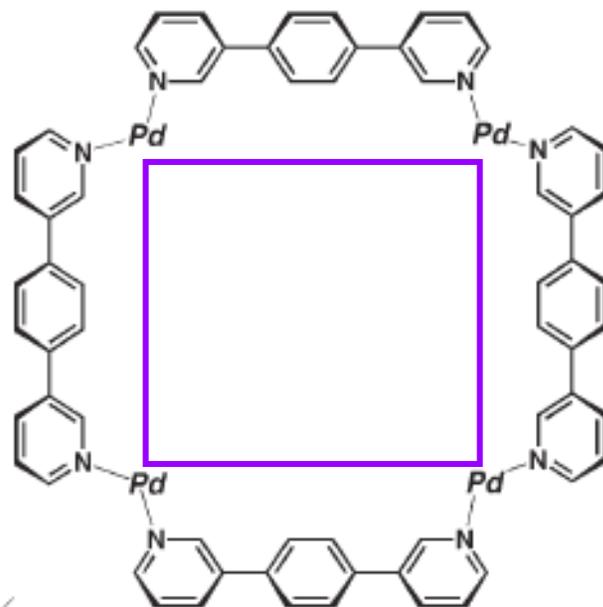
Pd =



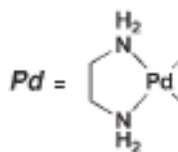
2



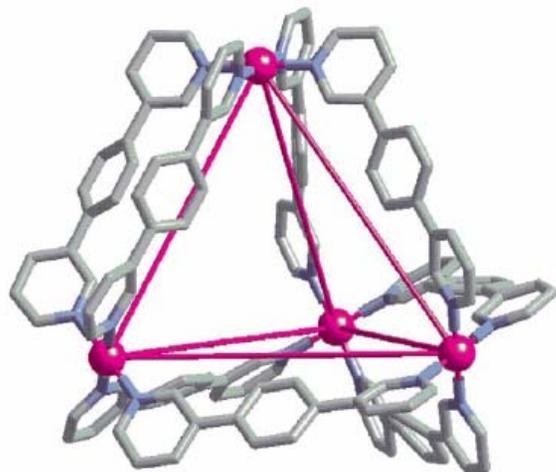
4



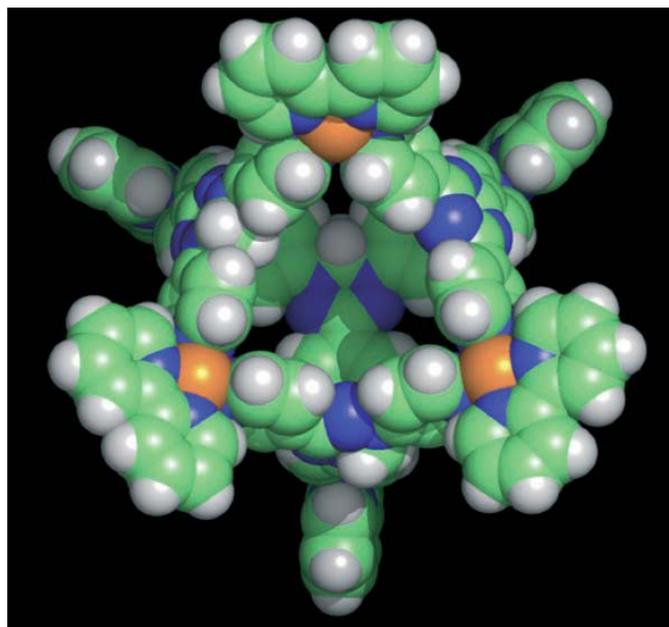
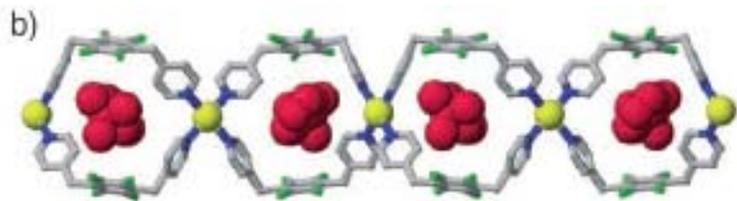
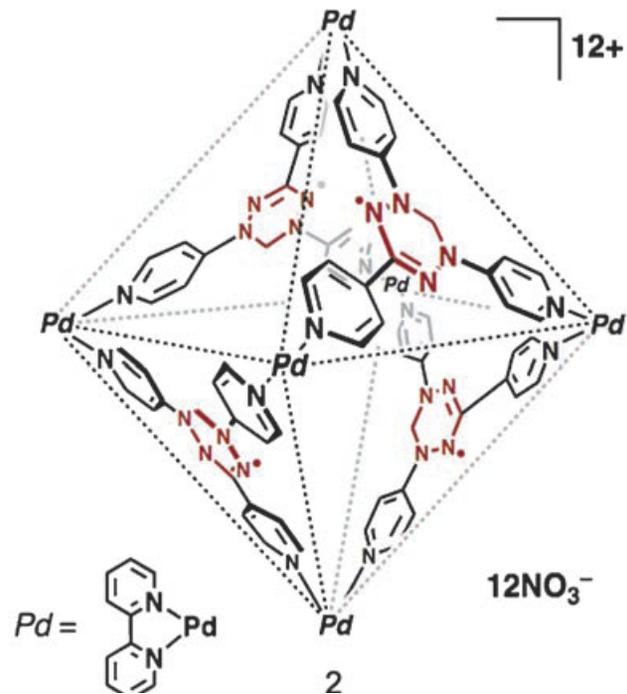
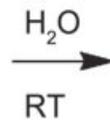
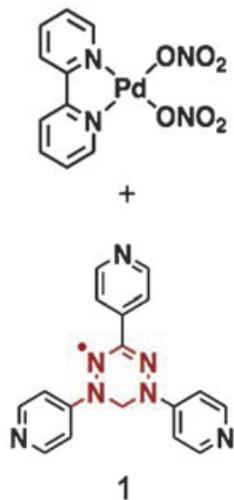
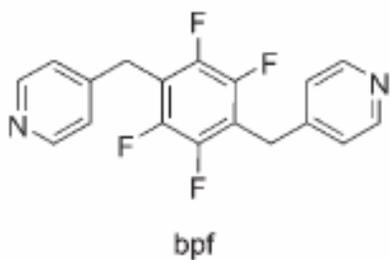
5



Pd =



*Chem. Asian. J.* 2006, 1–2, 82–90



Through self assembly large cavities can be generated that can be employed for space specific reactions

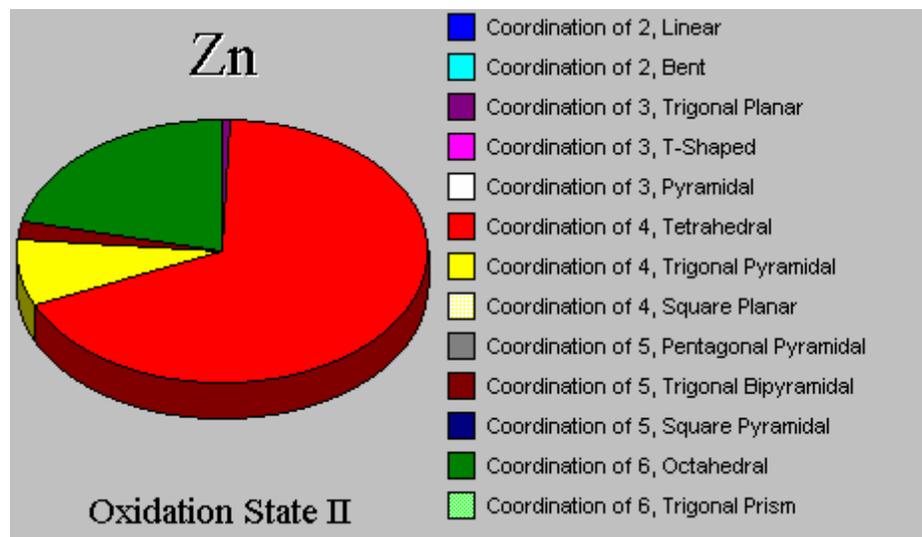
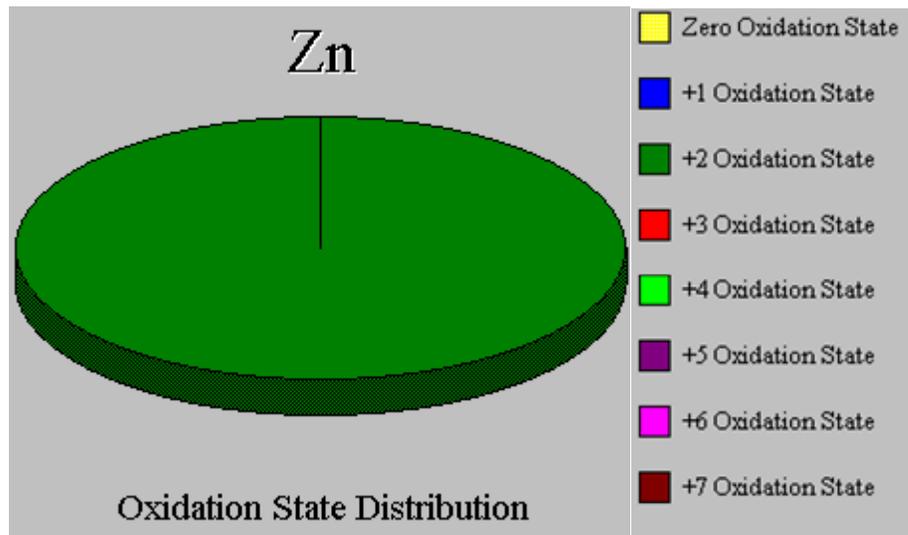


# Effect of Ligand Spacer ...



If we take  $Zn^{2+}$  as an example, then one finds that Zn exhibits only one oxidation state = +2

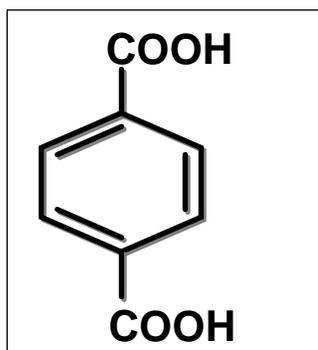
The coordination geometry does not show much diversity - tetrahedral, trigonal pyramidal, trigonal bipyramidal and octahedral





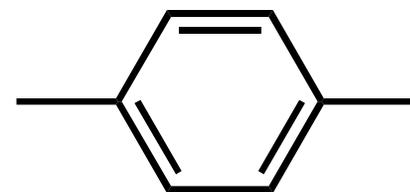
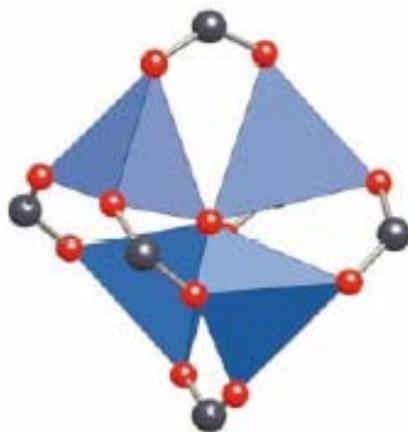
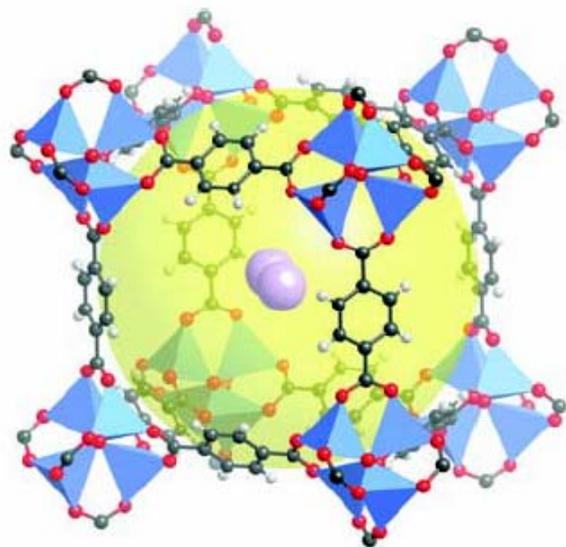
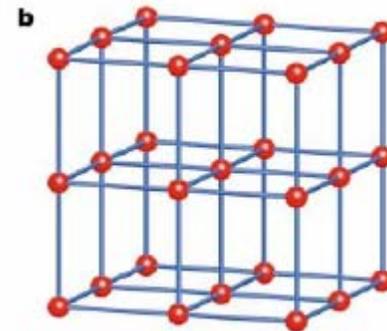
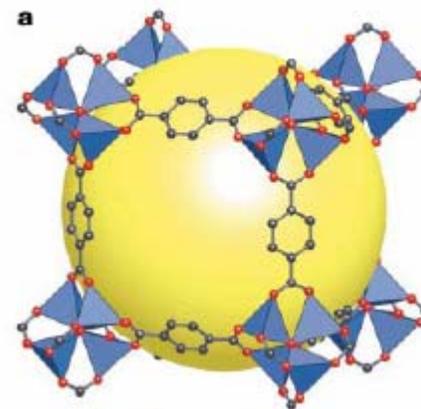
# Metal Organic Framework - MOF-5

Prepared using DMF as the solvent  
and at 65°C



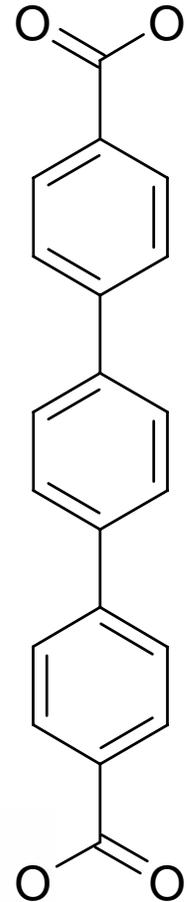
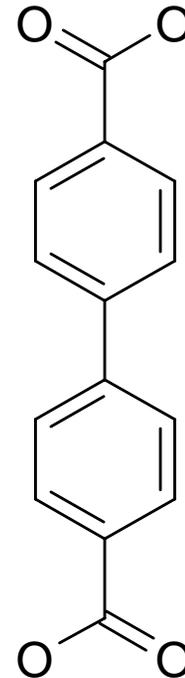
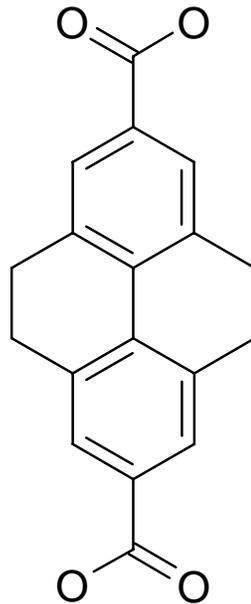
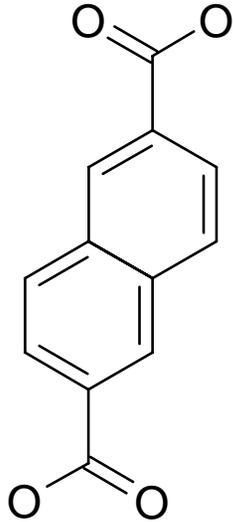
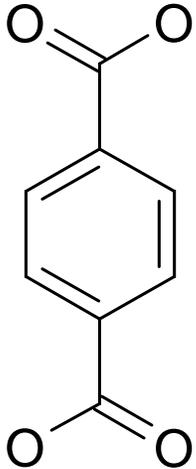
+

ZnO

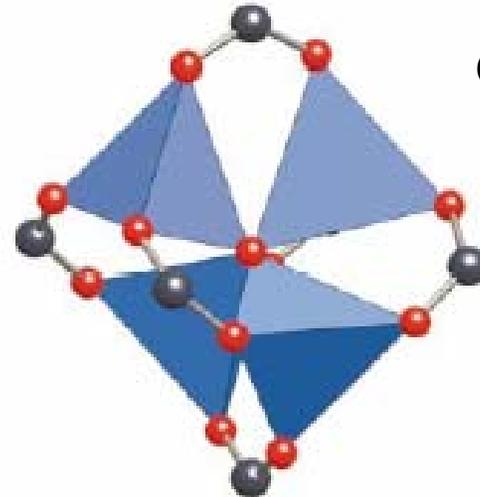




## Tuning the ligand to obtain larger space

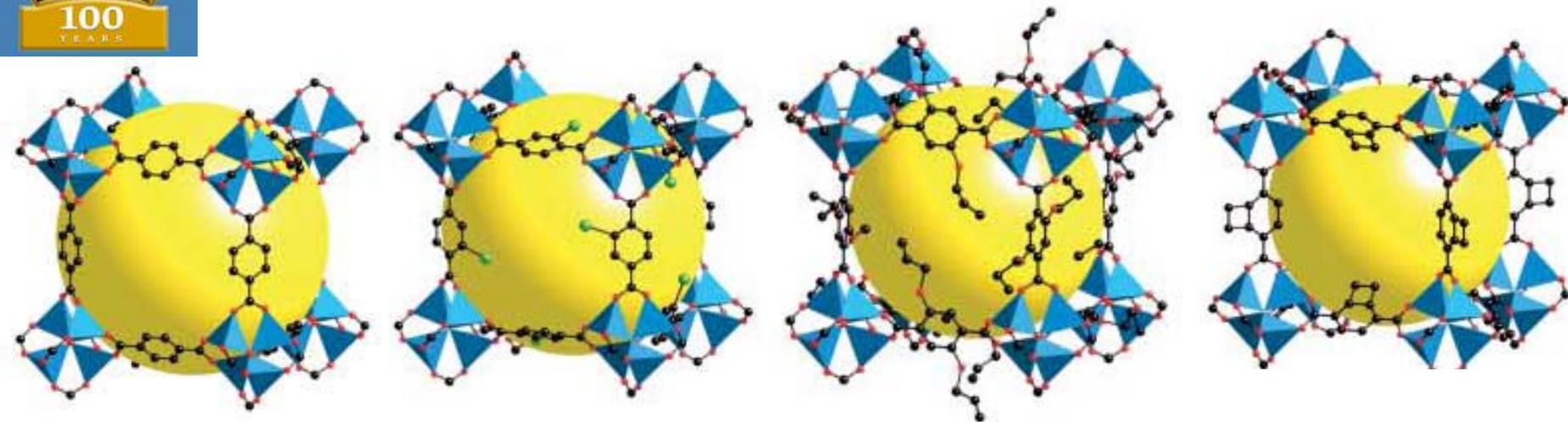


If the metal site does not alter the binding preference, then we can carefully choose ligands to change the size of the channels - which would allow us to carry out some interesting studies!!

