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Metal-Organic Frameworks I

Lecture 36

Surfaces: adhesion, friction, lubrication

Lecture 37

Metal-organic frameworks: structures and structural properties

Lecture 38

Metal-organic frameworks: surfaces and host-guest chemistry

Nobel Prize in Chemistry 2025



Ill. Niklas Elmehed © Nobel Prize Outreach

Susumu Kitagawa

Prize share: 1/3



Ill. Niklas Elmehed © Nobel Prize Outreach

Richard Robson

Prize share: 1/3



Ill. Niklas Elmehed © Nobel Prize Outreach

Omar M. Yaghi

Prize share: 1/3

"for the development of metal–organic frameworks"

https://www.nobelprize.org/prizes/chemistry/2025/summary/

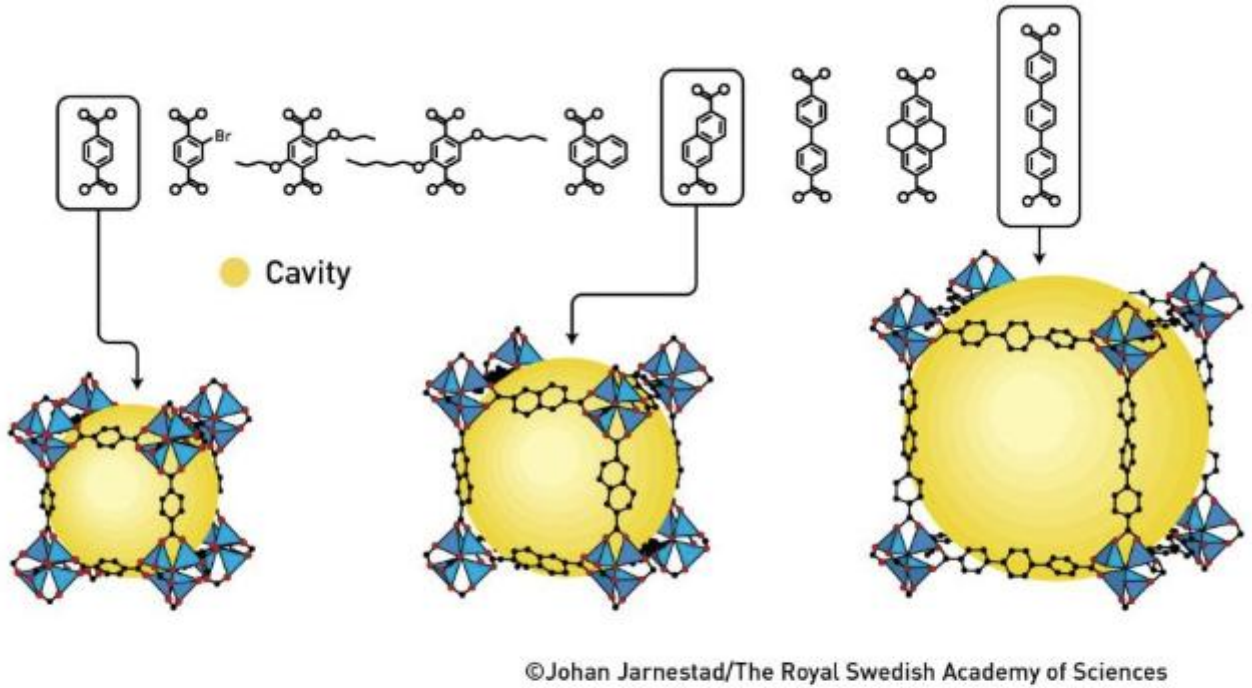
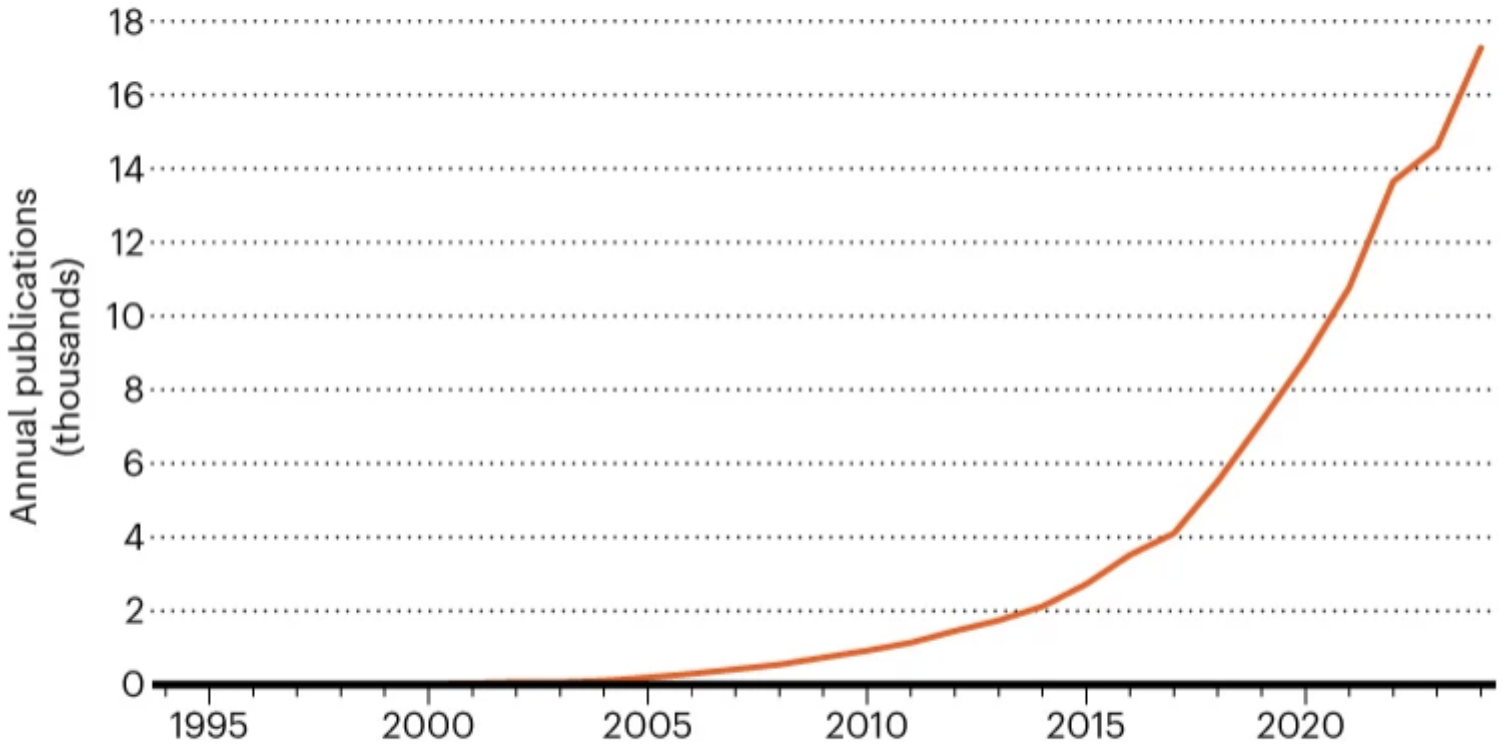


Figure 6. In the early 2000s, Yaghi showed that it is possible to produce entire families of MOF materials. He varied the molecular links, which resulted in materials with different properties. These include 16 variants of MOF-5, with cavities of various sizes. ©Johan Jarnestad/The Royal Swedish Academy of Sciences

PAPERS ON METAL–ORGANIC FRAMEWORKS

More than 100,000 journal articles have been published about metal–organic frameworks in the past three decades.



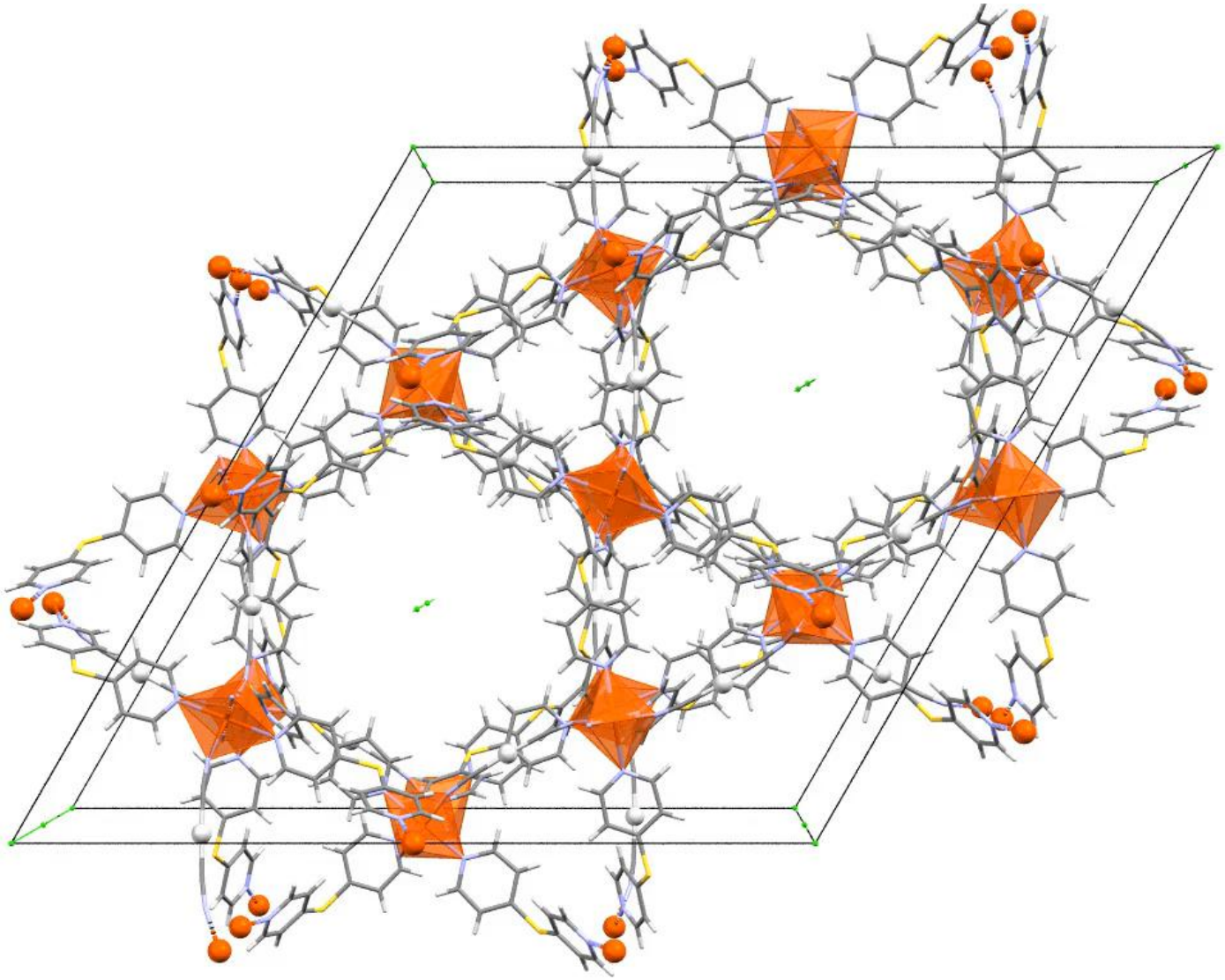
Dimensions database search for metal–organic frameworks, covalent organic frameworks and MOFs in the title, abstract or keyword of research and review articles. Alternative definitions of MOF, such as 'multiple organ failure', were excluded.