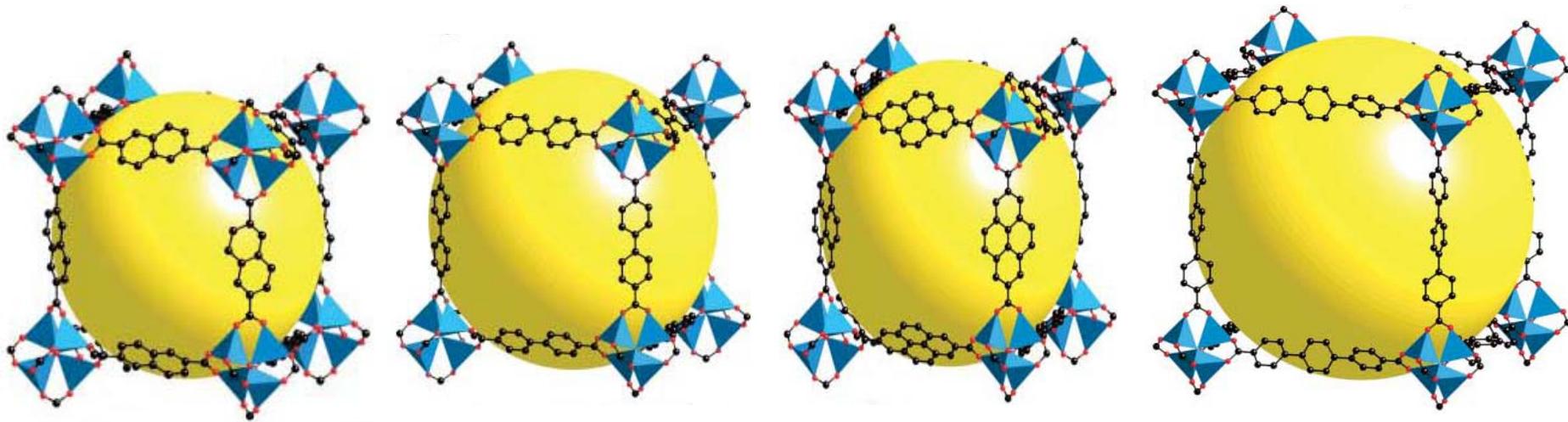




# Introducing Functional Groups - Reactive Centers

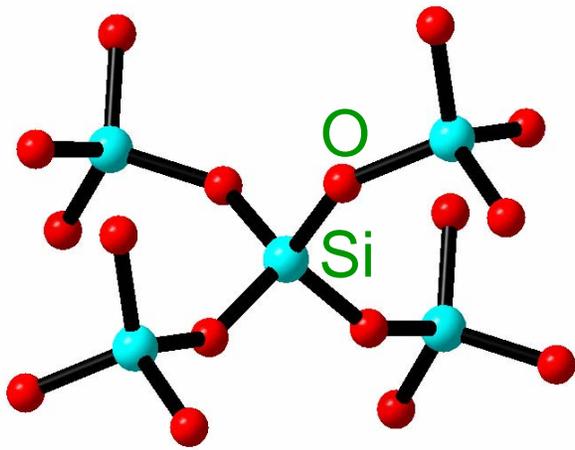


Larger Channels - add Functional Groups - Larger Reactive spaces

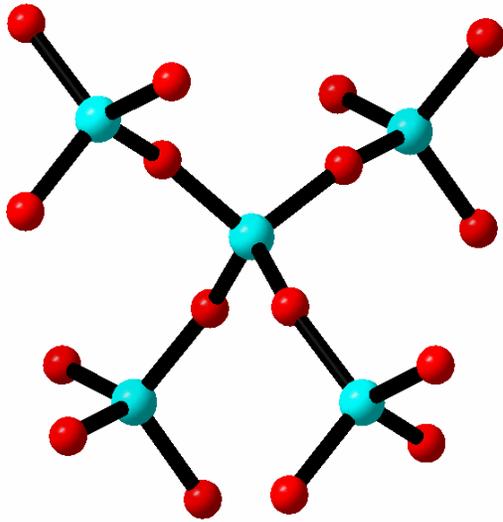
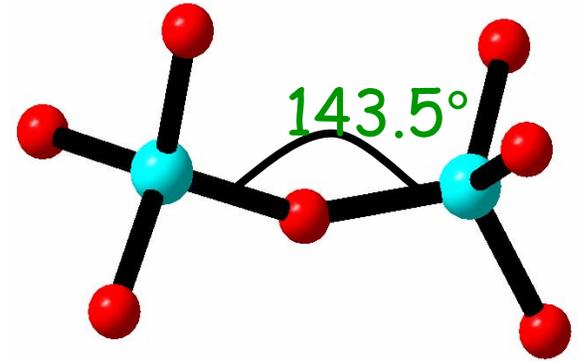




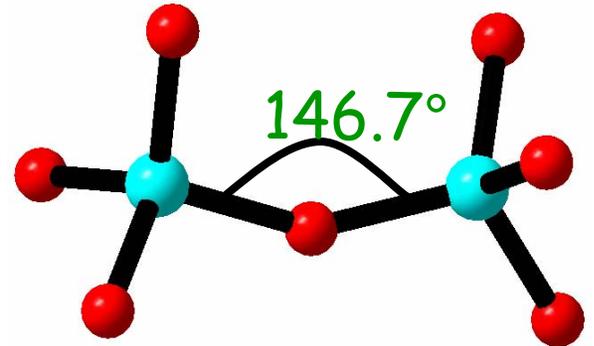
New frameworks - Newer strategies -  
but still part of Coordination Chemistry



Quartz



Cristobalite



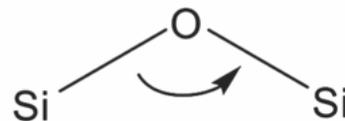


# Imidazole based compounds



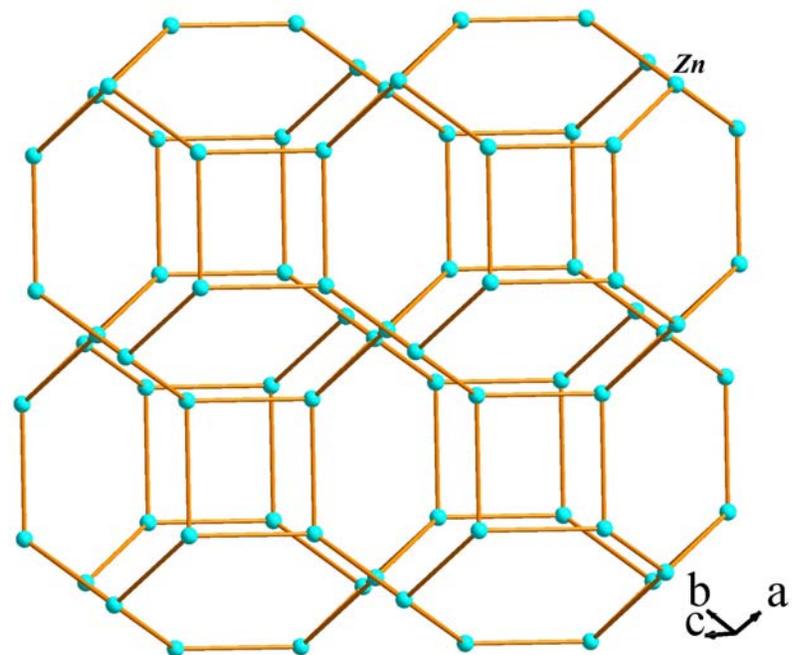
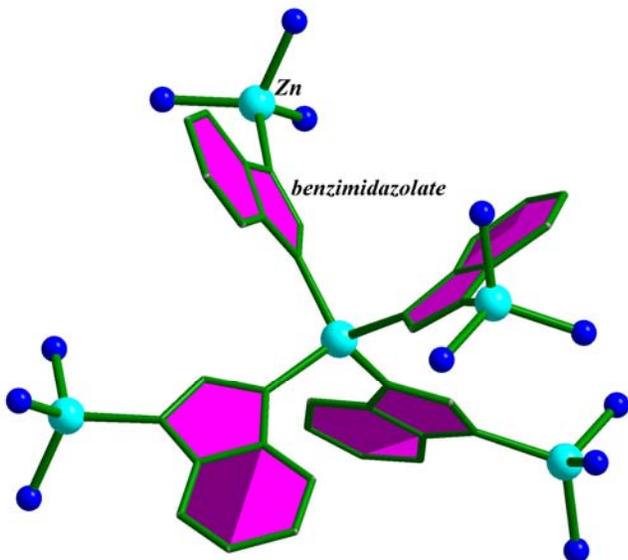
M - IM - M

1



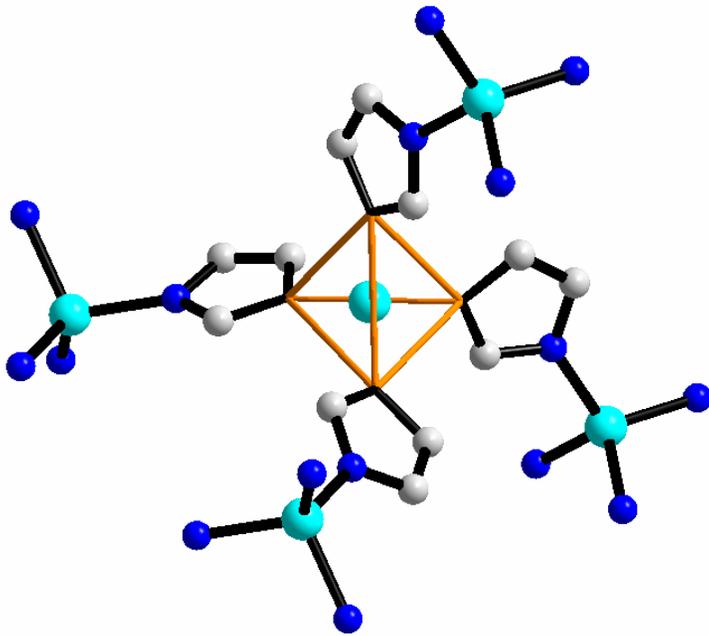
Si - O - Si

2

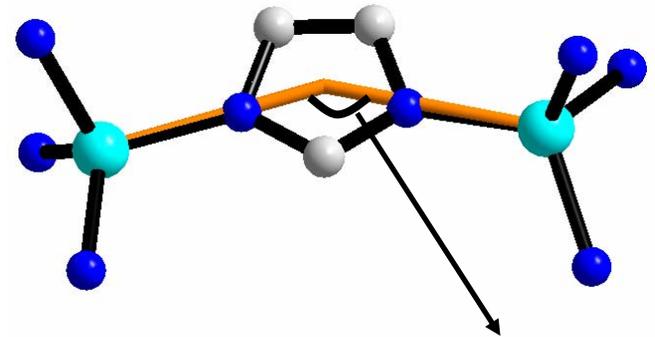
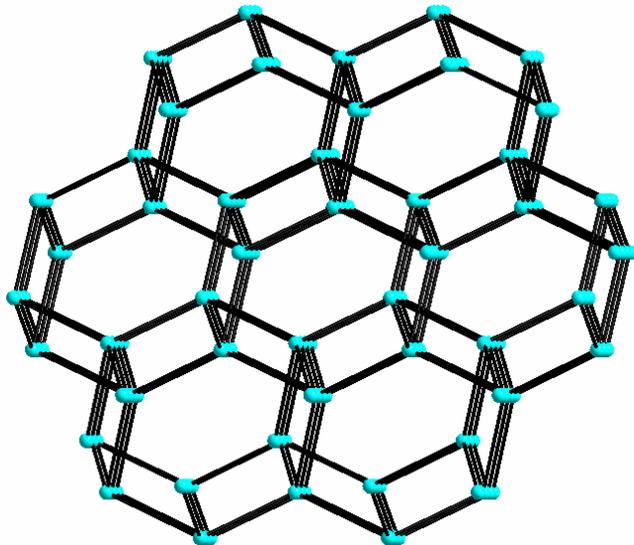