©nature

Inversion Axes ($\bar{n}$) in Crystals

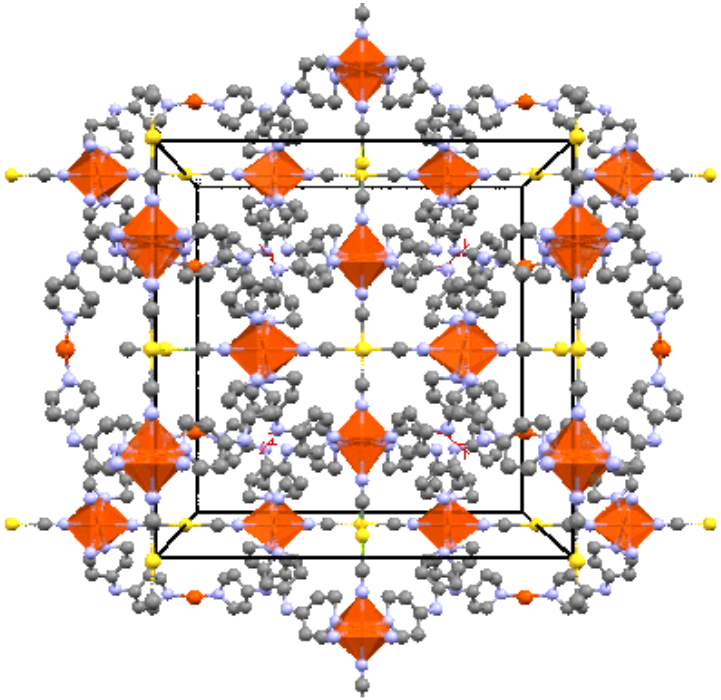
Symbol: $\bar{n}$

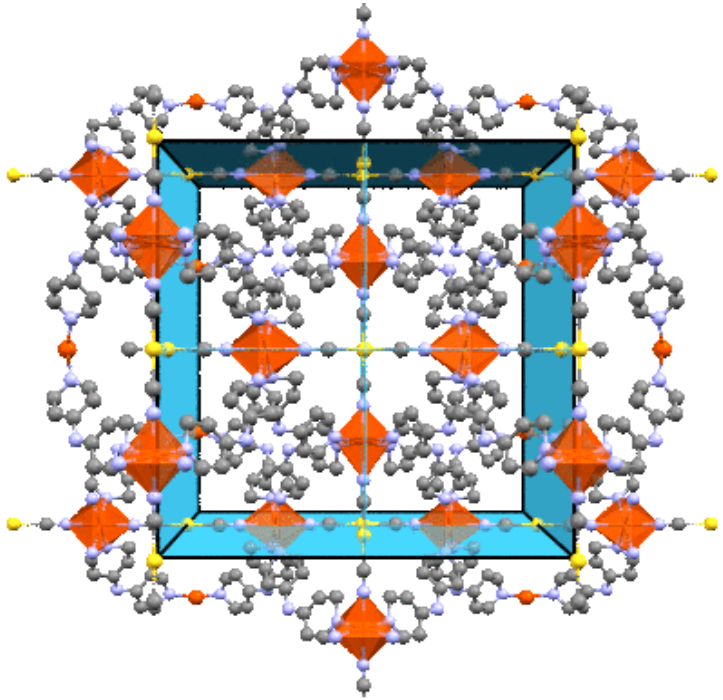
$\bar{3}$ rotary inversion (rotation then inversion) axes (green) in a Metal-Organic Framework (materials of this type will be covered in lectures 37-39 in week 13).

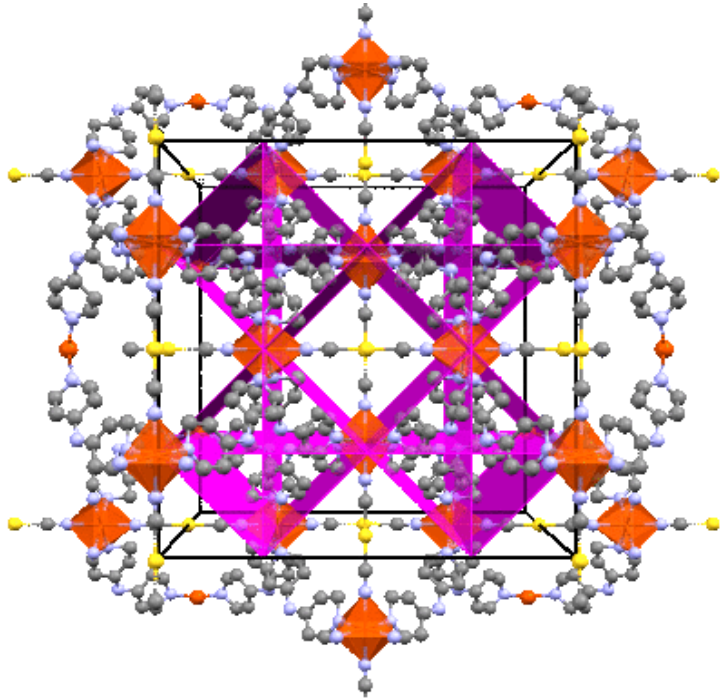


A crystal structure with space group $I4_1/amd$

- Body-centred tetragonal cell
- A lot of symmetry! (32 symmetry elements)

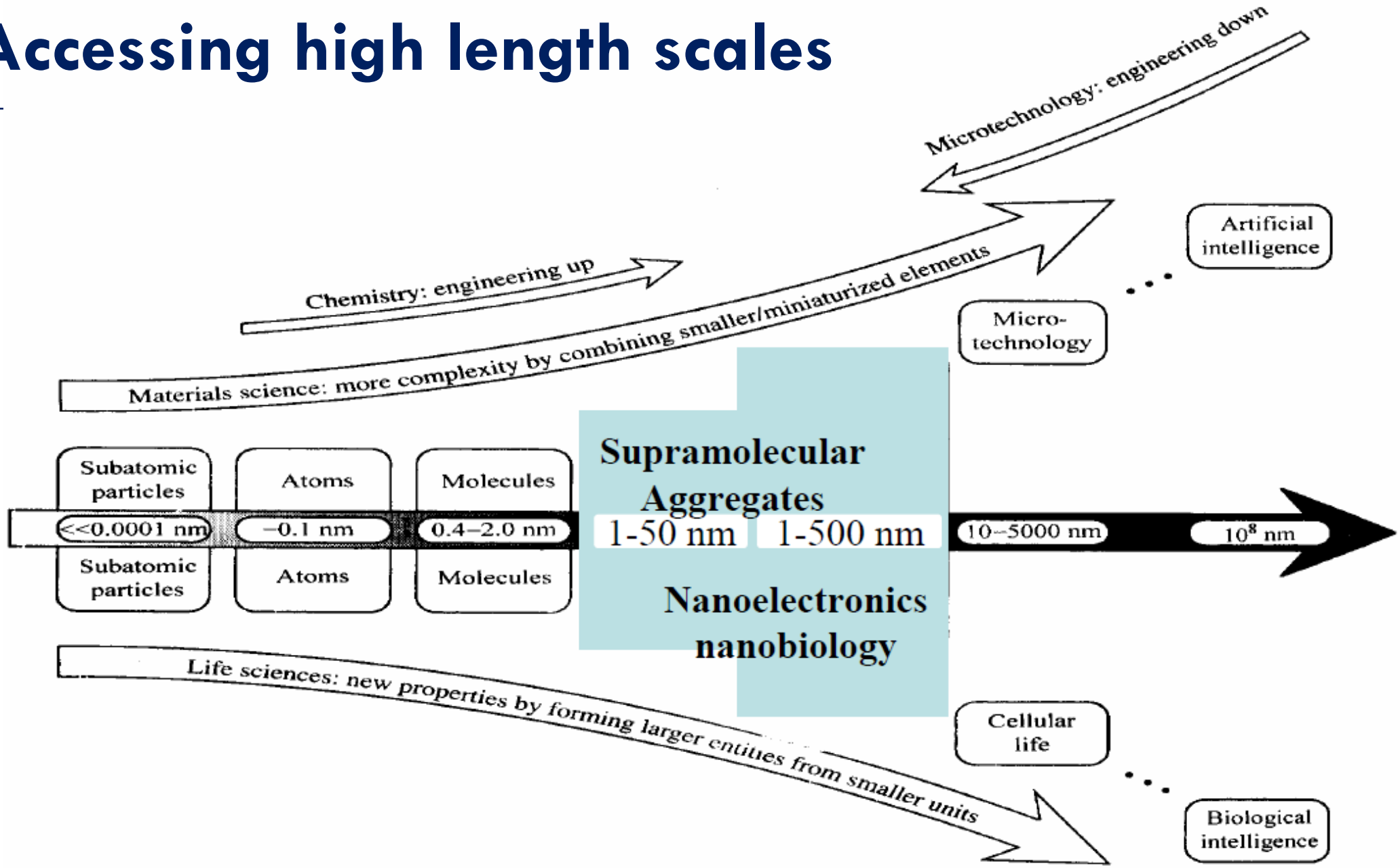




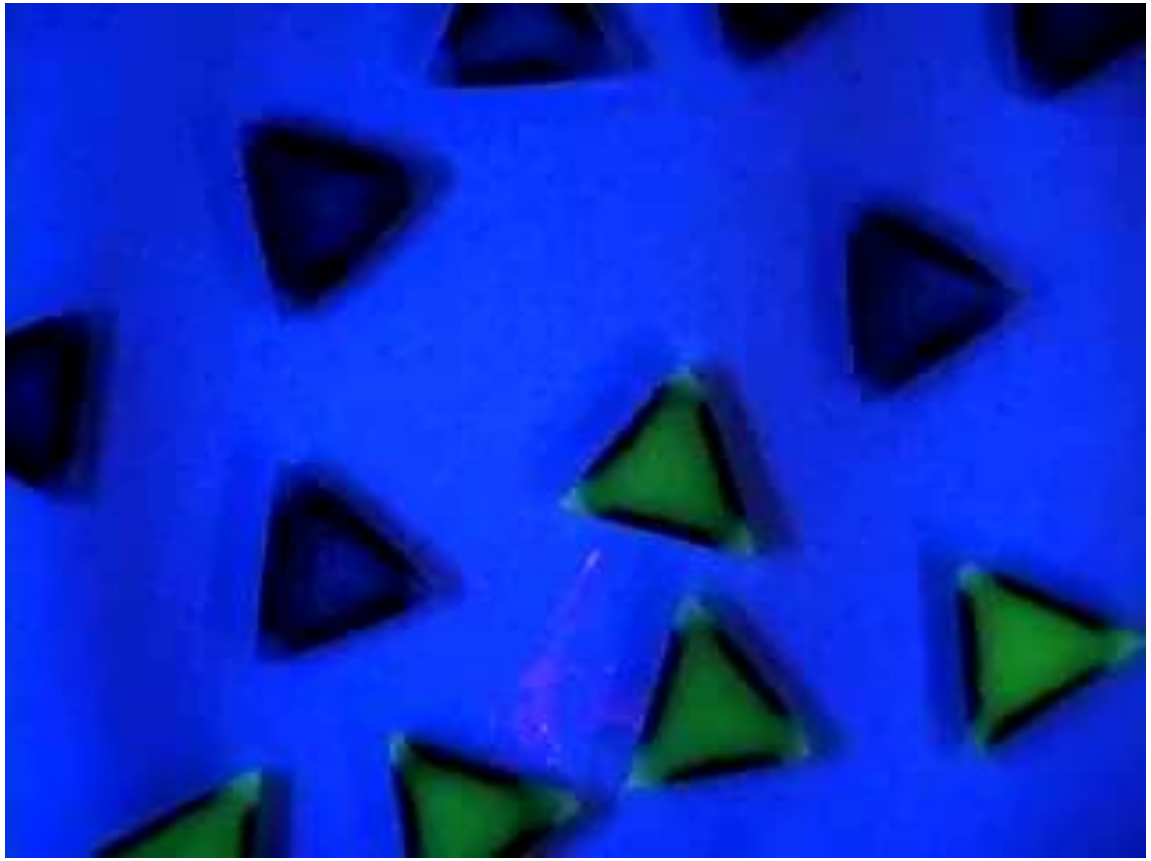


4_1 screw axes (red), 2-fold rotation axes (green), mirror planes (blue), two different types of glide planes

Accessing high length scales



Self-assembly on the macroscale



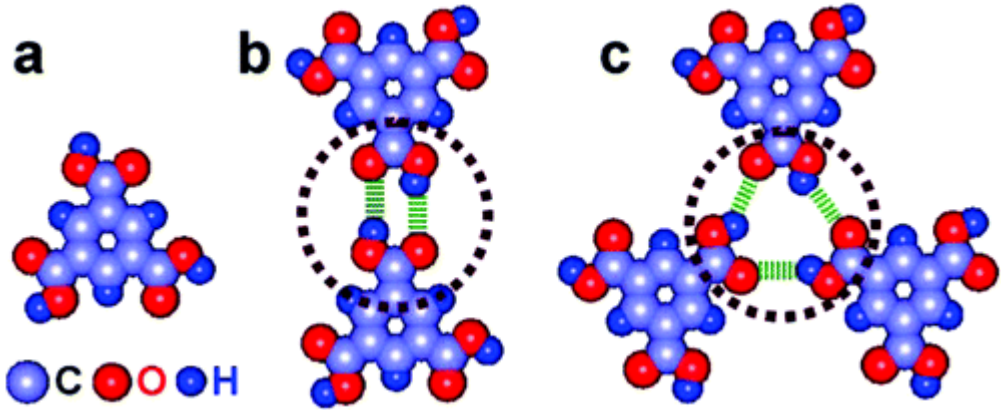
http://mrsec.wisc.edu/Edetc/background/selfassembly/index.html

Here, coloured triangles floating on water are used to illustrate self-assembly.

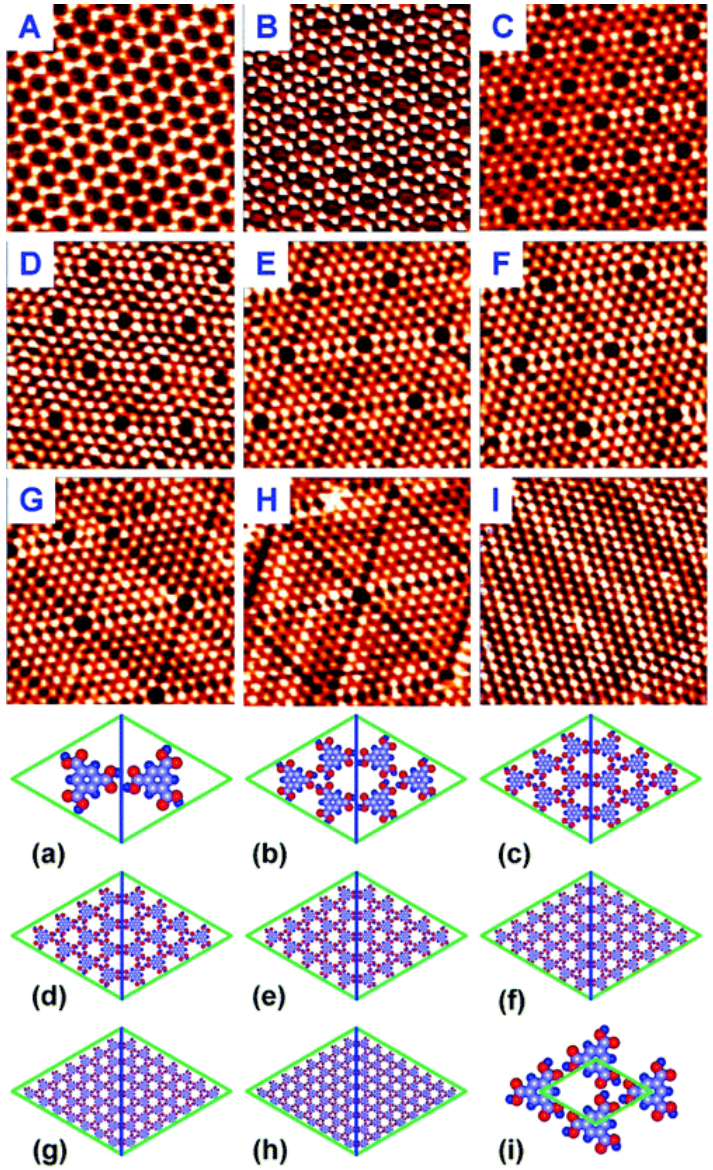
Over time as the system cools, it explores many different configurations and finds a thermodynamically stable configuration.

Molecular self-assembly

Self-Assembly of trimesic acid (1,3,5-benzenetricarboxylate) on surfaces

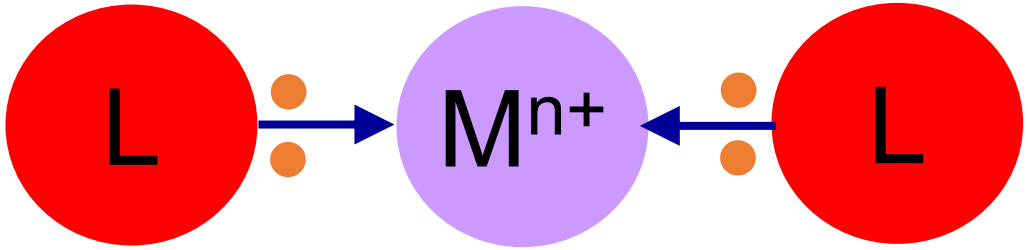


Two hydrogen bonding motifs: dimer (b) and trimer (c)

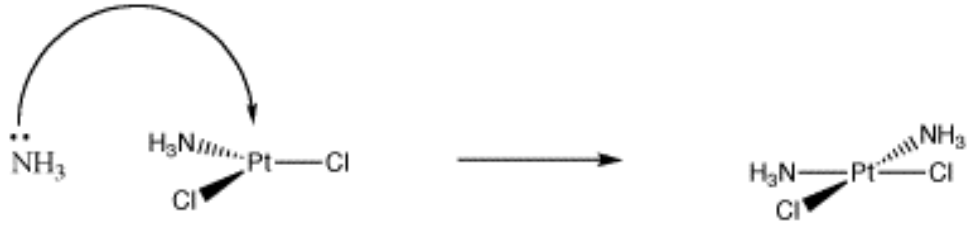


Self-assembly through the coordinate Bond

Coordinate bond formation

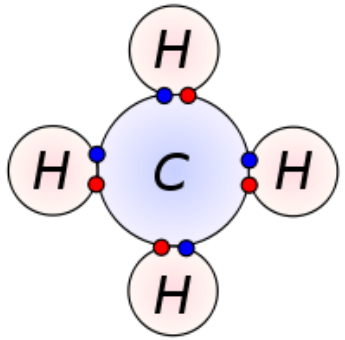


Coordinate bond



Ligand **Metal ion** **Coordination complex**

Covalent bond



Metal-Organic Frameworks (MOFs)

Two connecting ligand



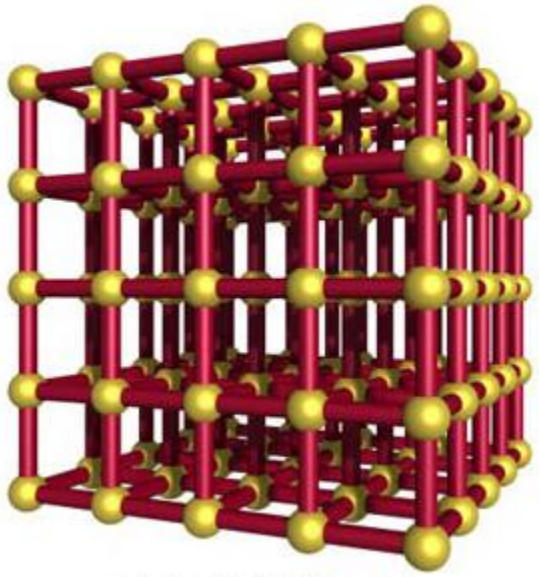
+

Six connecting **metal**

Octahedral



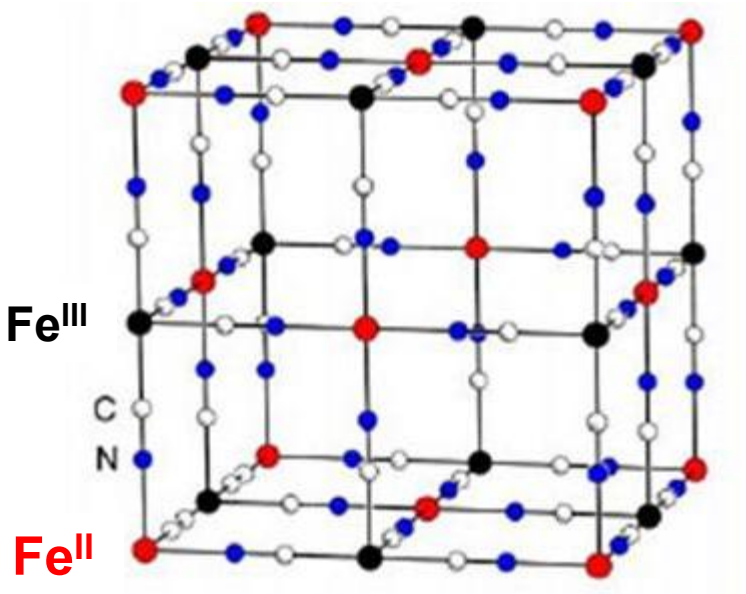
=



Cubic framework
(three-dimensional)

History

Prussian Blue (1710)