ZIF-1



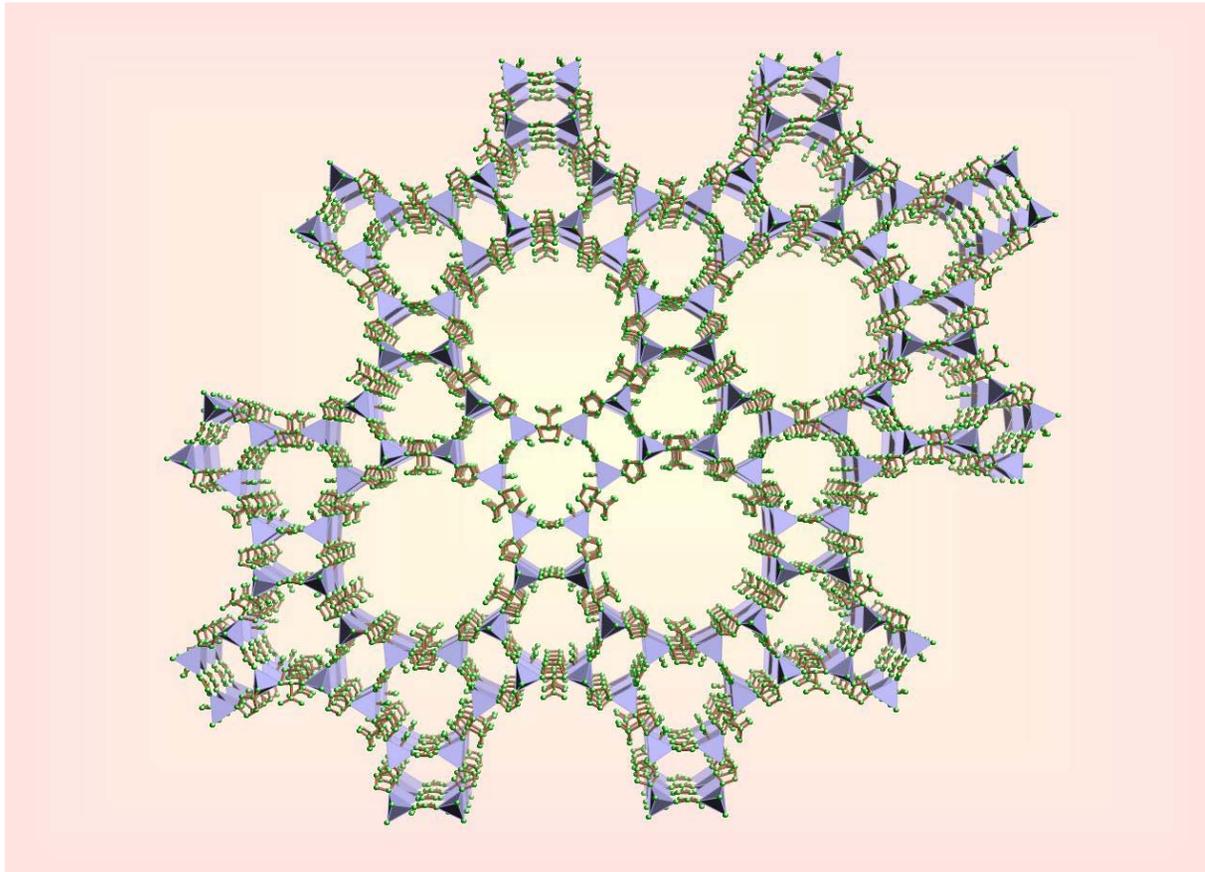
CrB<sub>4</sub> topology



136.7, 137.3, 147 and 143.5°

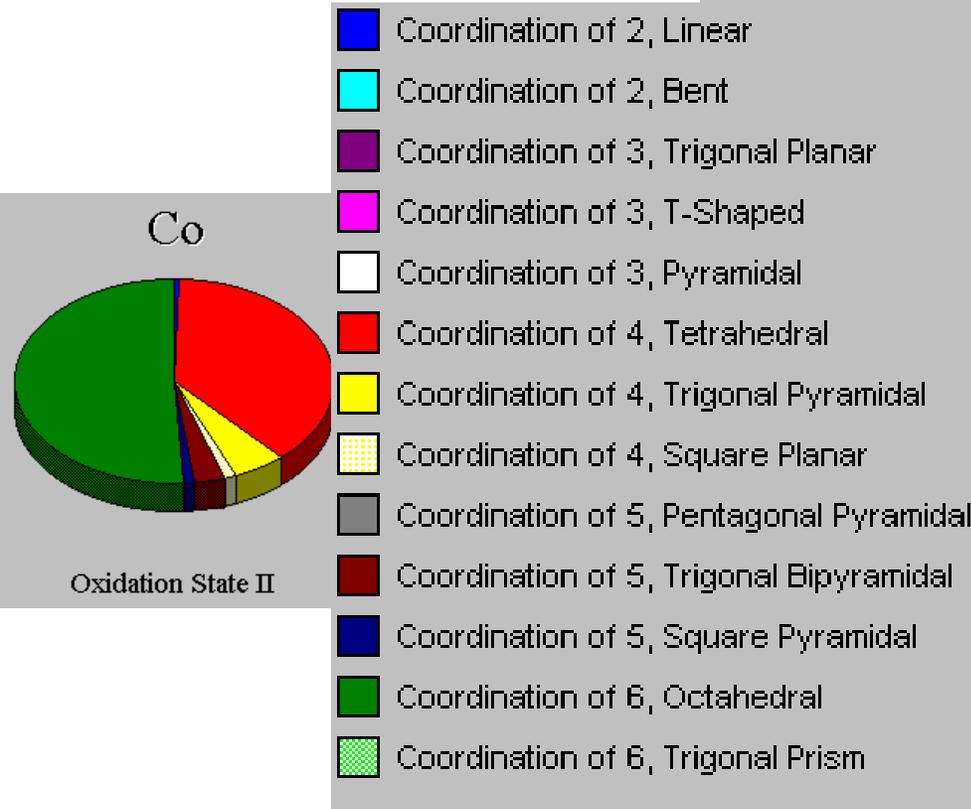
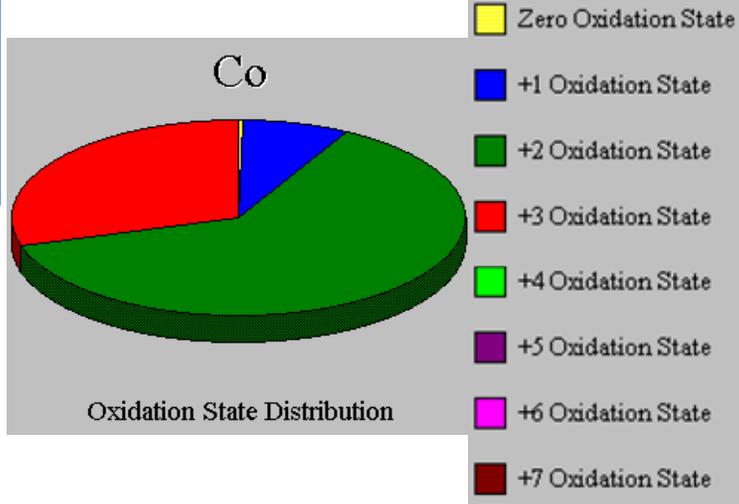


# Zeolite-like Frameworks





Effect of temperature? ...  
- Few Examples



The variations in oxidation states and geometrical arrangement observed for Cobalt based compounds - complexes

### Experimental Results

Coordination of 2, Linear	1
Coordination of 2, Bent	0
Coordination of 3, Trigonal Planar	0
Coordination of 3, T-Shaped	0
Coordination of 3, Pyramidal	0
Coordination of 4, Tetrahedral	71
Coordination of 4, Trigonal Pyramidal	10
Coordination of 4, Square Planar	2
Coordination of 5, Pentagonal Pyramidal	0
Coordination of 5, Trigonal Bipyramidal	6
Coordination of 5, Square Pyramidal	2
Coordination of 6, Octahedral	96
Coordination of 6, Trigonal Prism	0

What happens to compounds during the formation under different temperature??



# What happens when di-carboxylic acids are used?

*Identical reaction mixture is employed*

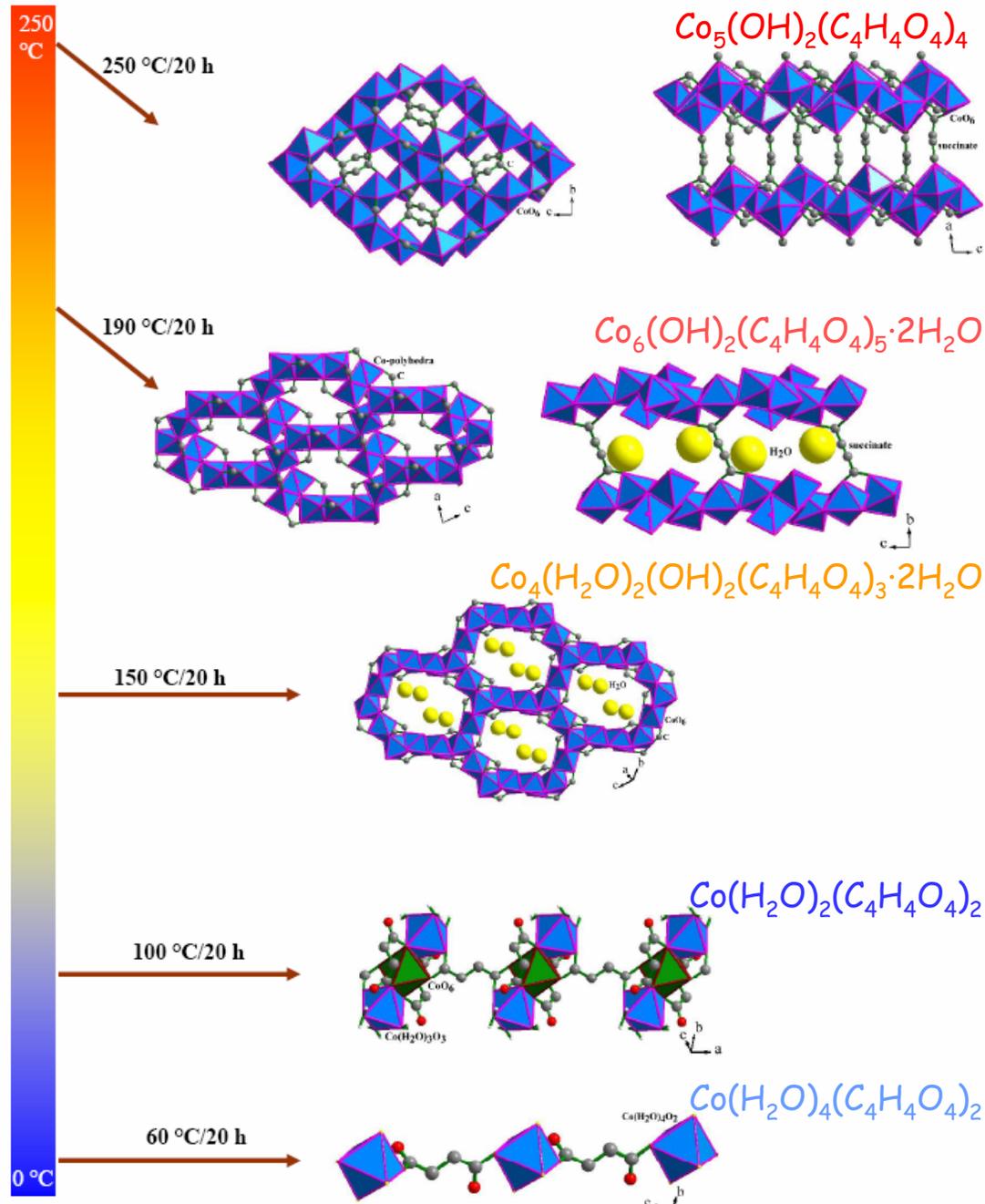
The reaction between  $\text{Co}^{2+}$  and succinic acid forms a variety of complexes depending on the temperature.

There is an overall decrease of bound water (coordinated) as the temperature raises.

At high temperature ( $> 150\text{ }^\circ\text{C}$ ), the compound possesses  $\text{M} - \text{O} - \text{M}$  linkages, but has channels with water molecules.

At ( $250\text{ }^\circ\text{C}$ ), the compound has a Cobalt oxide layer connected by the succinate!! - gives empty voids

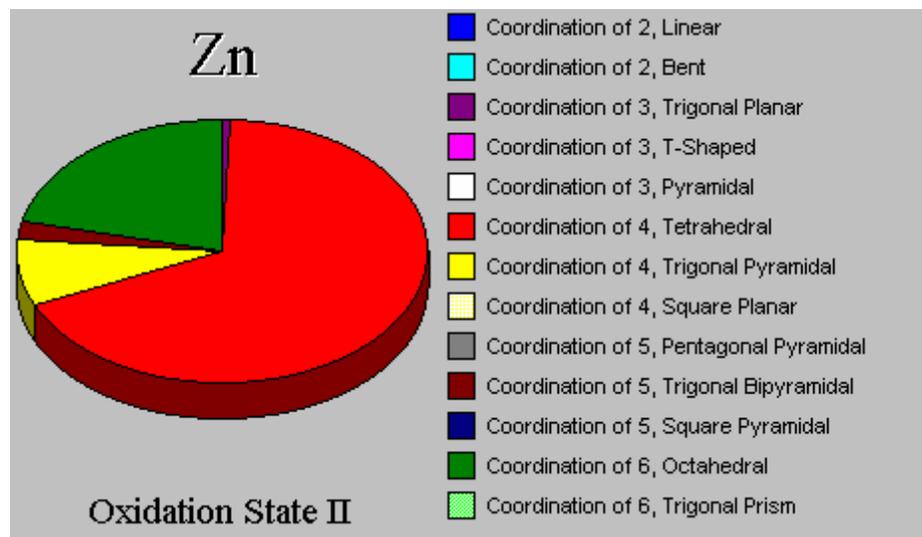
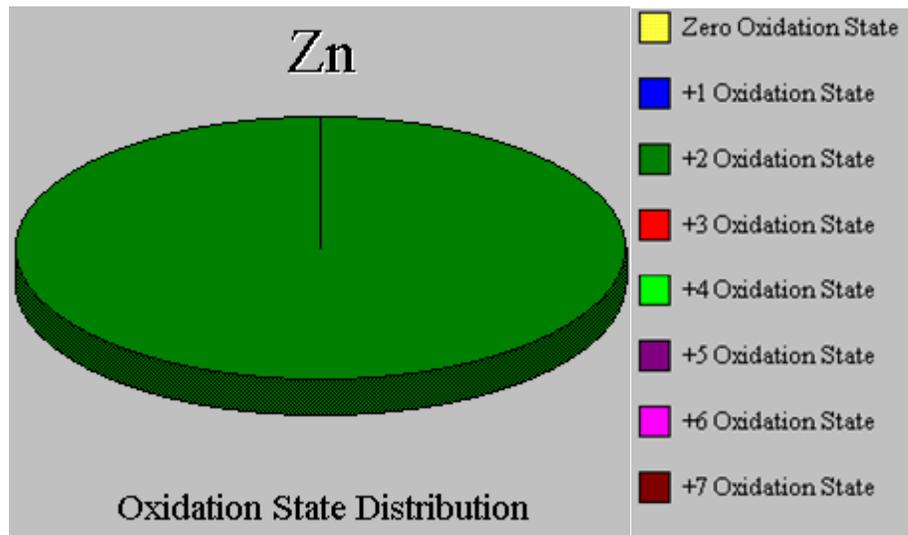
Novosibirsk, 2009





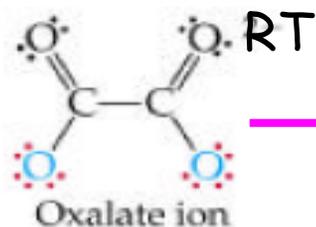
If we take  $Zn^{2+}$  as an example, then one finds that Zn exhibits only one oxidation state = +2

The coordination geometry does not show much diversity - tetrahedral, trigonal pyramidal, trigonal bipyramidal and octahedral

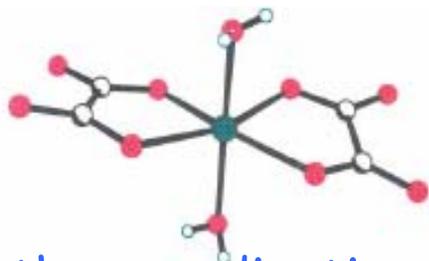




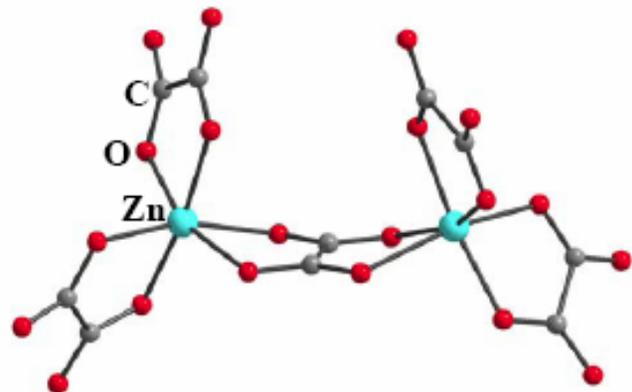
# The effect of Temp on the reaction between oxalic acid and $Zn^{2+}$