$Fe^{III}_4[Fe^{II}(CN)_6]_3$



Octahedral metal node

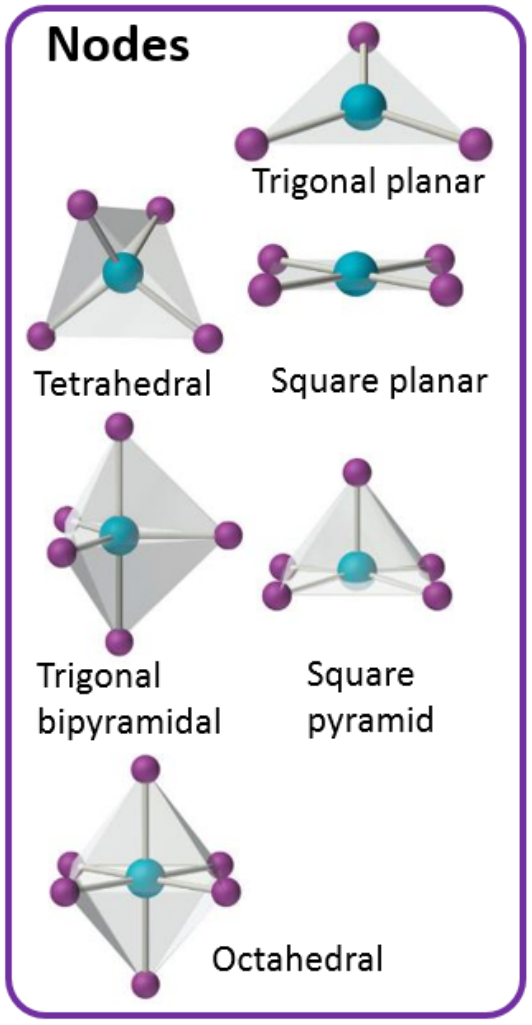
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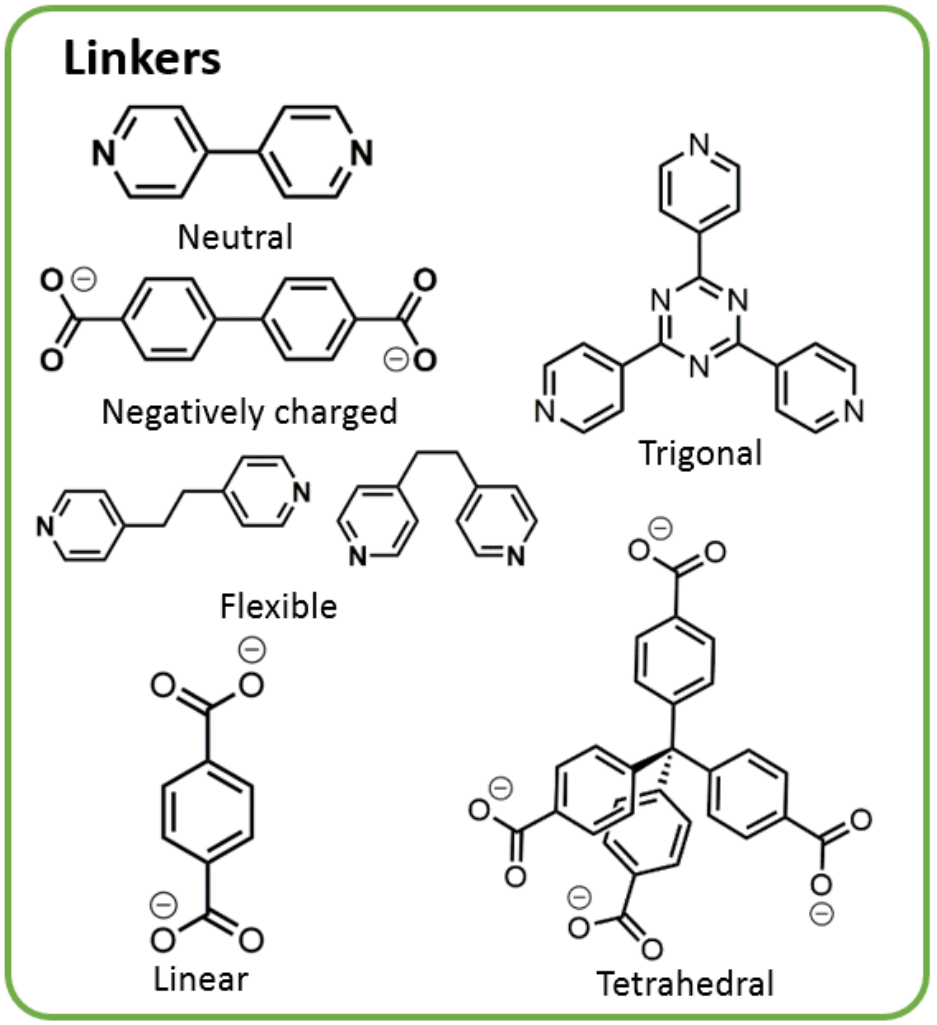
Linear CN^- linker

⬇

Coordination Framework

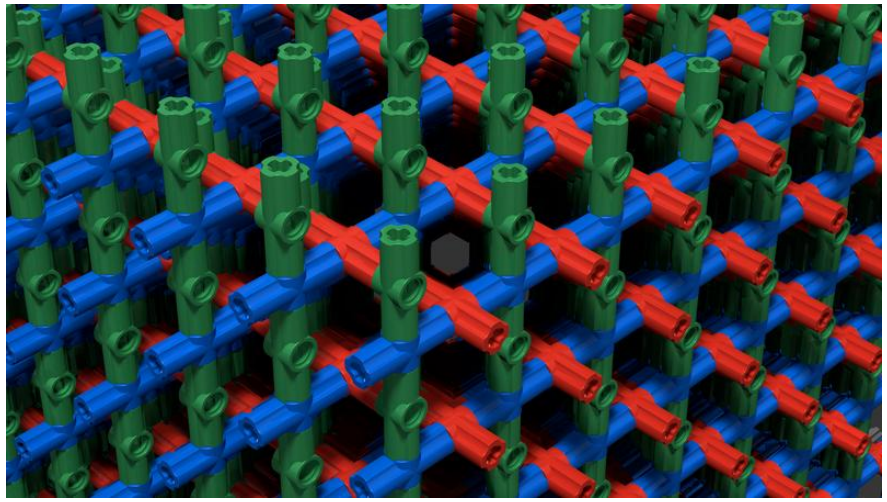
MOF formation: ‘nodes + linkers’

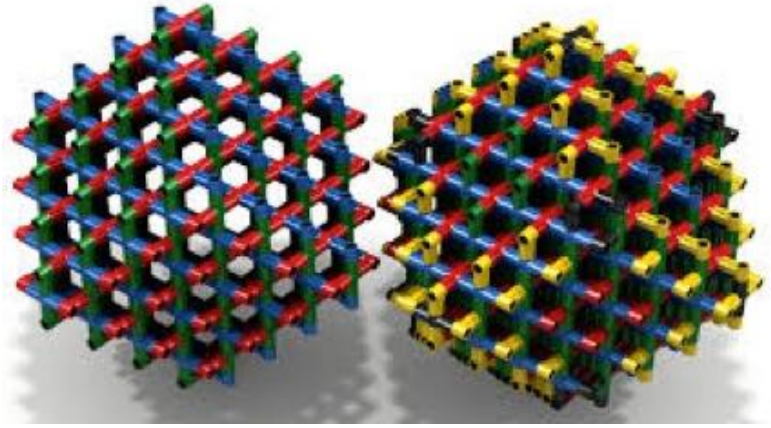


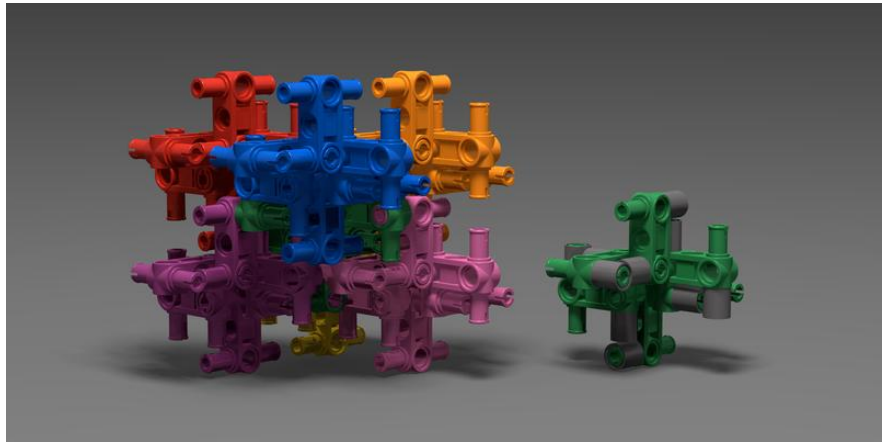


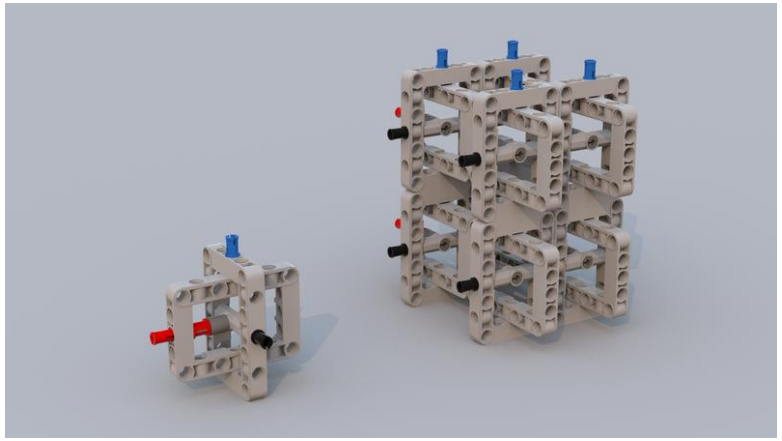
- Factors to consider
  - Metal coordination
  - Ligand coordination
  - Ligand charge
  - Ligand flexibility
  - Ligand sterics
- And…
  - Synthetic conditions (solvent, temperature)
  - Counter ions
  - Mixed ligand systems
  - Other ligand interactions

‘Molecular LEGO’



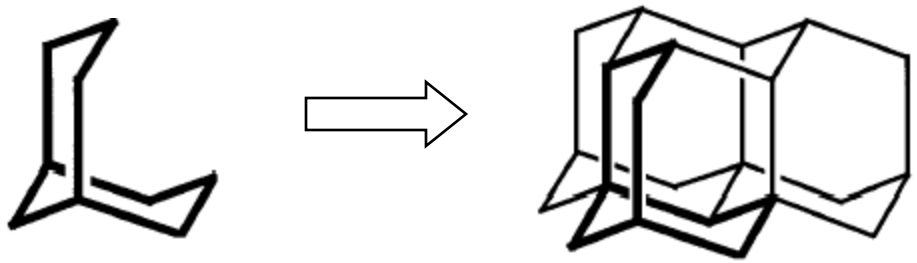






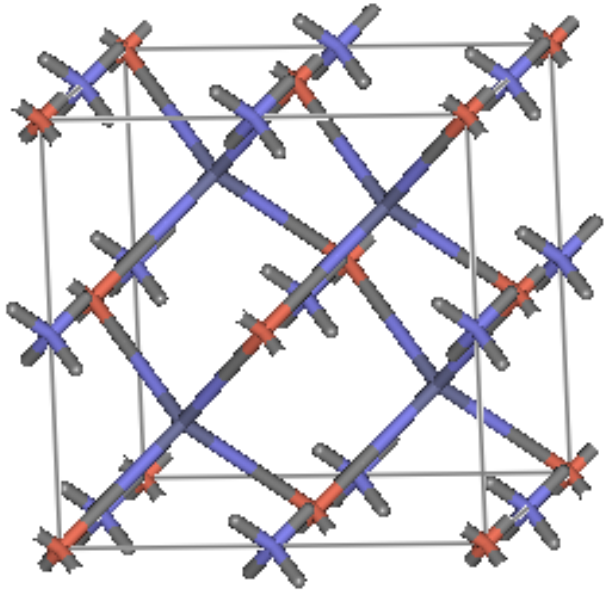
Design and construction ("crystal engineering")

Diamond structure built from tetrahedral centres



Robson (1990) - generated the first family of compounds where it was possible to reliably predict the structures before the crystals were actually made.

$$Cu^{I} + [Zn^{II}(CN)_4]^{2-} + N(CH_3)_4^{+} \Longrightarrow$$

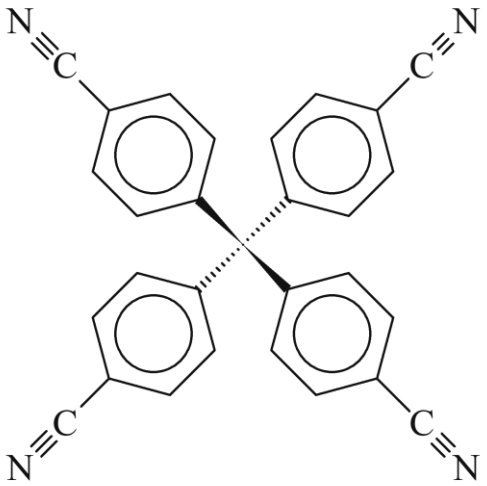


J. Am. Chem. Soc. 1990, 112, 4, 1546–1554

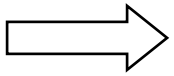
Design and construction ("crystal engineering")

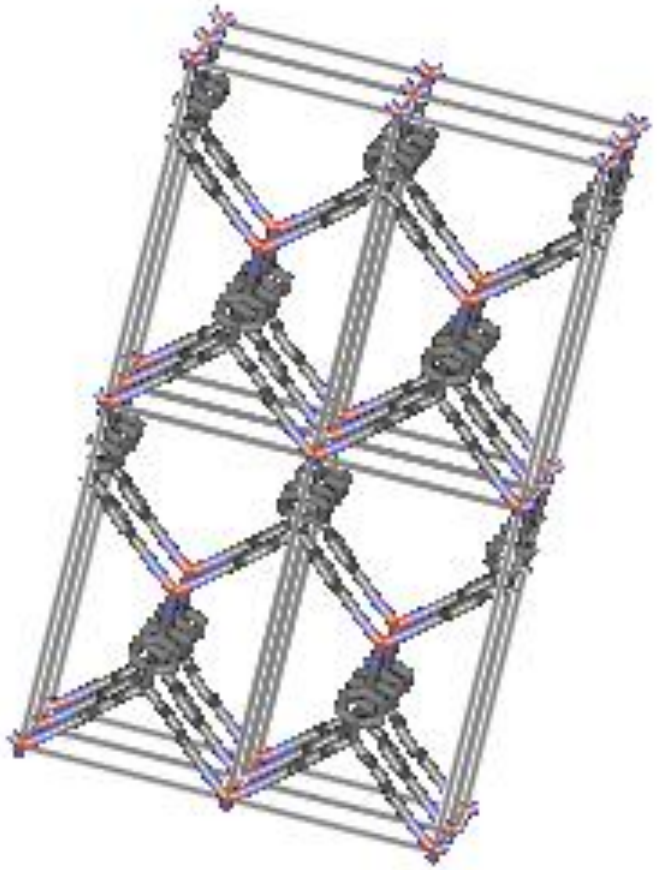
Robson (1990) - expanded diamond-type frameworks using larger tetrahedral building units

Cu^{I} +



Ligand with a central carbon (tetrahedral) and benzonitrile "arms"

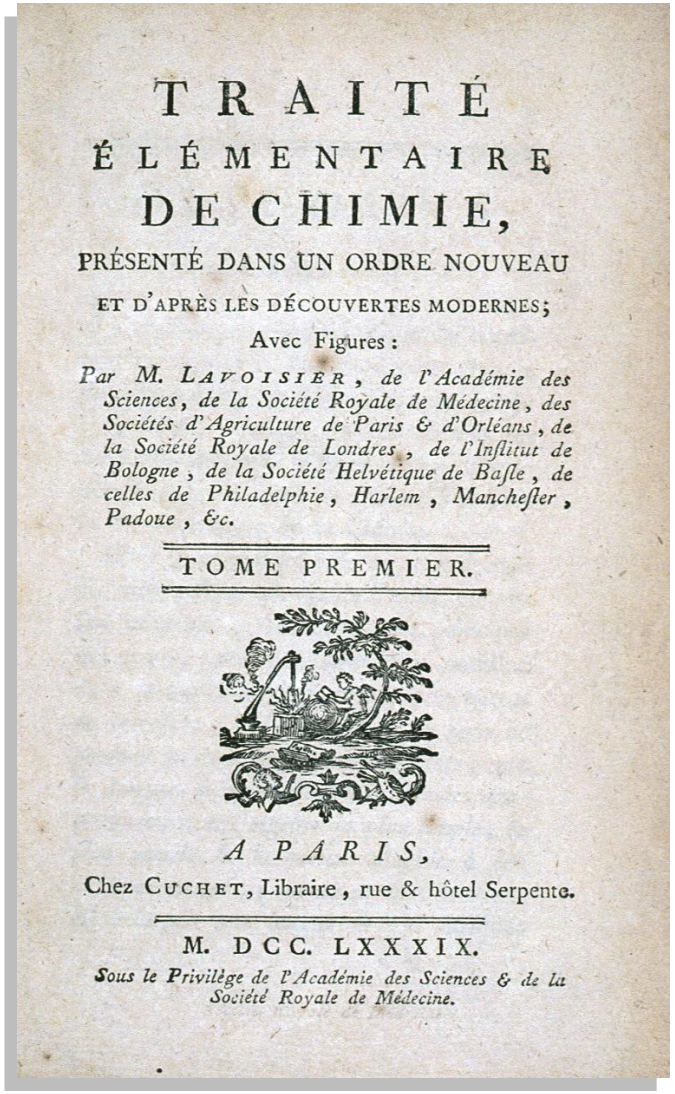




Void regions are filled with anions and solvent of crystallisation ⇒ opportunity for host-guest chemistry

J. Am. Chem. Soc. 1990, 112, 4, 1546–1554

Thermal expansion



TRAITÉ
ÉLÉMENTAIRE
DE CHIMIE,
PRÉSENTÉ DANS UN ORDRE NOUVEAU
ET D'APRÈS LES DÉCOUVERTES MODERNES;
Avec Figures :
Par M. LAVOISIER, de l'Académie des Sciences, de la Société Royale de Médecine, des Sociétés d'Agriculture de Paris & d'Orléans, de la Société Royale de Londres, de l'Inſtitut de Bologne, de la Société Helvétique de Baſle, de celles de Philadelphie, Harlem, Manchester, Padoue, &c.
TOME PREMIER.
A PARIS,
Chez CUCHET, Libraire, rue & hôtel Serpente.
M. DCC. LXXXIX.
Sous le Privilège de l'Académie des Sciences & de la Société Royale de Médecine.



Lavoisier, 1789

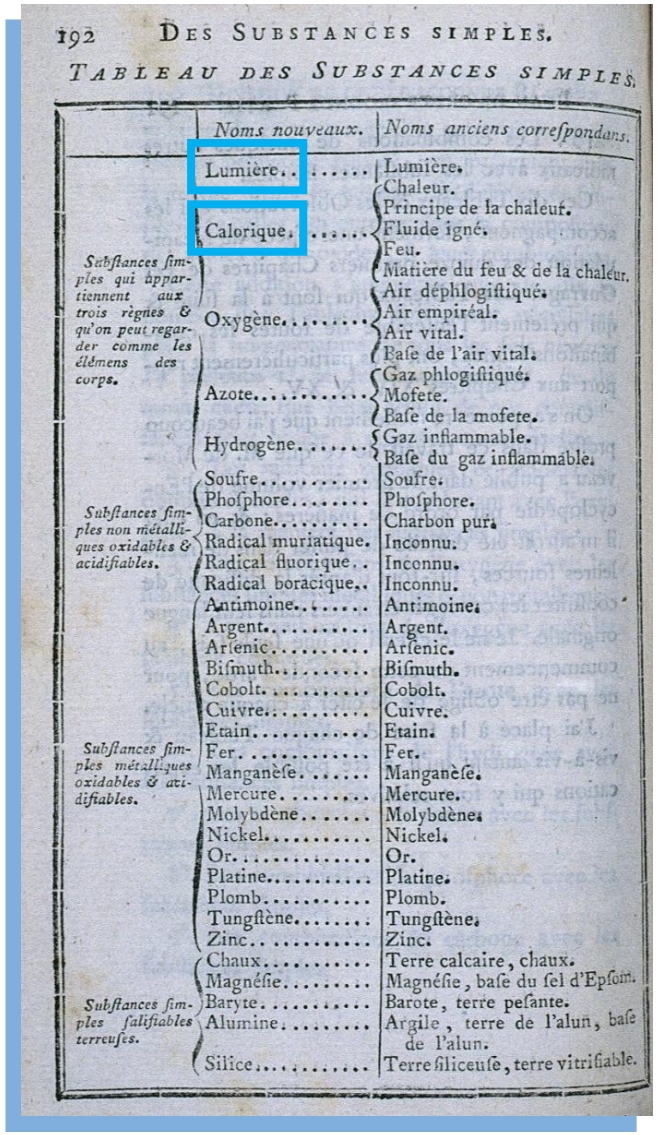
"It is a universal phenomenon in nature, of which the generality has been well established… that any material whatsoever, solid or fluid, increases in size in each dimension when heated. Any claims that this principle is of limited generality are based on arguments which lead only to fallacious results …"

Mechanism of thermal expansion

Lavoisier thought that light (lumiere) and heat (calorique) were substances and that heat got into materials and pushed it outwards.

Lavoisier, 1789

"It is difficult to comprehend these phenomena without conceding that they are the effect of a real and material substance, a particularly pervasive fluid, which insinuates itself between the particles of bodies and thus separates them."



192 DES SUBSTANCES SIMPLES.

TABLEAU DES SUBSTANCES SIMPLES.

	Noms nouveaux.	Noms anciens correſpondans.
	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Mofete. Baſe de la mofete.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobolt	Cobolt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtène.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'Epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

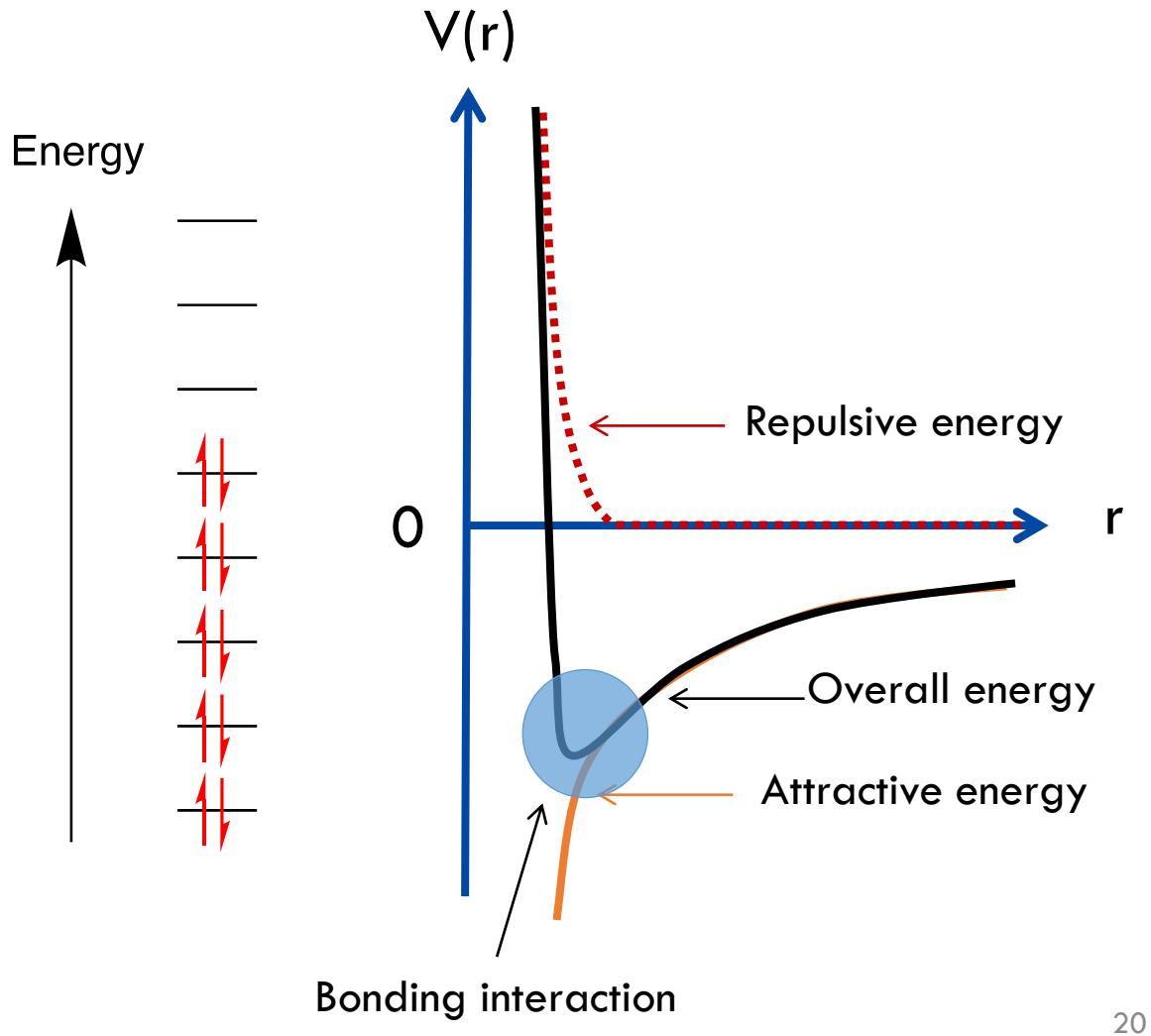
https://phet.colorado.edu/sims/html/states-of-matter/latest/states-of-matter_en.html

Bonding: Potential Energy Curves

Pauli Exclusion Principle

No two electrons in an atom may be in the same quantum state.