RT



50 °C

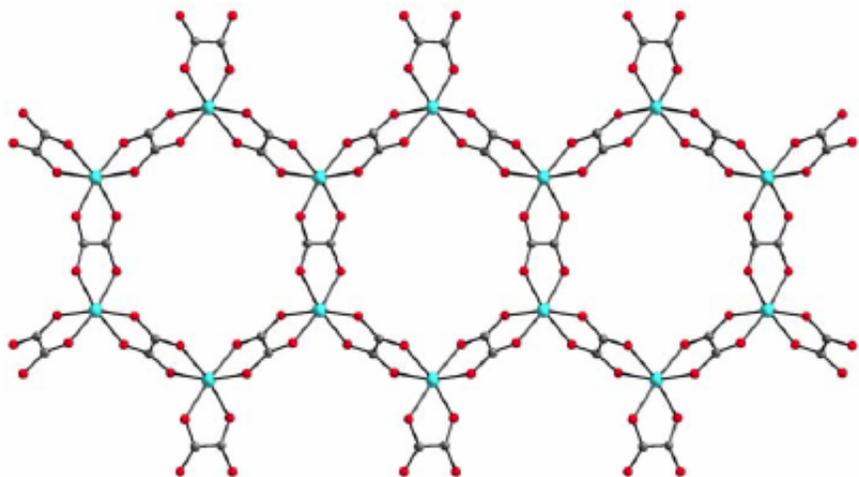


Dimer,  $[Zn_2(C_2O_4)_5][C_4N_2H_{12}]_3 \cdot 8H_2O$

During the heating, the coordination around  $Zn^{2+}$  does not change - the oxalate changes the connectivity to give rise to higher dimensional structures

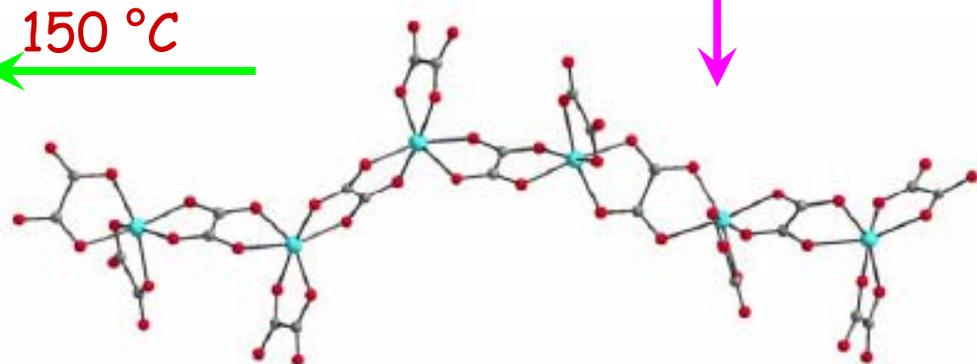
100 °C

150 °C



Pseudolayer,  $[Zn_4(C_2O_4)_7][C_4N_2H_{12}]_3 \cdot 4H_2O$ , III

Novosibirsk, 2009

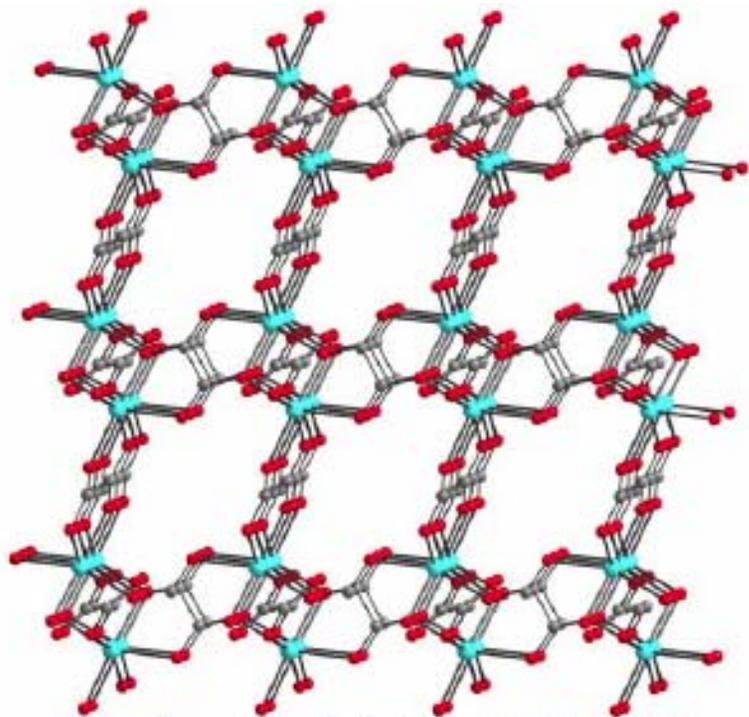


Chain,  $[Zn_2(C_2O_4)_4][C_4N_2H_{12}]_2 \cdot 3H_2O$ , II

Rao et al, *Angew. Chem.*, 2005



What happens if the temperature is raised further??? - say to 180 °C



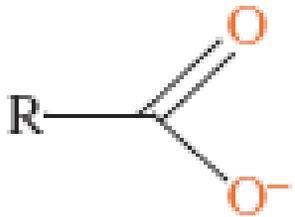
3D,  $[\text{Zn}_2(\text{C}_2\text{O}_4)_3][\text{C}_4\text{N}_2\text{H}_{12}]$ , IV

It forms a three-dimensional structure with channels/voids

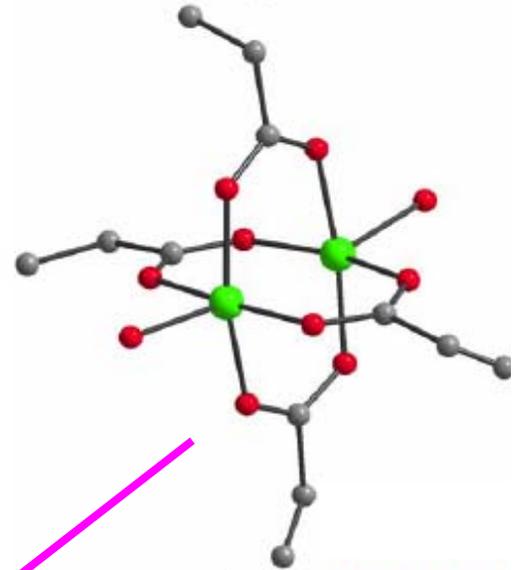
A simple coordination compound has become a new material - the channels can be used for adsorption and other related purposes



# Effect of temperature on simple carboxylates

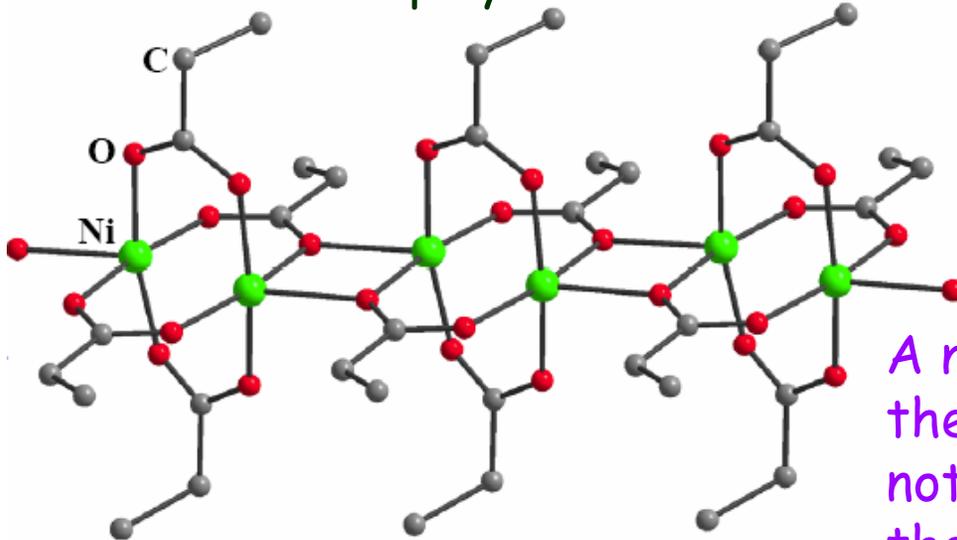


Carboxylate



A simple monomeric complex at RT

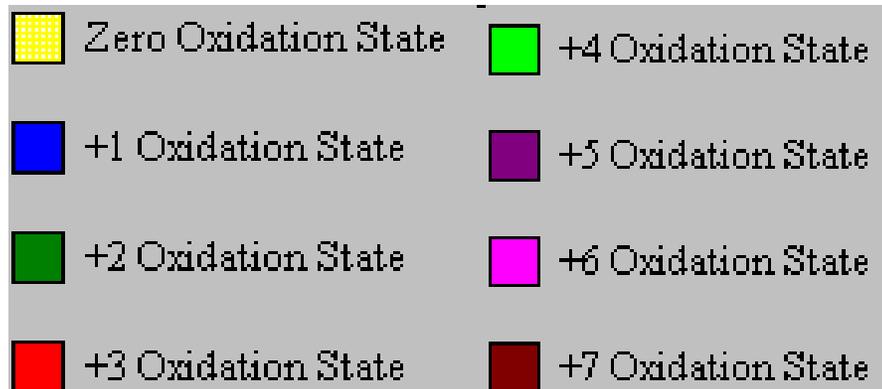
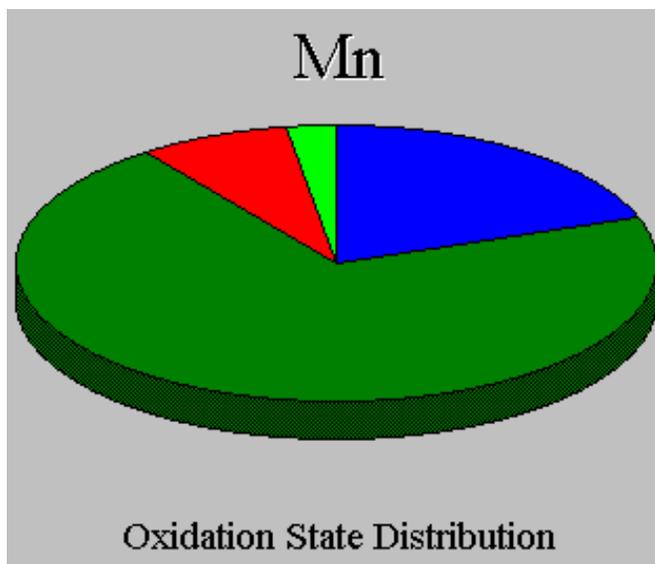
On heating becomes polymeric



A new chain compound is formed - the coordination around Ni<sup>2+</sup> ion does not change, but the connectivity of the ligand changes

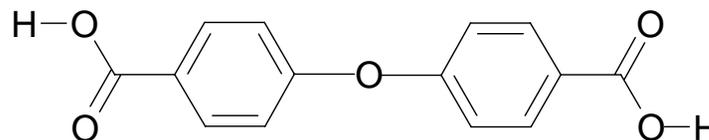


We have considered Mn - especially oxidation states and coordination preferences



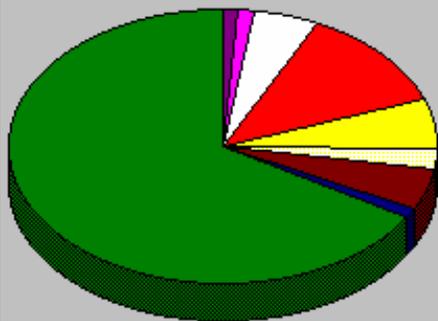
$Mn^{2+}$  salt + secondary base

+





Mn



Oxidation State II



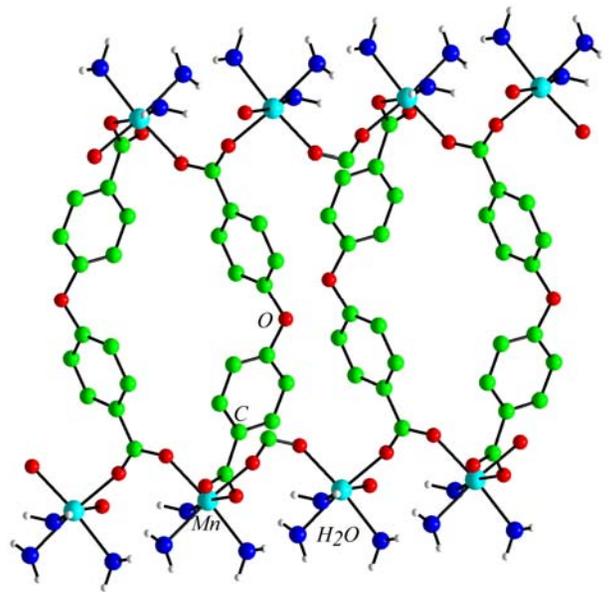
The table lists the different complexes that have been formed by the use of  $Mn^{2+}$  ions - different geometrical arrangements

## Experimental Results

Coordination of 2, Linear	0
Coordination of 2, Bent	0
Coordination of 3, Trigonal Planar	1
Coordination of 3, T-Shaped	1
Coordination of 3, Pyramidal	4
Coordination of 4, Tetrahedral	10
Coordination of 4, Trigonal Pyramidal	5
Coordination of 4, Square Planar	2
Coordination of 5, Pentagonal Pyramidal	0
Coordination of 5, Trigonal Bipyramidal	4
Coordination of 5, Square Pyramidal	1
Coordination of 6, Octahedral	55
<b>Coordination of 6, Trigonal Prism</b>	<b>0</b>



The important point here is that the octahedral  $Mn^{2+}$  ion changes coordination from octahedral (6) to trigonal bi-pyramidal (5) and then to octahedral - the dimensionality from one- to two- to three-

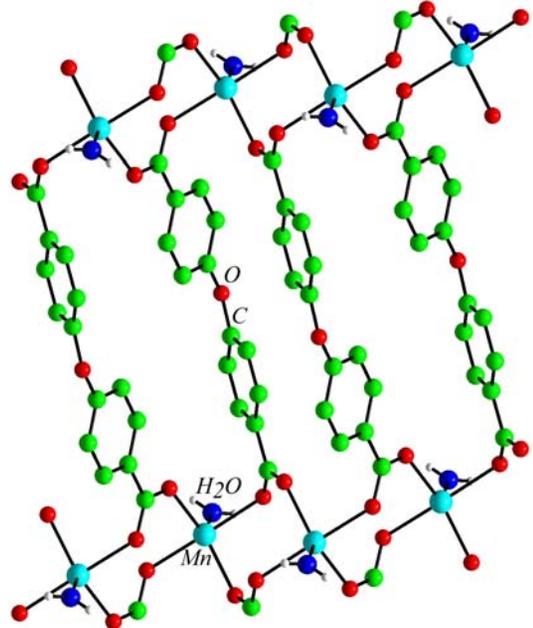
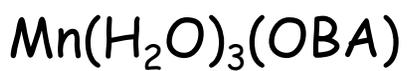


110 ° C (2D), **I**

$$d_{(Mn - Mn)} = 4.85 \text{ \AA}$$

Density: 1.578 g cm<sup>-3</sup>

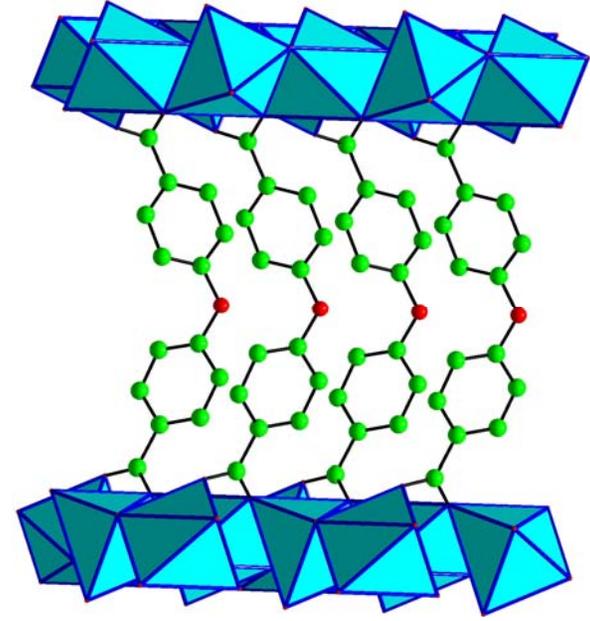
L.T.