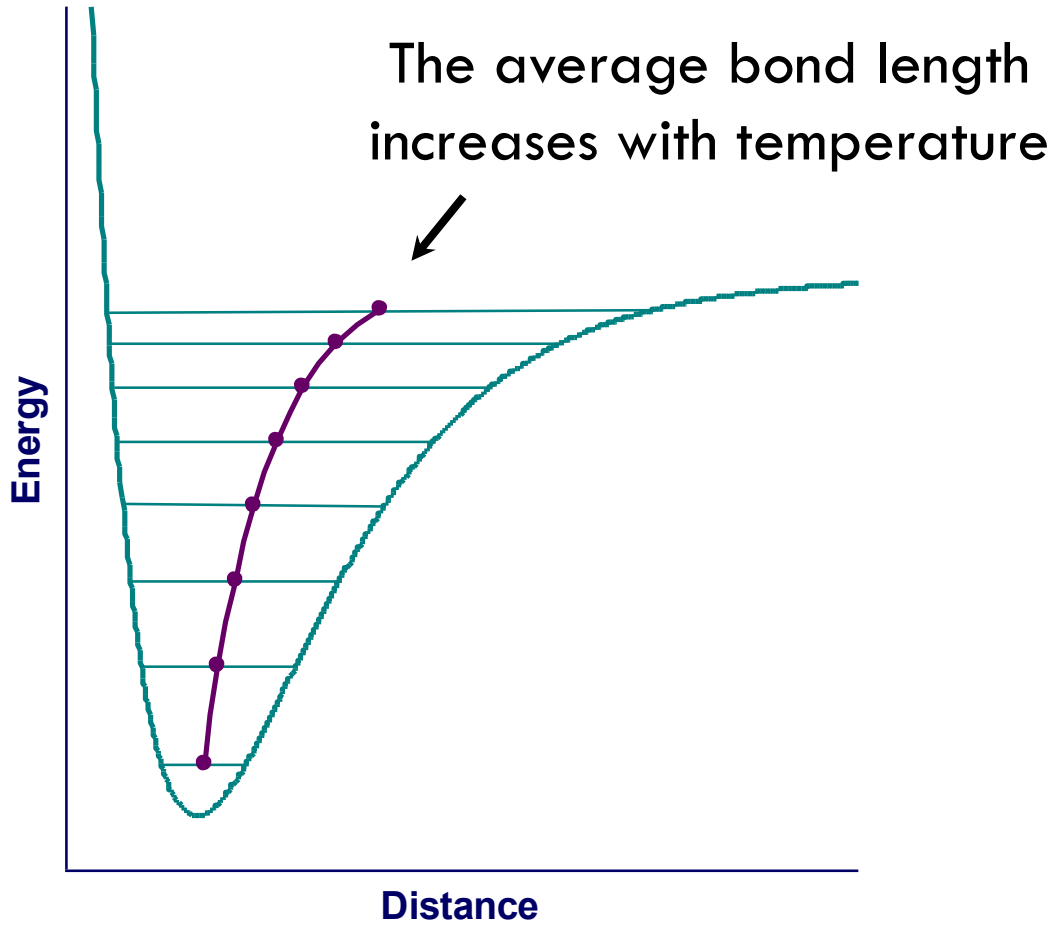
- No two electrons can have same four quantum numbers, *n*, *l*, *m*, and s.
- No orbital (specified by *n*, *l*, *m*) can be occupied by more than two electrons.



Mechanism of thermal expansion

As temperature is raised:

- The atoms have more thermal energy.
- The amplitude of the longitudinal vibrations (i.e., the vibrations running along the length of the bond) increases.
- The asymmetric nature of the potential well means that the average inter-atomic spacing (bond length) increases.



Coefficient of thermal expansion

The **coefficient of thermal expansion,** α , is the relative change in linear dimensions, per unit of temperature change.

Volumetric expansion:

$$\alpha_V = \frac{1}{V}\left(\frac{dV}{dT}\right)$$

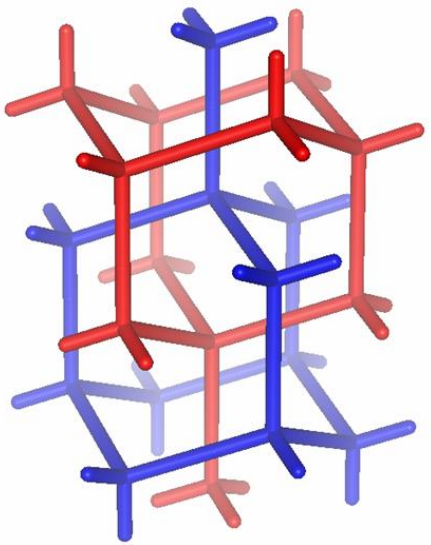
Linear expansion:

$$\alpha_l = \frac{1}{l}\left(\frac{dl}{dT}\right)$$

Material	α_l /10^{-6} K^{-1} at 20 °C
Mercury	60
Lead	29
Aluminium	23
Brass	19
Stainless steel	17
Copper	17
Gold	14
Nickel	13
Concrete	12
Steel	12
Platinum	9
Glass	8
GaAs	6
Indium phosphide	5
Pyrex	3
Silicon	3
Diamond	1

Negative Thermal Expansion (NTE) in MOFs

$M(CN)_2$ family

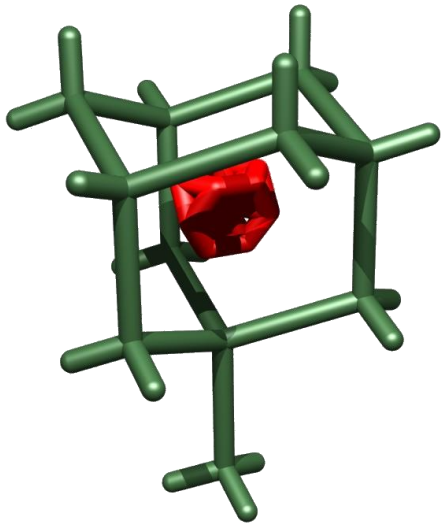


$M^{II}(CN)_2$

– two networks

– neutral framework

– no guests

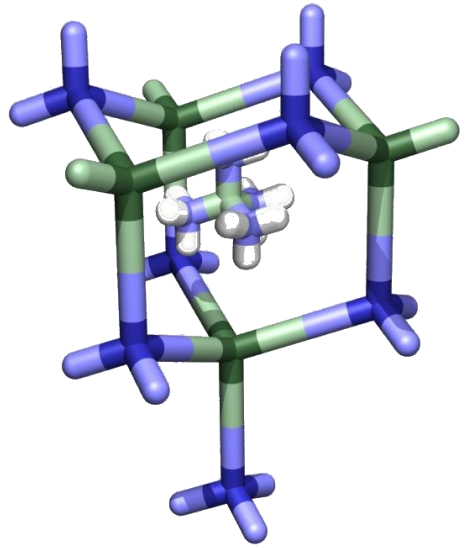


$Cd^{II}(CN)_2 \cdot G$

– single porous network

– neutral framework

– guest molecules



$N(CH_3)_4Cu^{I}Zn^{II}(CN)_4$

– single network

– anionic framework

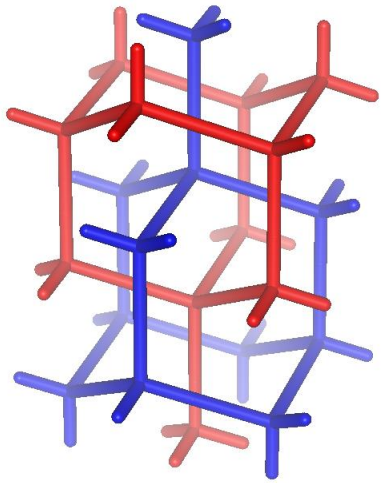
– $N(CH_3)_4^+$ cations in pores

Phys. Rev. B, 71, 140301 (2005).

Negative Thermal Expansion (NTE) in MOFs

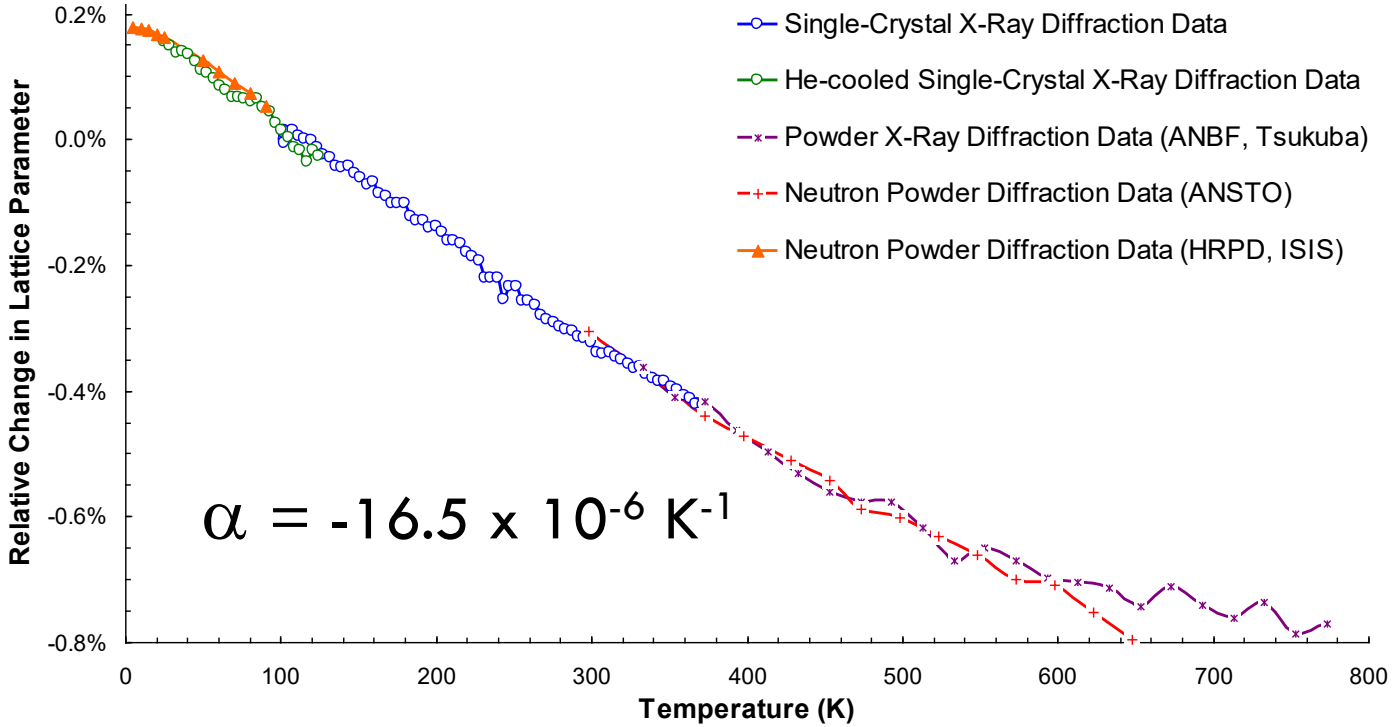
Example 1: Zinc cyanide

With increasing temperature, this material shows a contraction in the lattice parameter, characteristic of NTE behaviour.



$Zn(CN)_2$

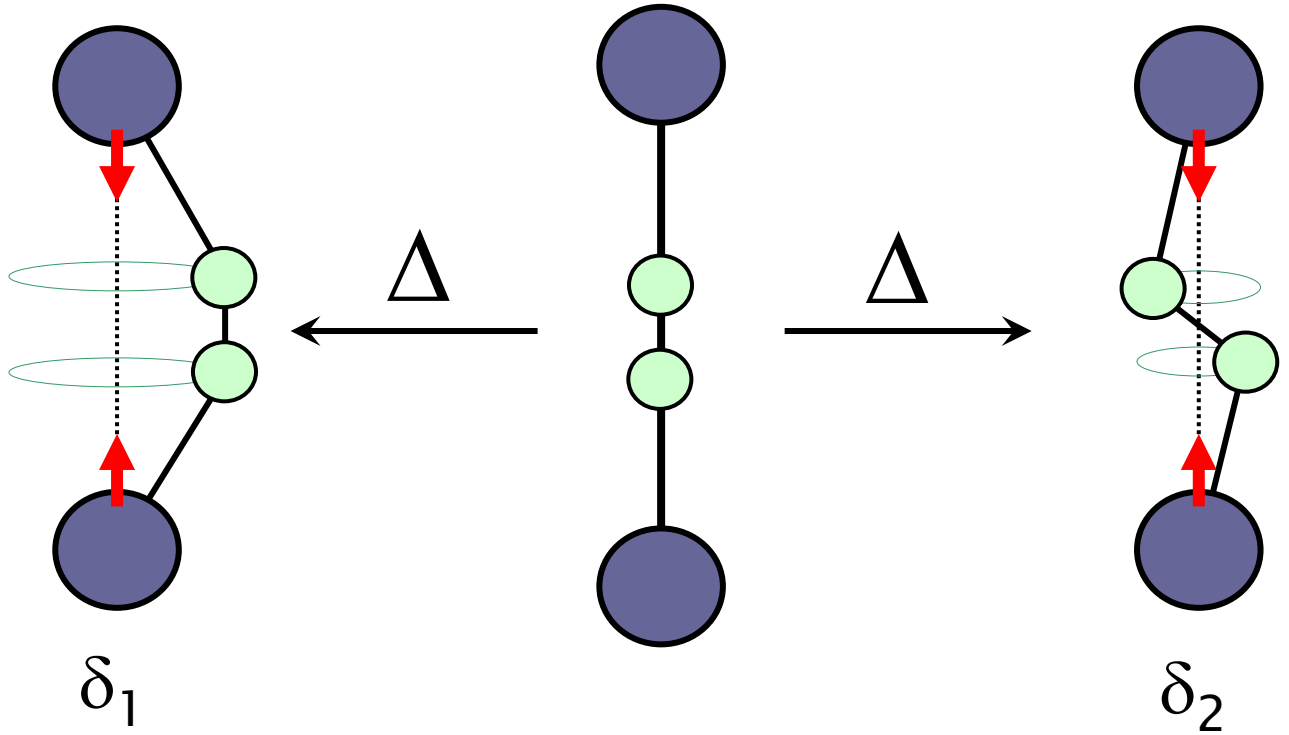
Unit cell lattice parameter vs. temperature measured using several diffraction techniques



Mechanism for NTE

While longitudinal vibrations make the bond lengths increase, other types of vibrations lead to a **decrease** in the distance between atoms with **increasing** temperature.

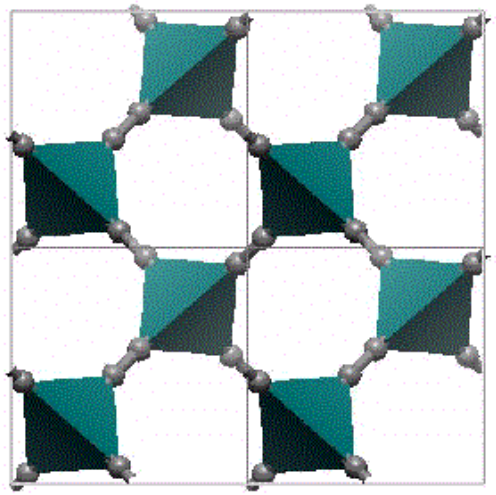
Low energy transverse (at a 90° angle) **vibrational modes**



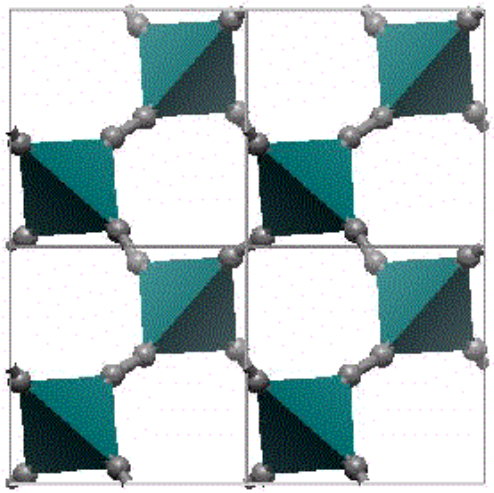
Phys. Rev. B, 71, 140301 (2005).

Mechanism for NTE

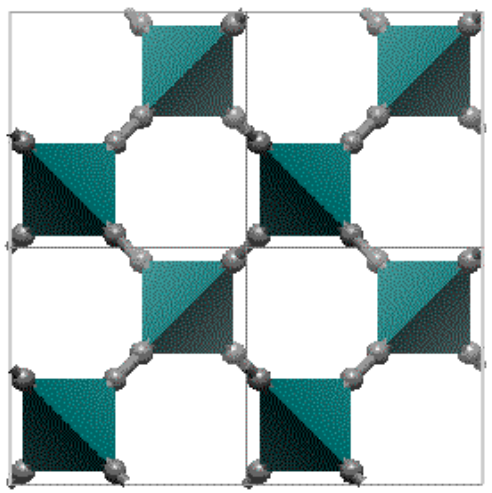
Low energy transverse vibrational modes in a crystal (phonons)