150 ° C (2D), **II**

$$d_{(Mn - Mn)} = 4.35 \text{ \AA}$$

Density: 1.659 g cm<sup>-3</sup>



220 ° C (3D), **III**

$$d_{(Mn - Mn)} = 3.2 \text{ \AA}$$

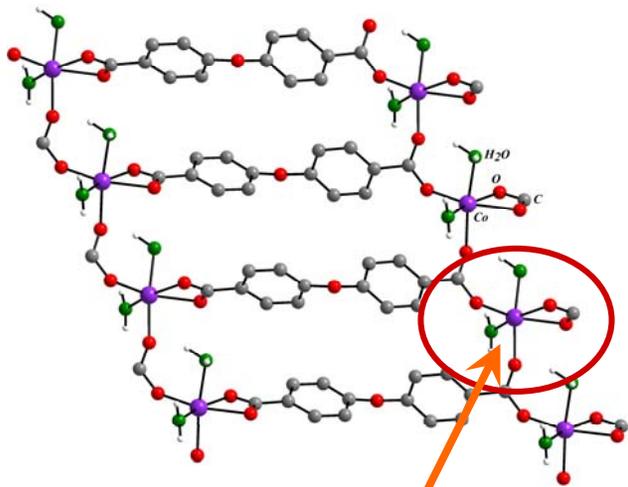
Density: 2.001 g cm<sup>-3</sup>

H.T.

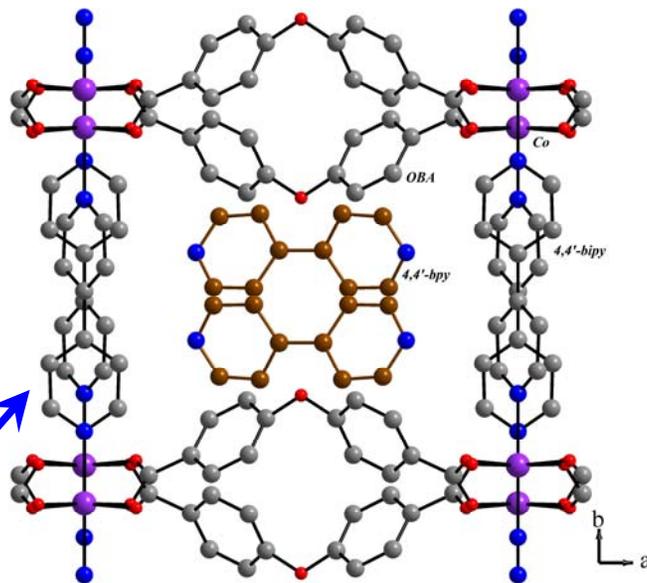
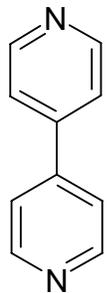




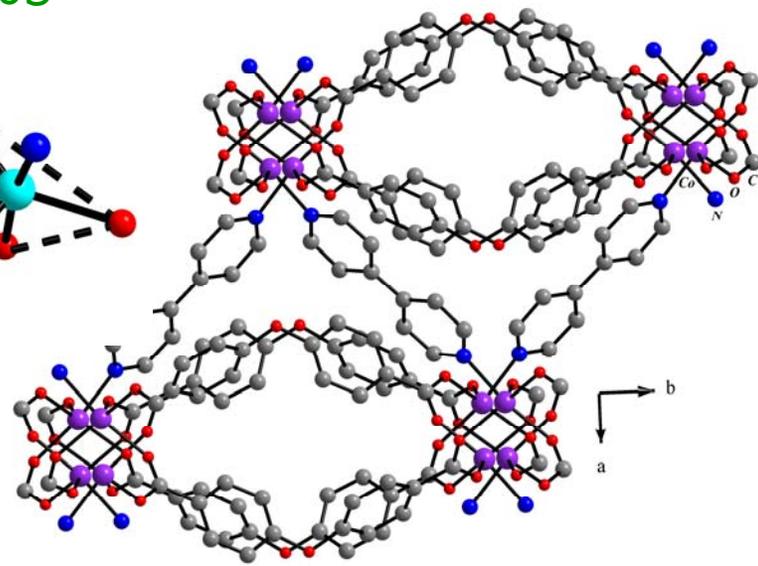
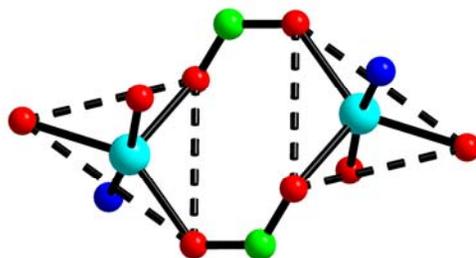
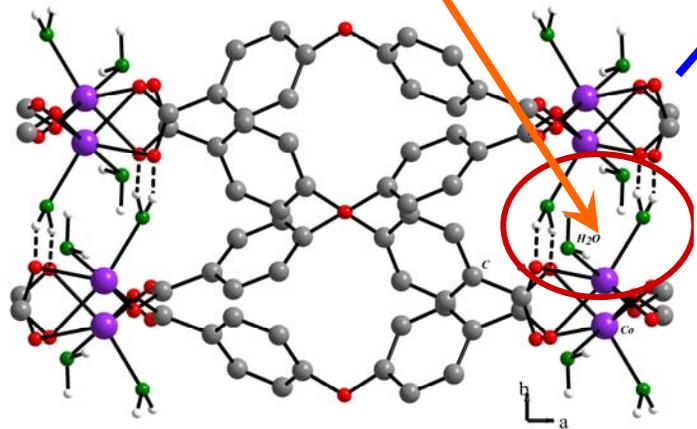
A well tested technique in inorganic coordination chemistry is to replace bound water molecules using simple organic ligands



+



The dimensionality here changes from 2D to 3D





What happens when the coordination requirement is higher - The case with lanthanides



8  
Dodecahedron



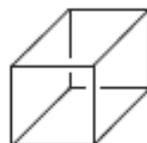
Most sterically  
efficient geometric  
arrangement for eight  
equivalent ligands

8  
Square  
antiprism



Uncommon

8  
Cube



Rare; found only  
with the largest  
metal ions

8  
Hexagonal  
bipyramid



Quite common for  
eight-coordinate  
complexes of metals  
with *trans*-dioxo  
ligands

The interest in  $\text{Ln}^{3+}$  compounds is due to its characteristic luminescence - line emission - generally used in many displays

C.N. 9

Tricapped  
trigonal prism



10

Bicapped square  
antiprism



11

Octadecahedron



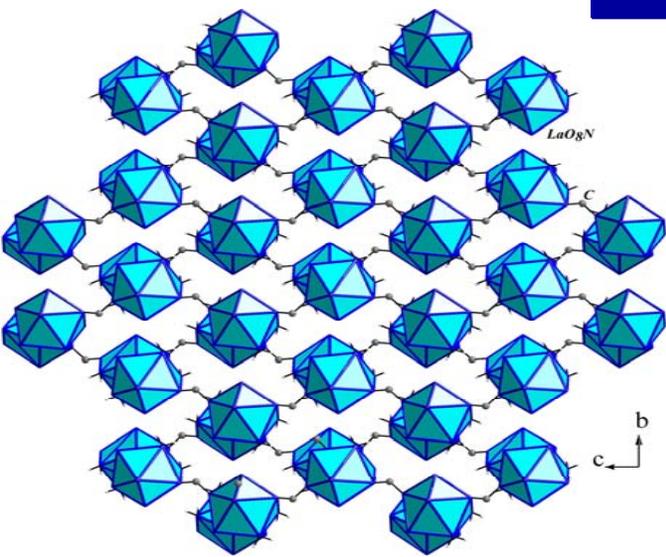
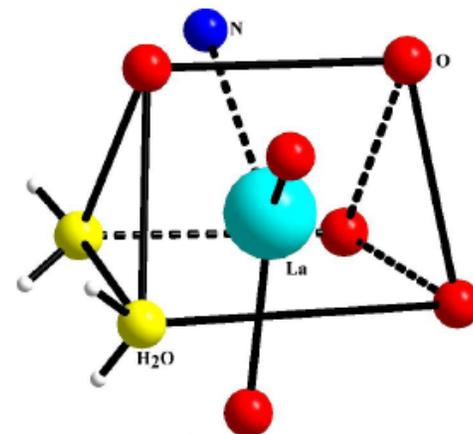
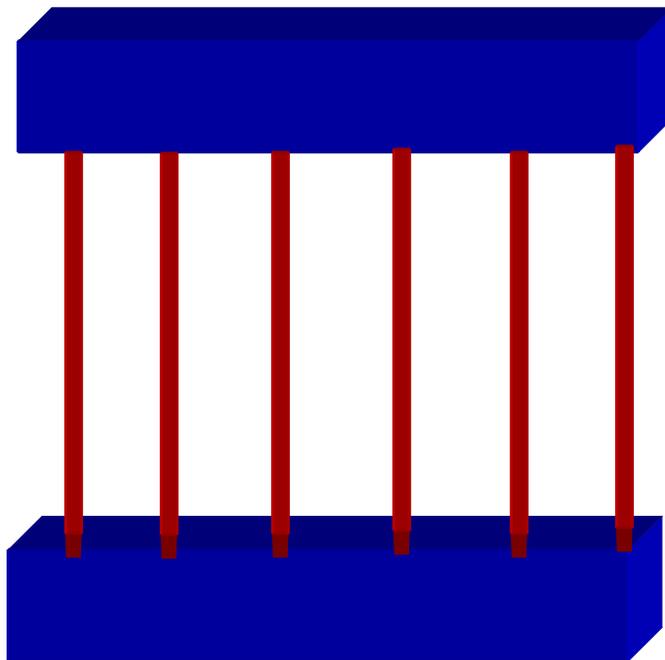
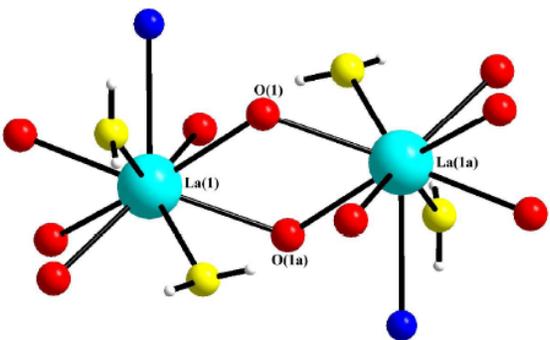
12

Icosahedron

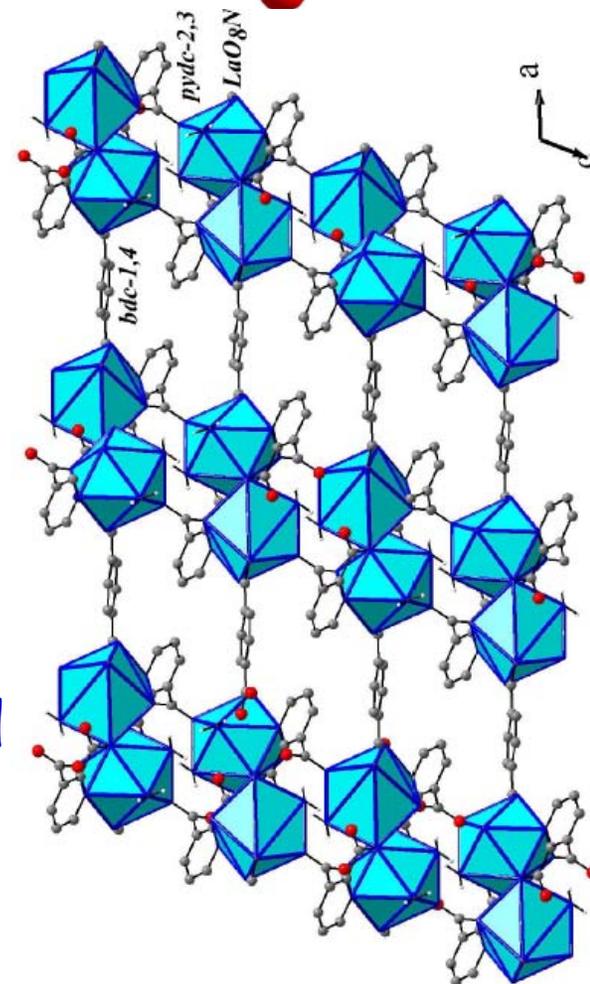




# $\text{Ln}^{3+}$ (py-2,3-diacid + 1,4-BDC)

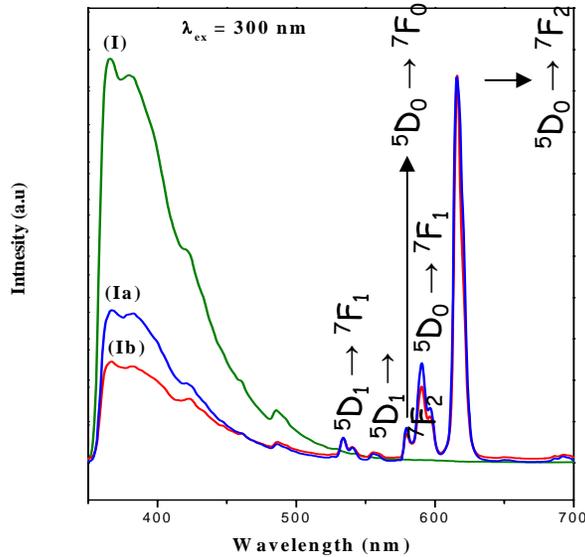


$\text{Ln}$  is 9-coordinated with two  $\text{H}_2\text{O}$  molecules

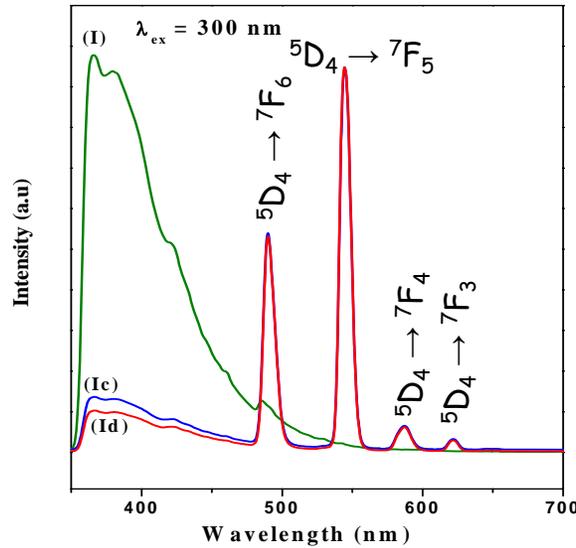




Eu doped sample

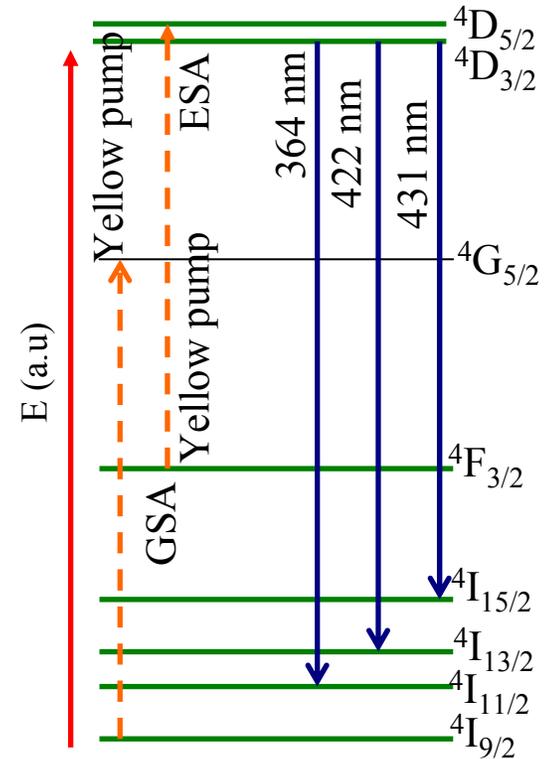


Tb doped sample

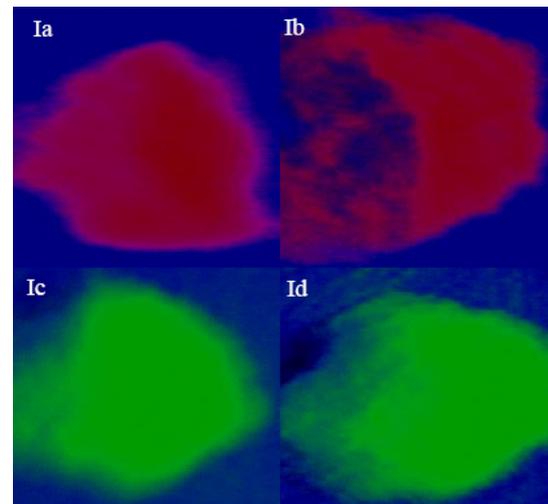


What happens when  $\text{La}^{3+}$  is doped with Eu/Tb ions?

Can we play around - look for newer properties



Nd - compound shows a 2-photon absorption behavior - one can view IR region in UV





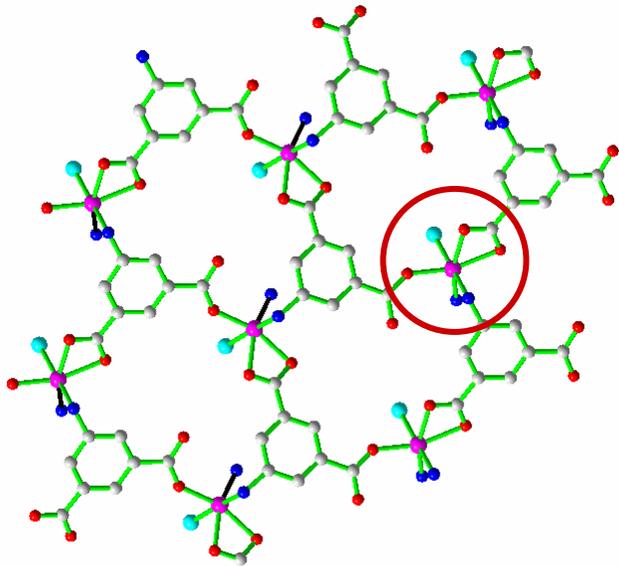
# Coordination Compounds in new properties



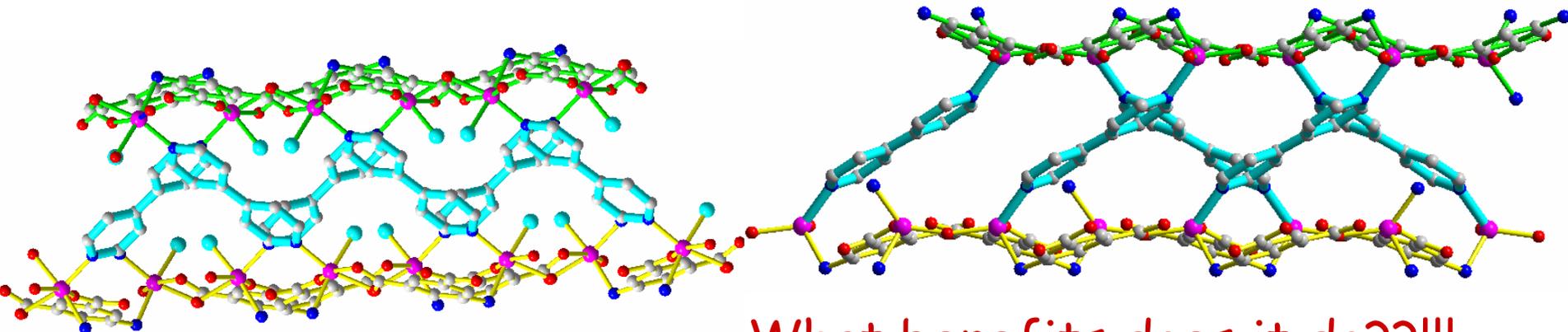
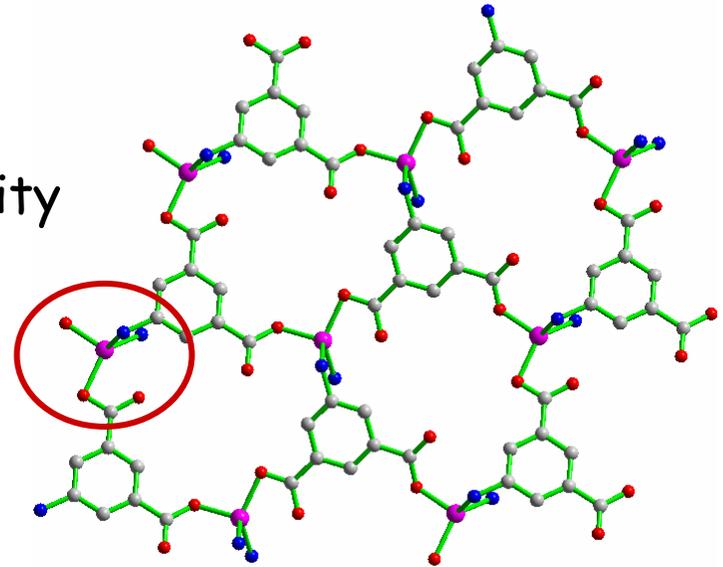
A tetrahedral cobalt is formed during dehydration

The structure is still a bi-layer structure

The bi-pyridine crosslinks individual layers for additional strength and interactions



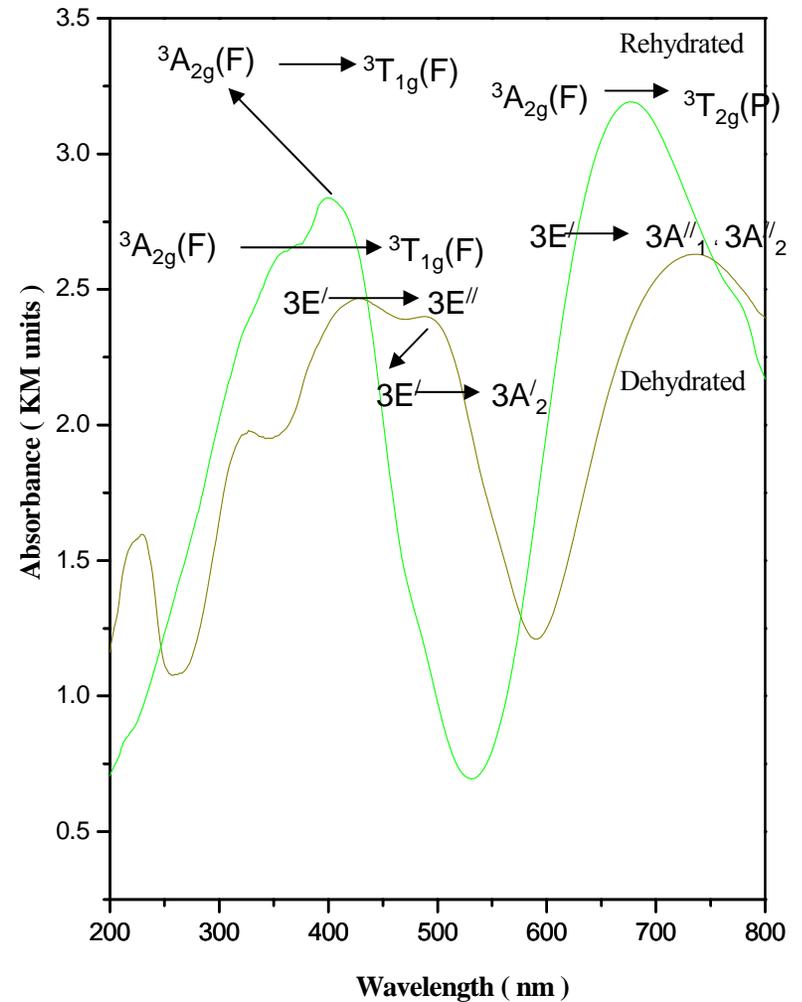
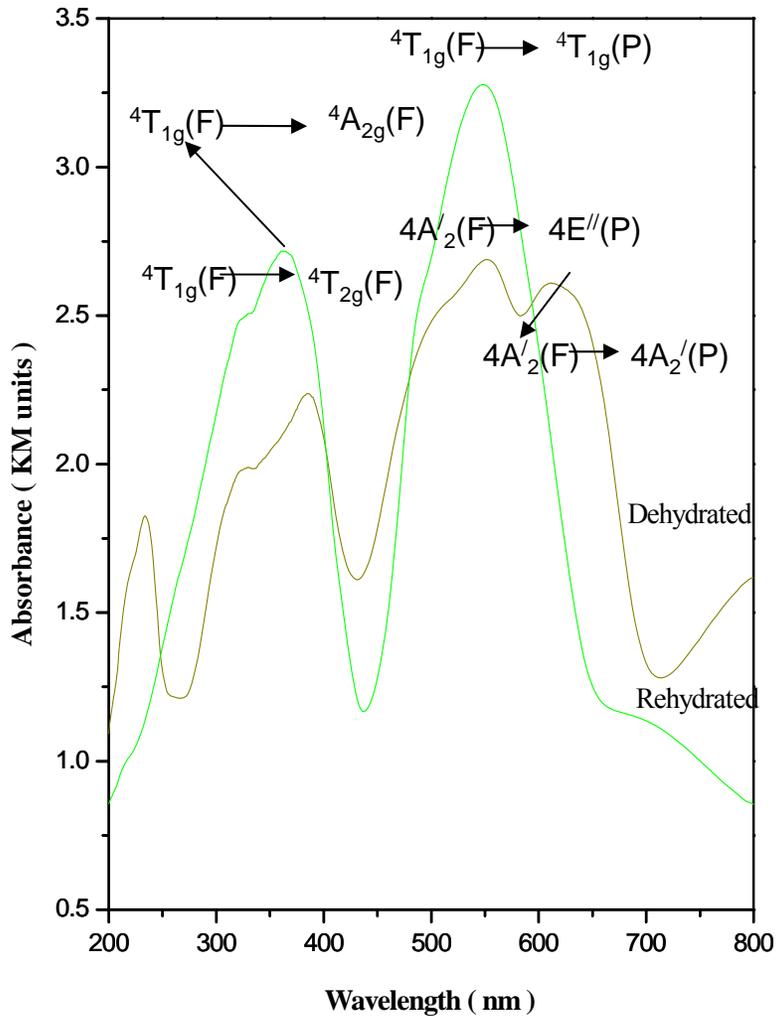
The acid-connectivity changes to fully mono-dentate on dehydration

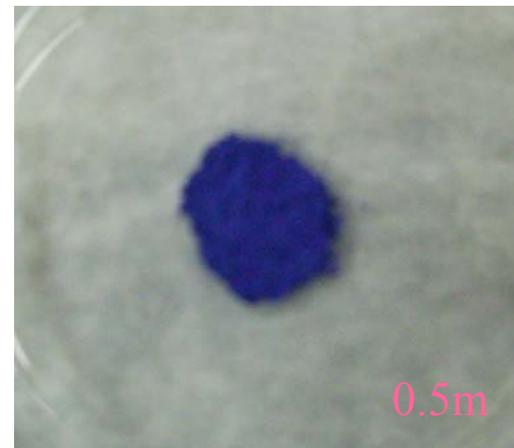
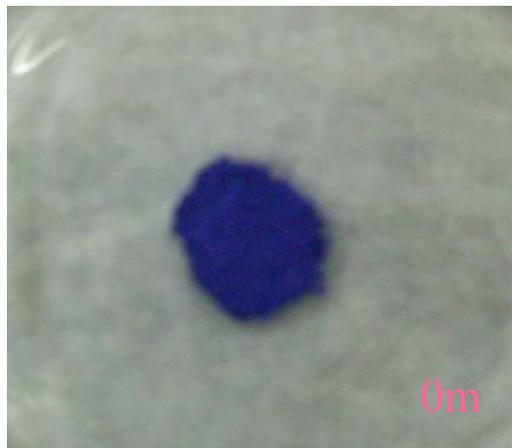


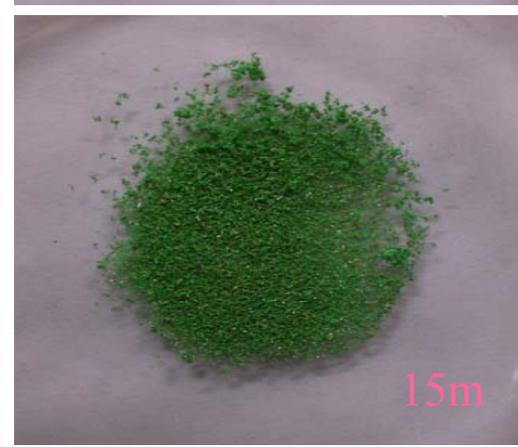
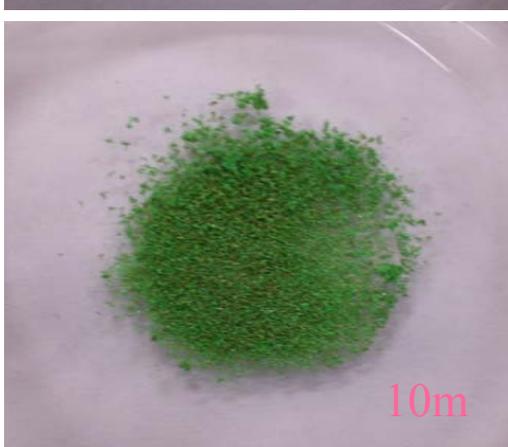
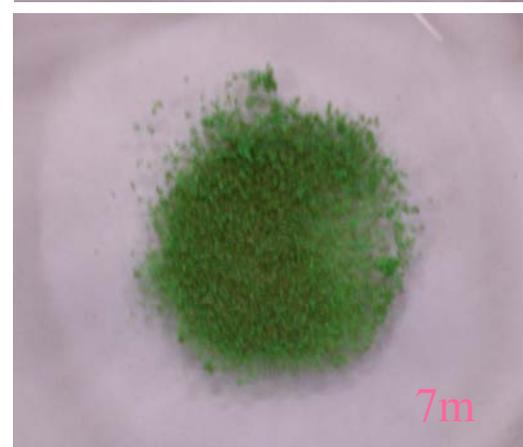
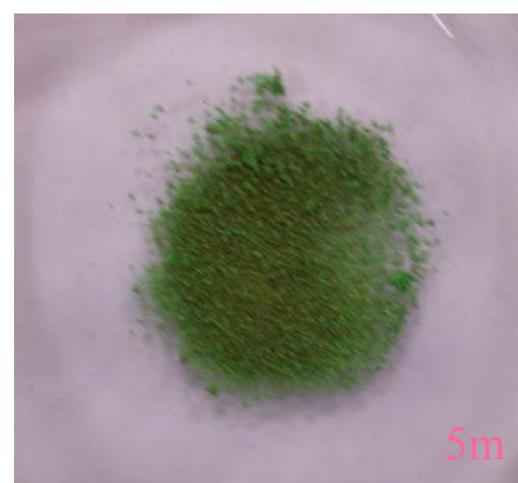
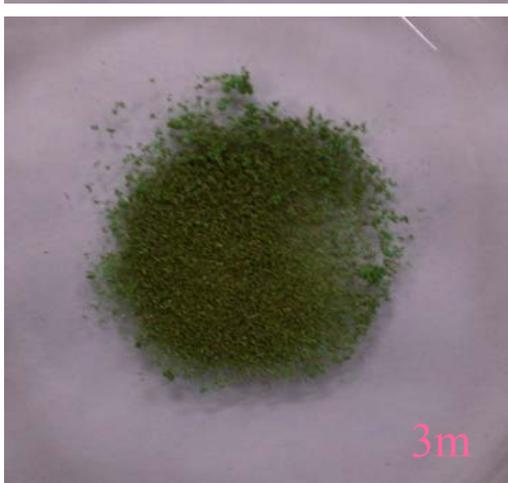
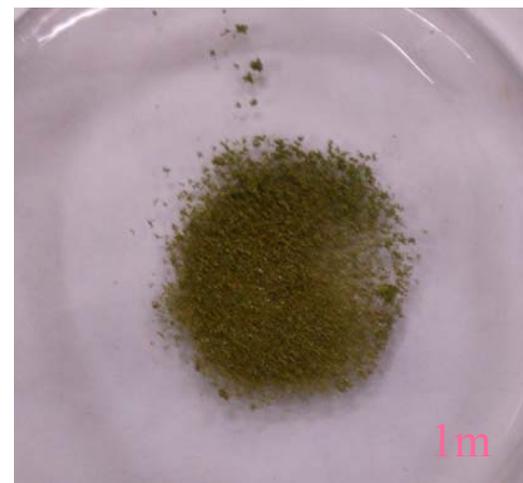
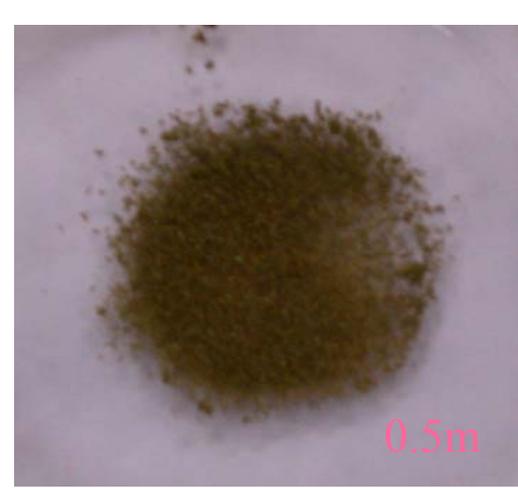
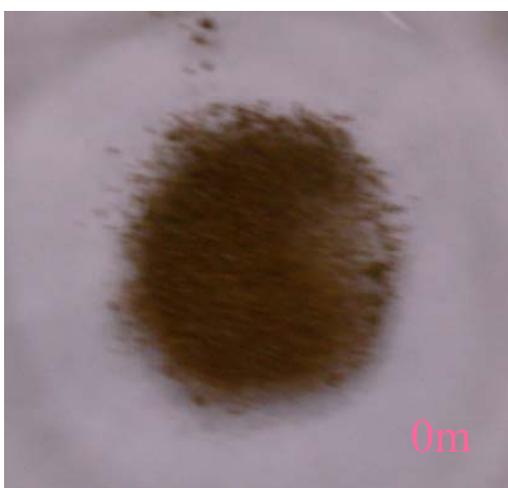
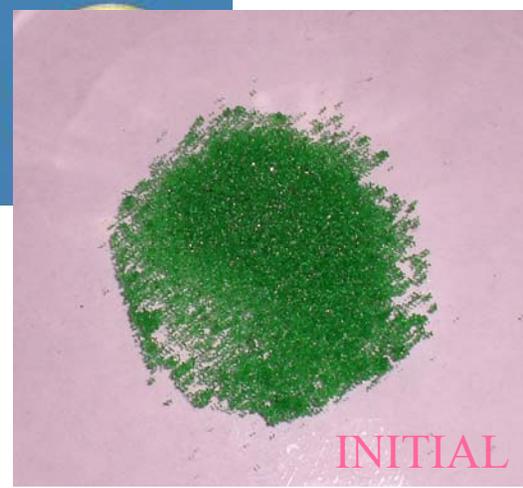
What benefits does it do??!!!

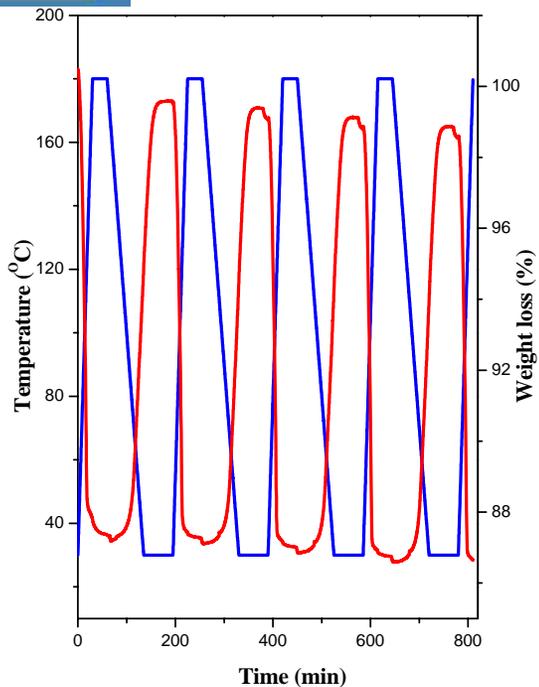


A simple UV study also indicates the change in the symmetry along with the observation of transitions corresponding to those.



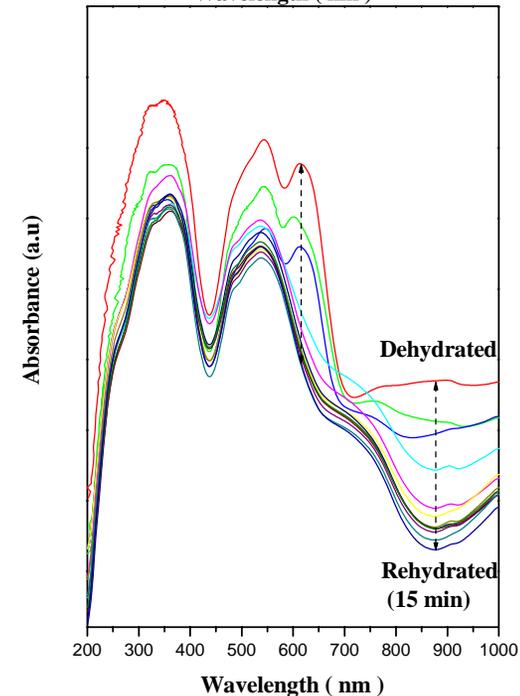
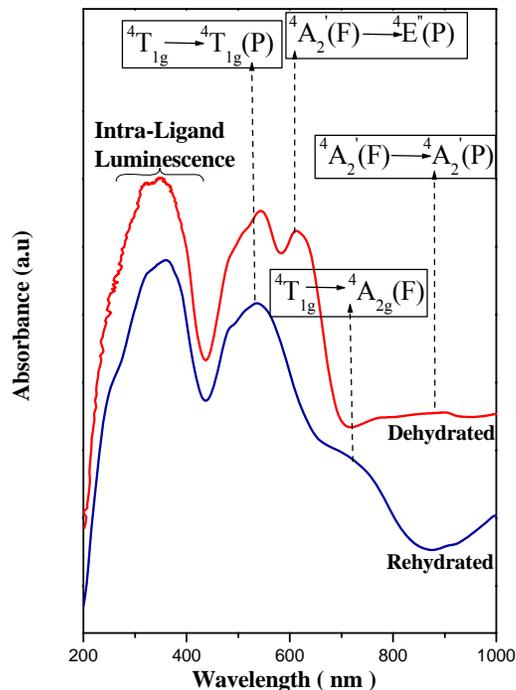
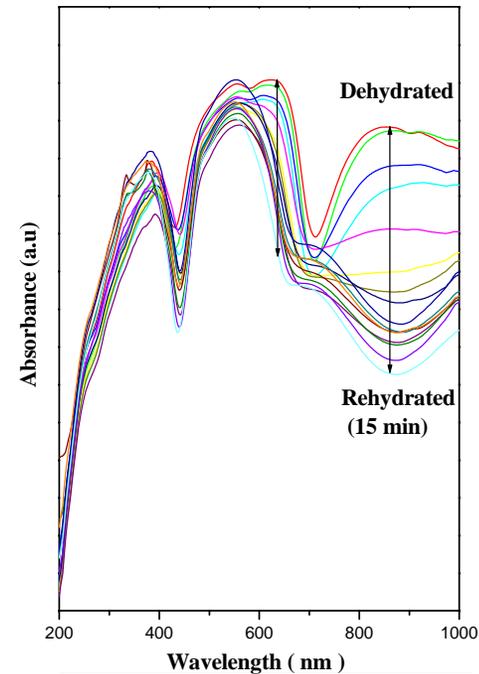
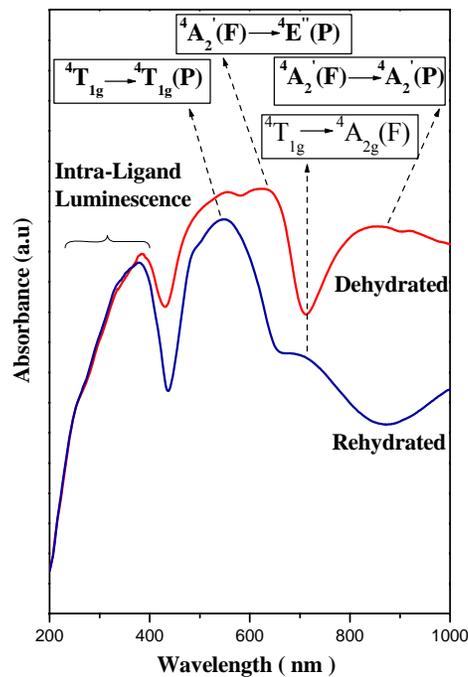


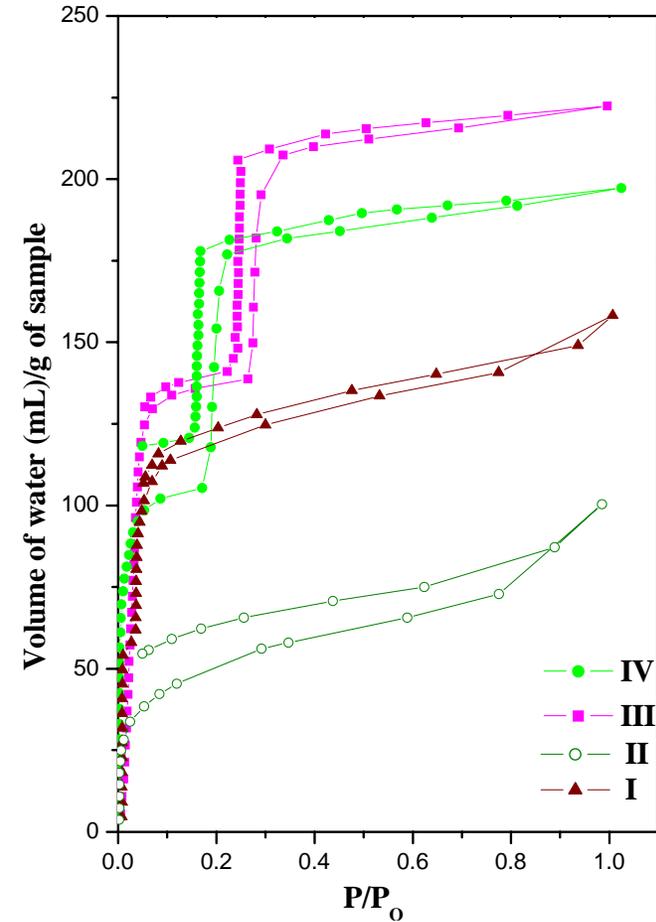




The dehydration is accompanied by change in coordination sphere around the metal, which can be studied by UV-Vis and IR spectroscopic studies. The reversibility can also be studied by SC-SC transformation studies

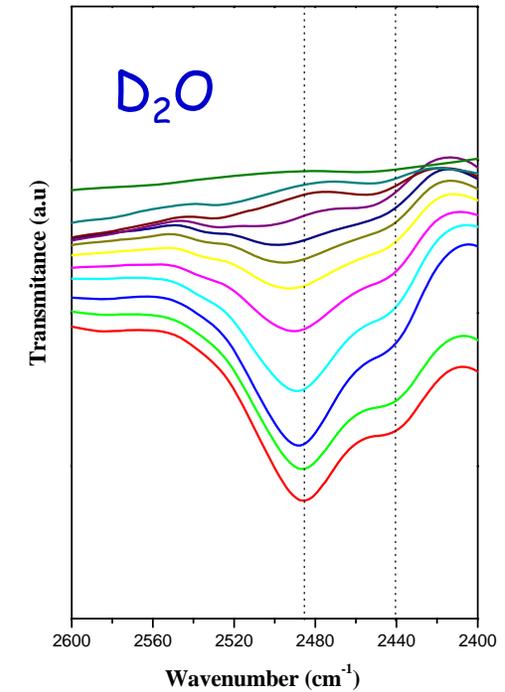
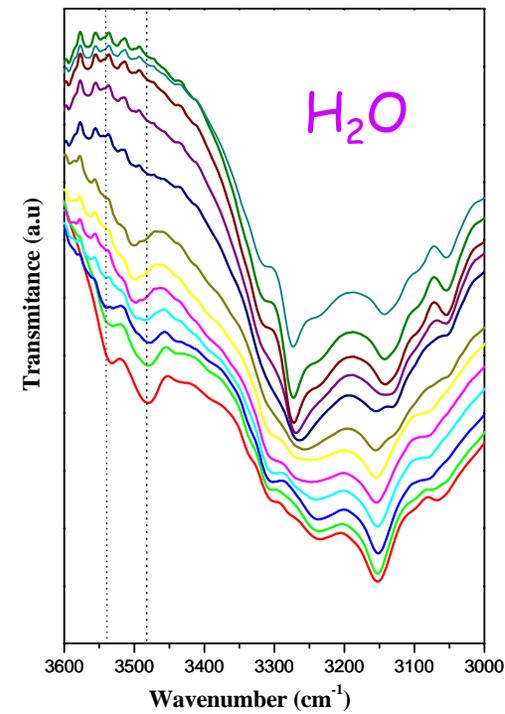
Novosibirsk, 2009





The dehydrated sample is exposed to D<sub>2</sub>O and we can study the dehydration *in-situ* using FT-IR spectroscopic investigations

The water adsorption studies also indicate that the uptake of water is rapid at low pressures - suggesting micropore behavior

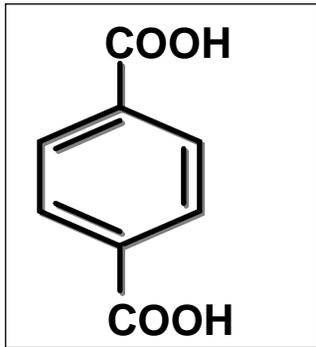




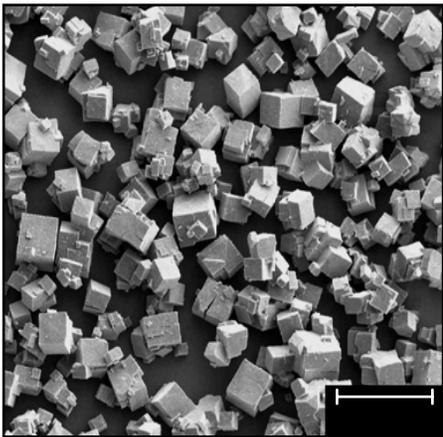
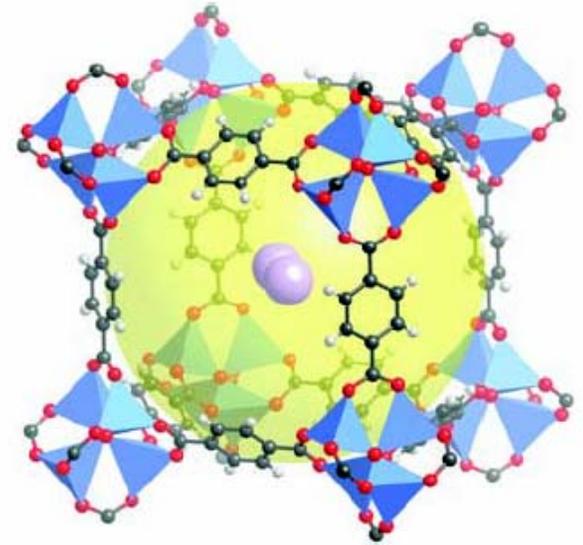
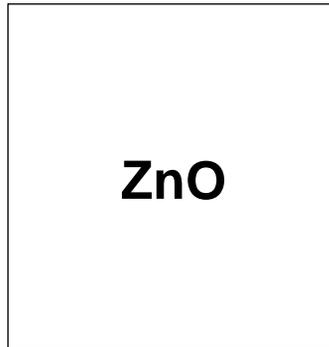
What about the Future - how can we use this knowledge further ?



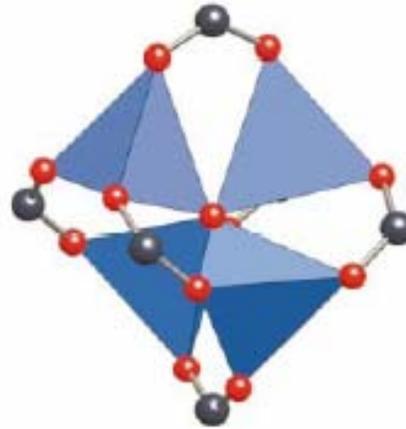
# Possible application for hydrogen storage and transportation in H<sub>2</sub>-fueled vehicles and portable electronics



+

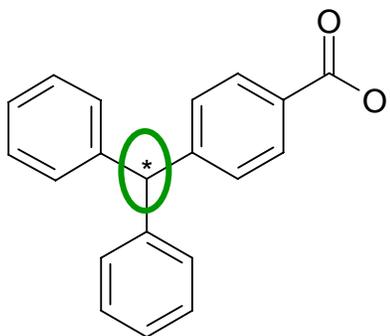
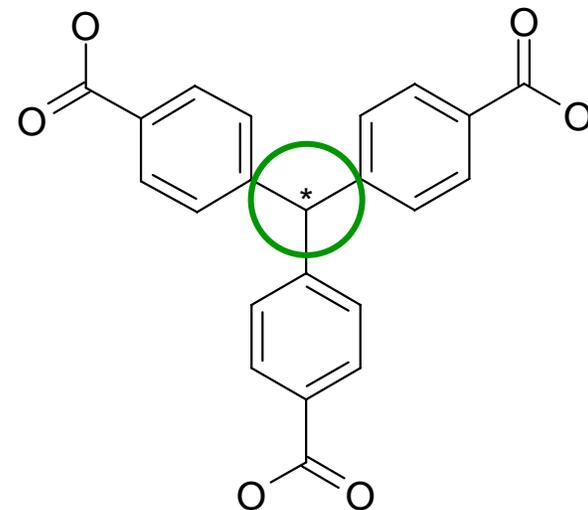
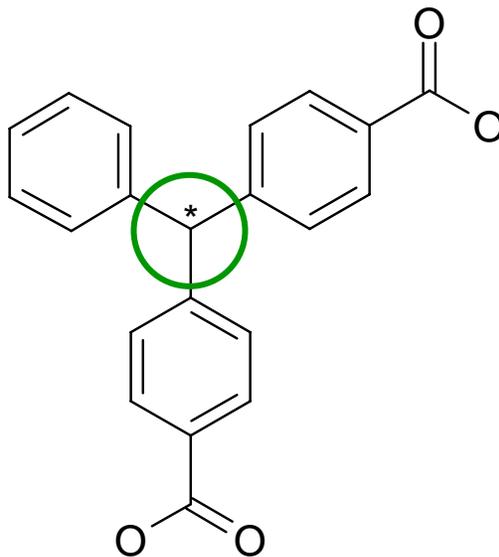
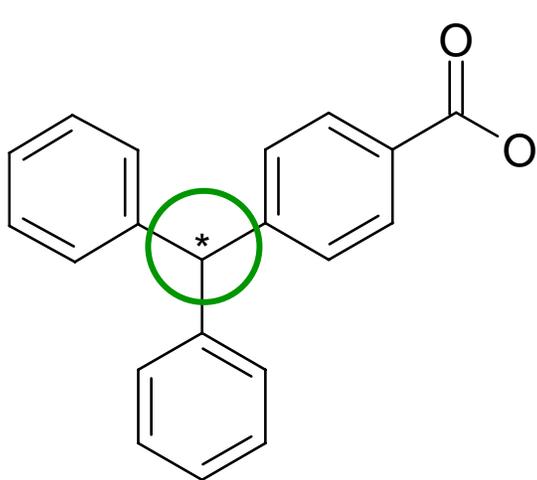


Produced by  
BASF for  
possible Gas  
Storage  
(BASOCUBES<sup>TM</sup>)

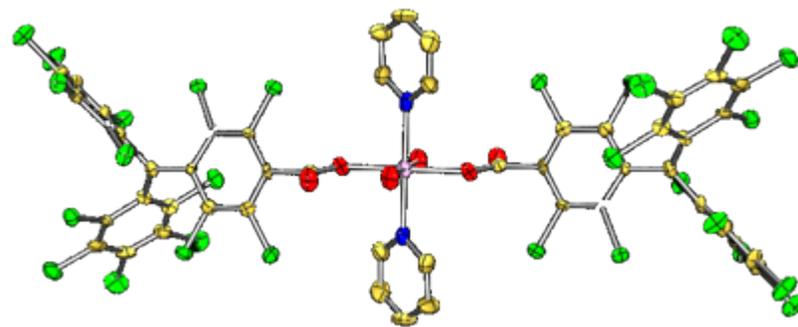


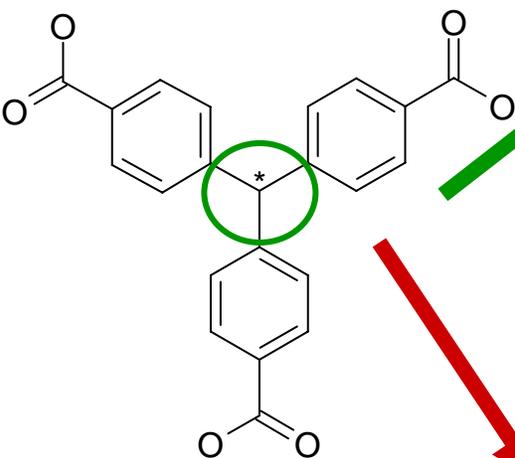
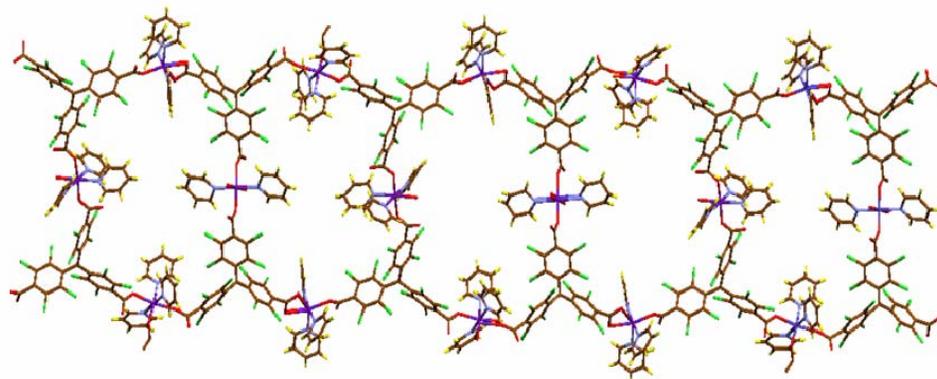
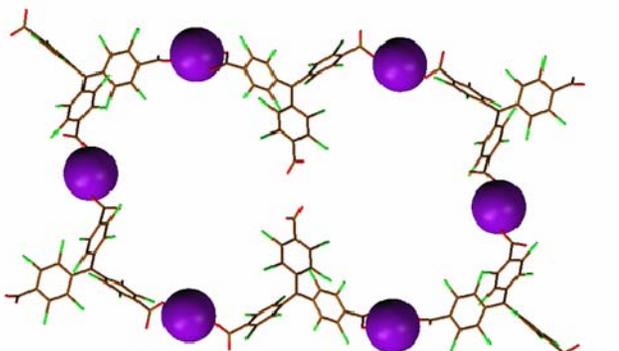


## Use of stable free radical acid as a ligand

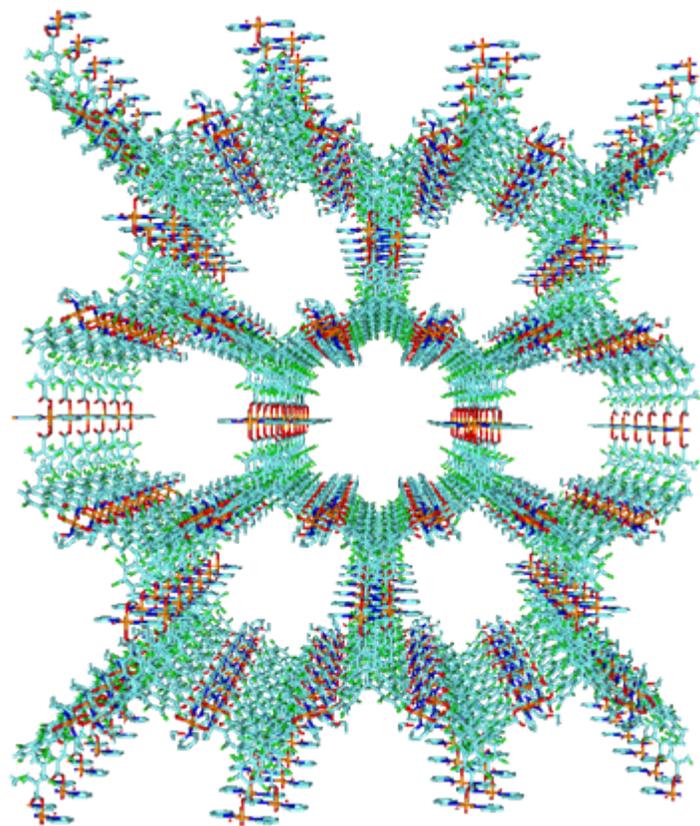
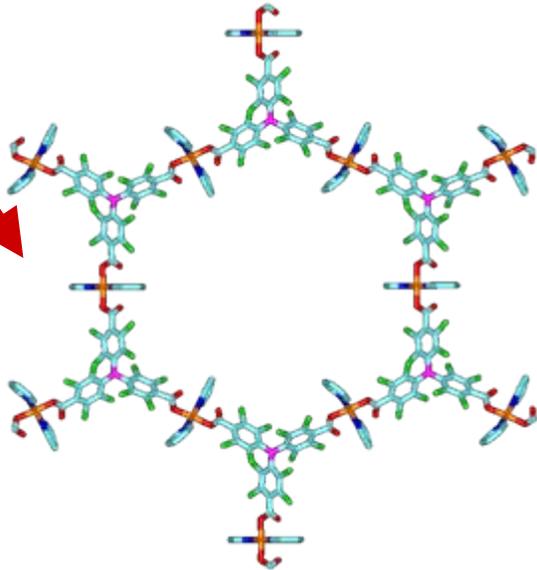


Presence of  
auxiliary ligand  
forms a simple  
complex





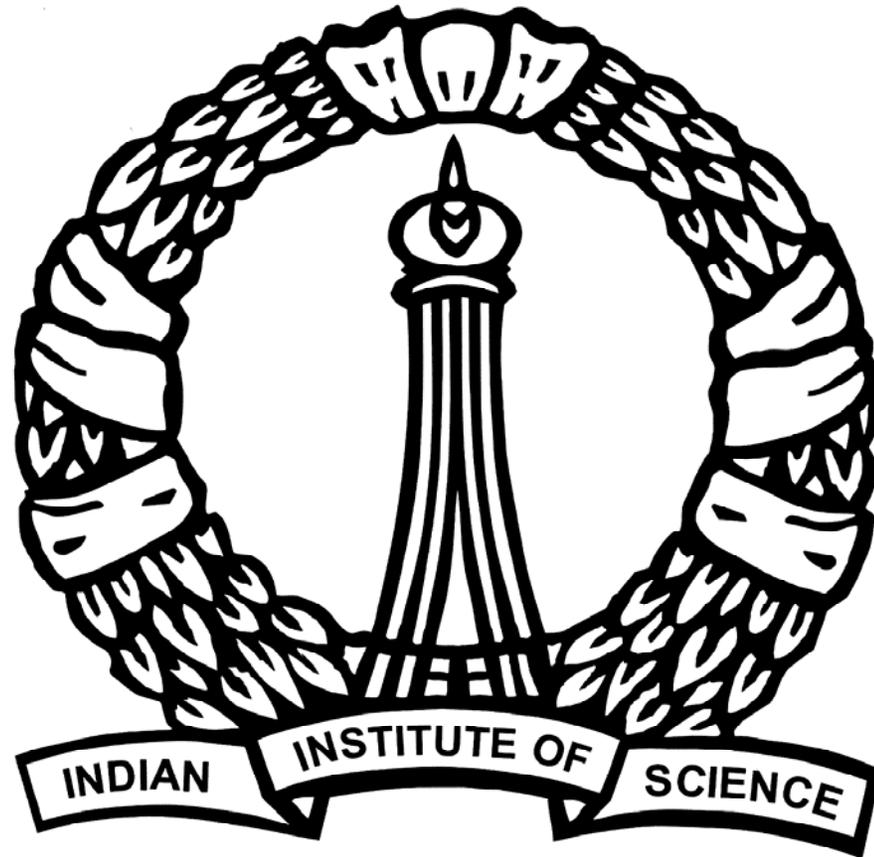
Presence of three  
carboxylate forms  
an open complex





RAMANNA Fellowship and the Department of Science & Technology (DST) and Council of Scientific and Industrial Research (CSIR), Government of India

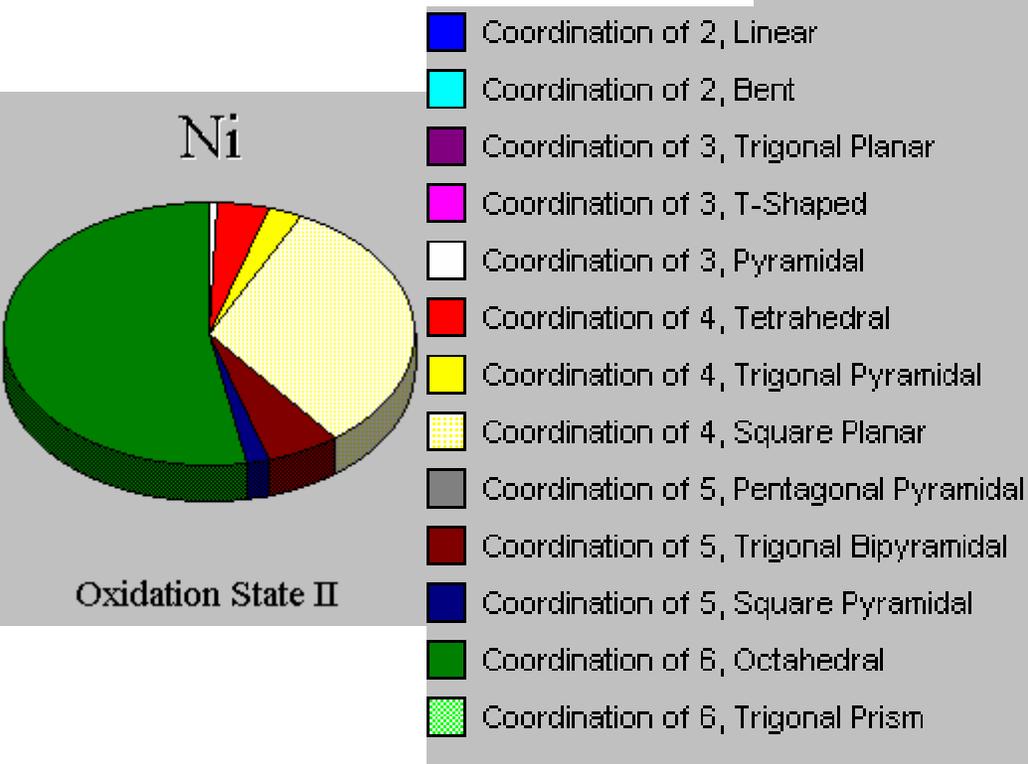
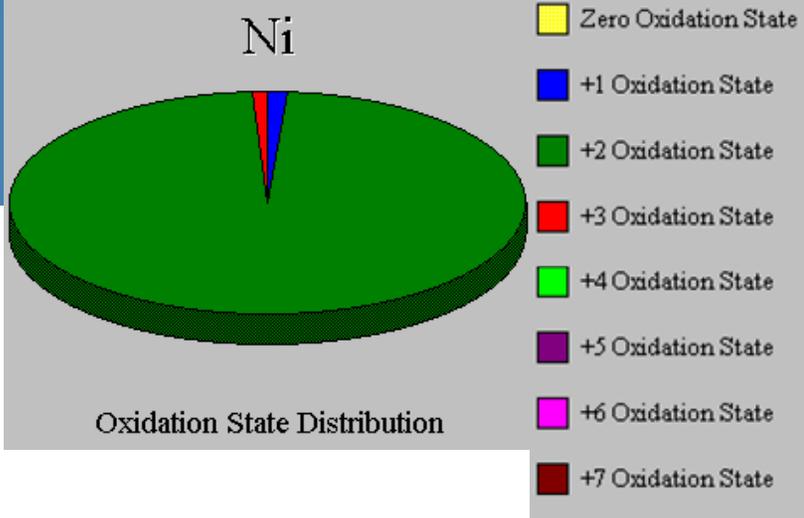
Indian Institute of Science, Bangalore



1909-2009 A century of Excellence

Thank you





Ni shows variations in oxidation states - predominantly +2, then we have +1 and +3

Coordination geometry has considerable variation with octahedral as the dominant followed by square planar - this is true in simple complexes - if there is some variations in reaction temperature - what would happen?