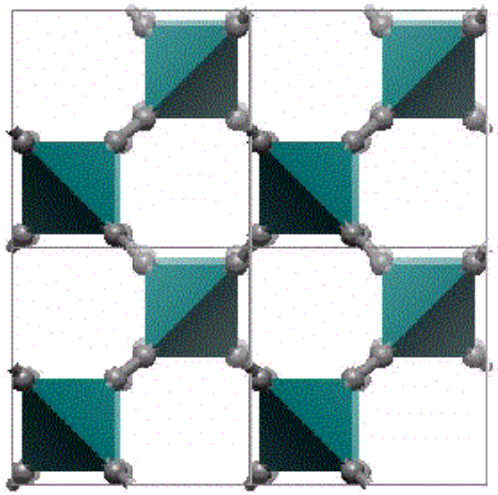
δ_1



δ_2



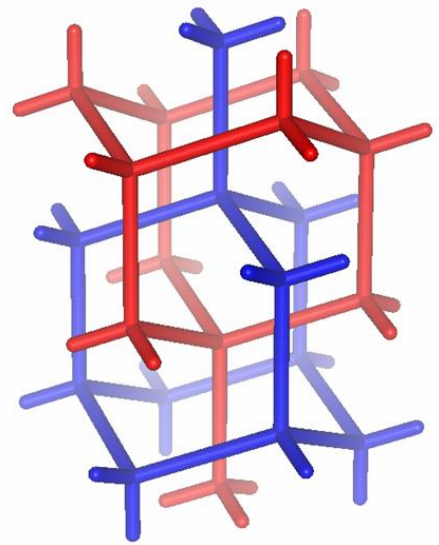
δ_1/δ_2



T

Negative Thermal Expansion (NTE) in MOFs

$M(CN)_2$ family

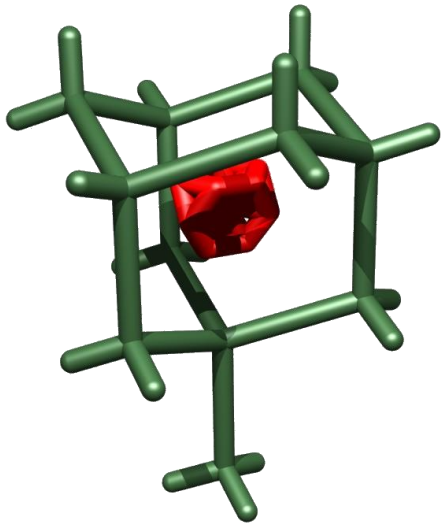


$M^{II}(CN)_2$

– two networks

– neutral framework

– no guests

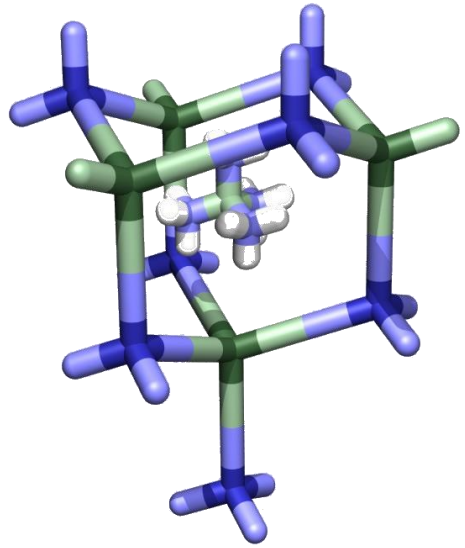


$Cd^{II}(CN)_2 \cdot G$

– single porous network

– neutral framework

– guest molecules



$N(CH_3)_4Cu^{I}Zn^{II}(CN)_4$

– single network

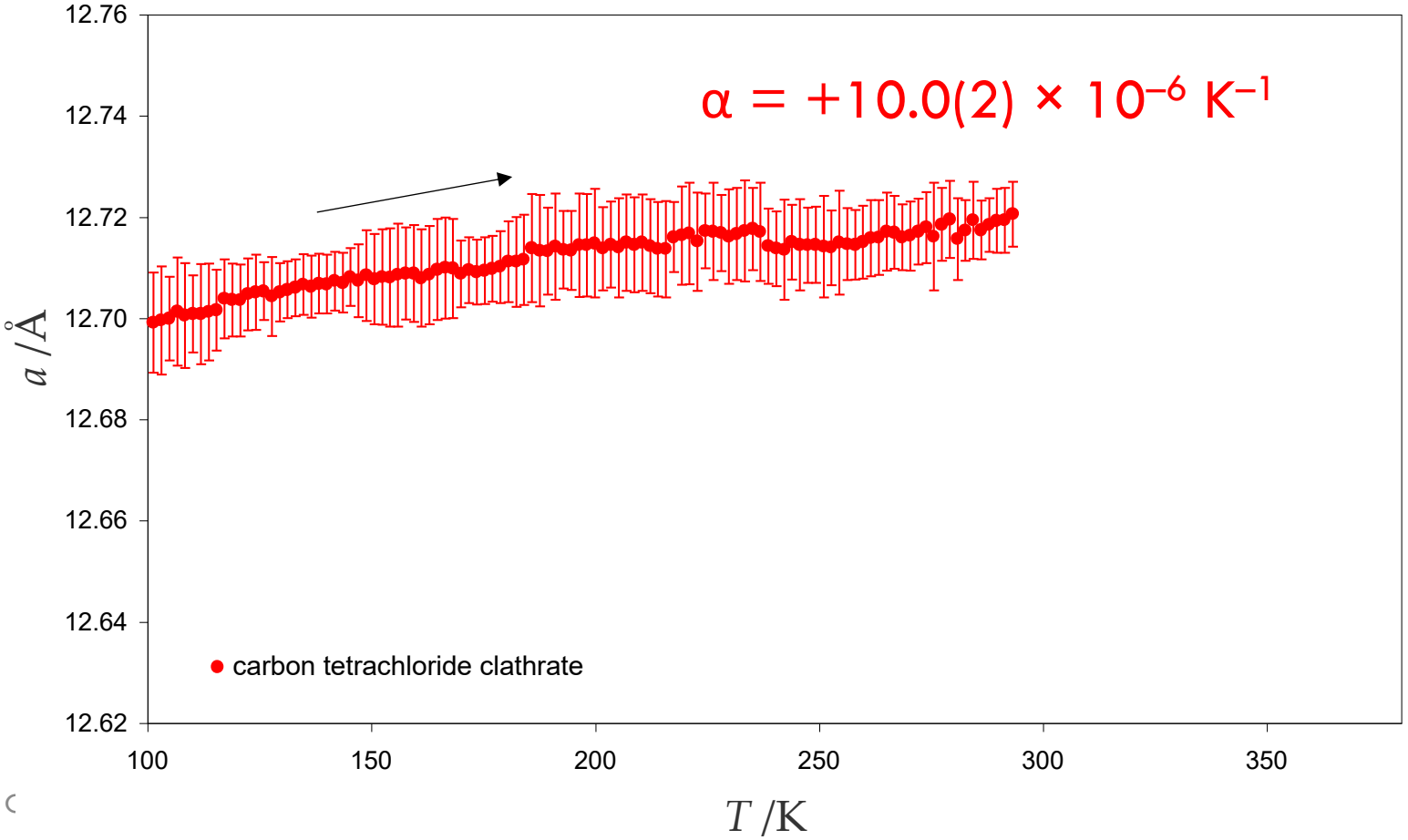
– anionic framework

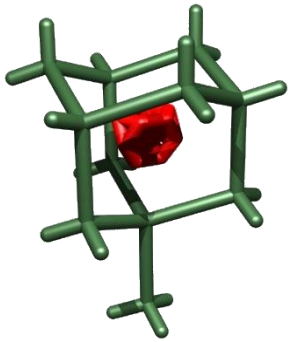
– $N(CH_3)_4^+$ cations in pores

Angew. Chem. Int. Ed., **47**, 1396 (2008).

NTE in MOFs: the $M(CN)_2$ family

Example 2: Cadmium cyanide with a carbon tetrachloride clathrate guest molecule in the cavity





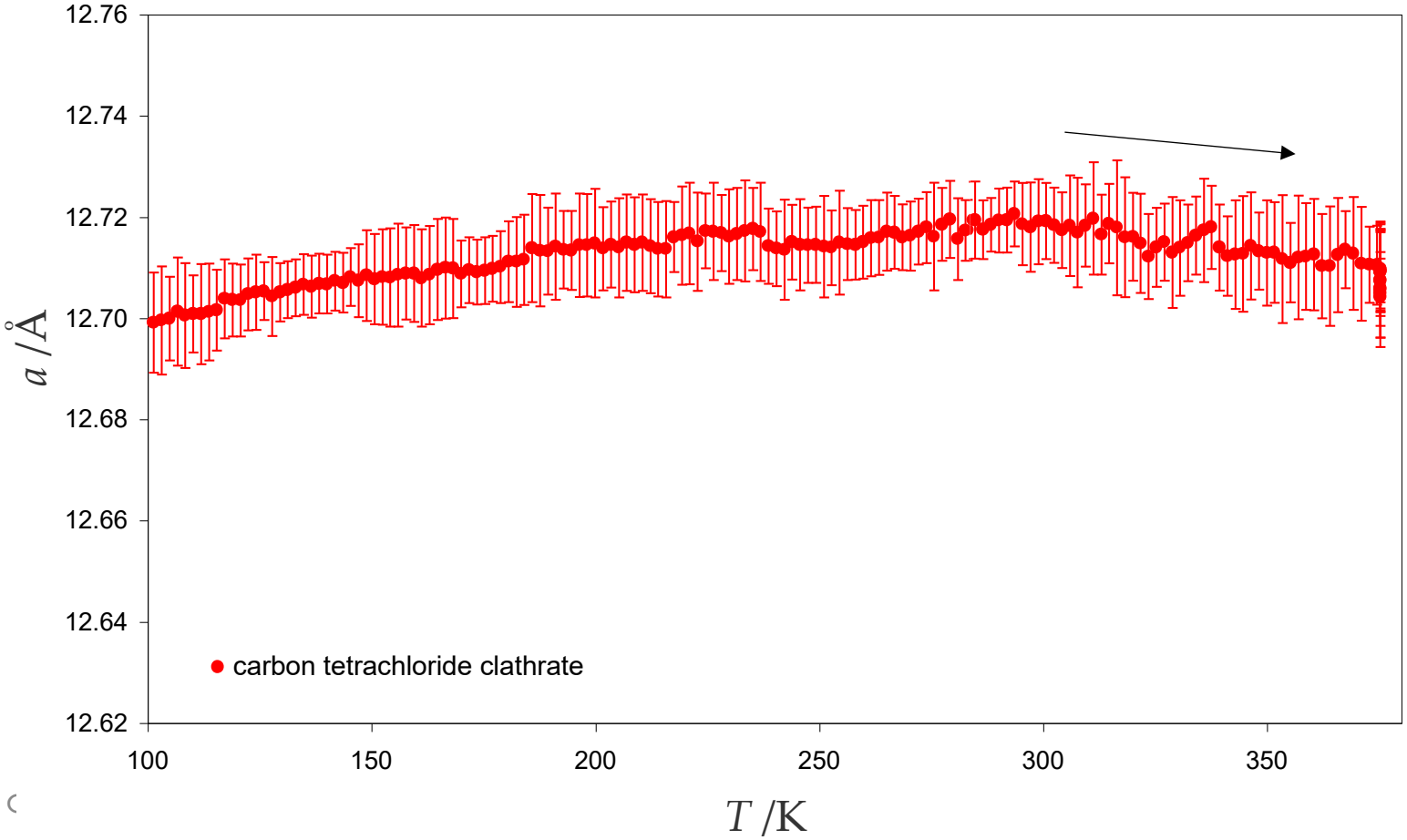
$Cd(CN)_2 \cdot G$

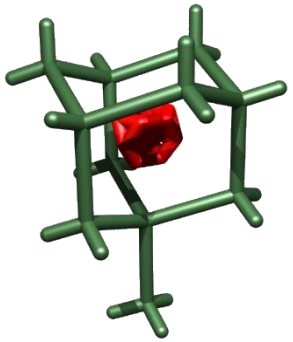
As temperature increase the lattice parameter increases, exhibiting thermal expansion behaviour.

Angew. Chem. Int. Ed., **47**, 1396 (2008).

NTE in MOFs: the $M(CN)_2$ family

Example 2: Cadmium cyanide with a carbon tetrachloride clathrate guest molecule in the cavity





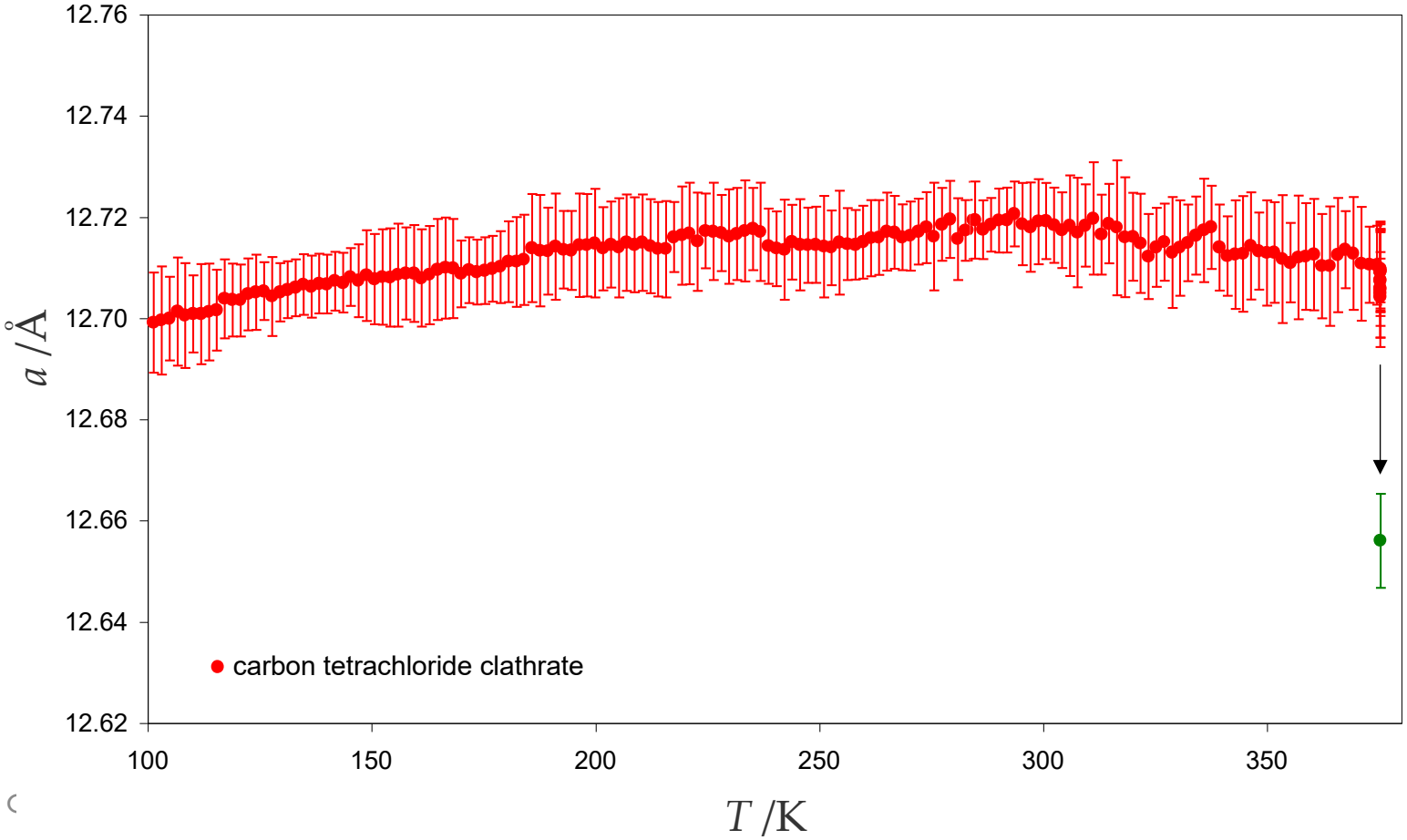
$Cd(CN)_2 \cdot G$

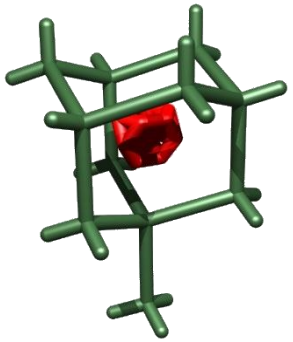
The lattice parameter starts to decrease slightly as the guest solvent molecule starts to evaporate, leaving the structure.

Angew. Chem. Int. Ed., **47**, 1396 (2008).

NTE in MOFs: the $M(CN)_2$ family

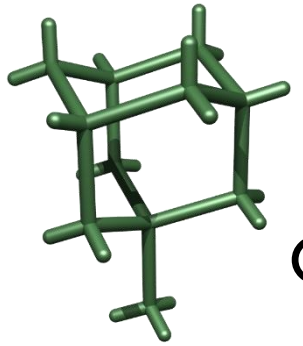
Example 2: Cadmium cyanide with a carbon tetrachloride clathrate guest molecule in the cavity





$Cd(CN)_2 \cdot G$

An abrupt lattice parameter collapse is seen at ~100 °C when all the solvent is removed.

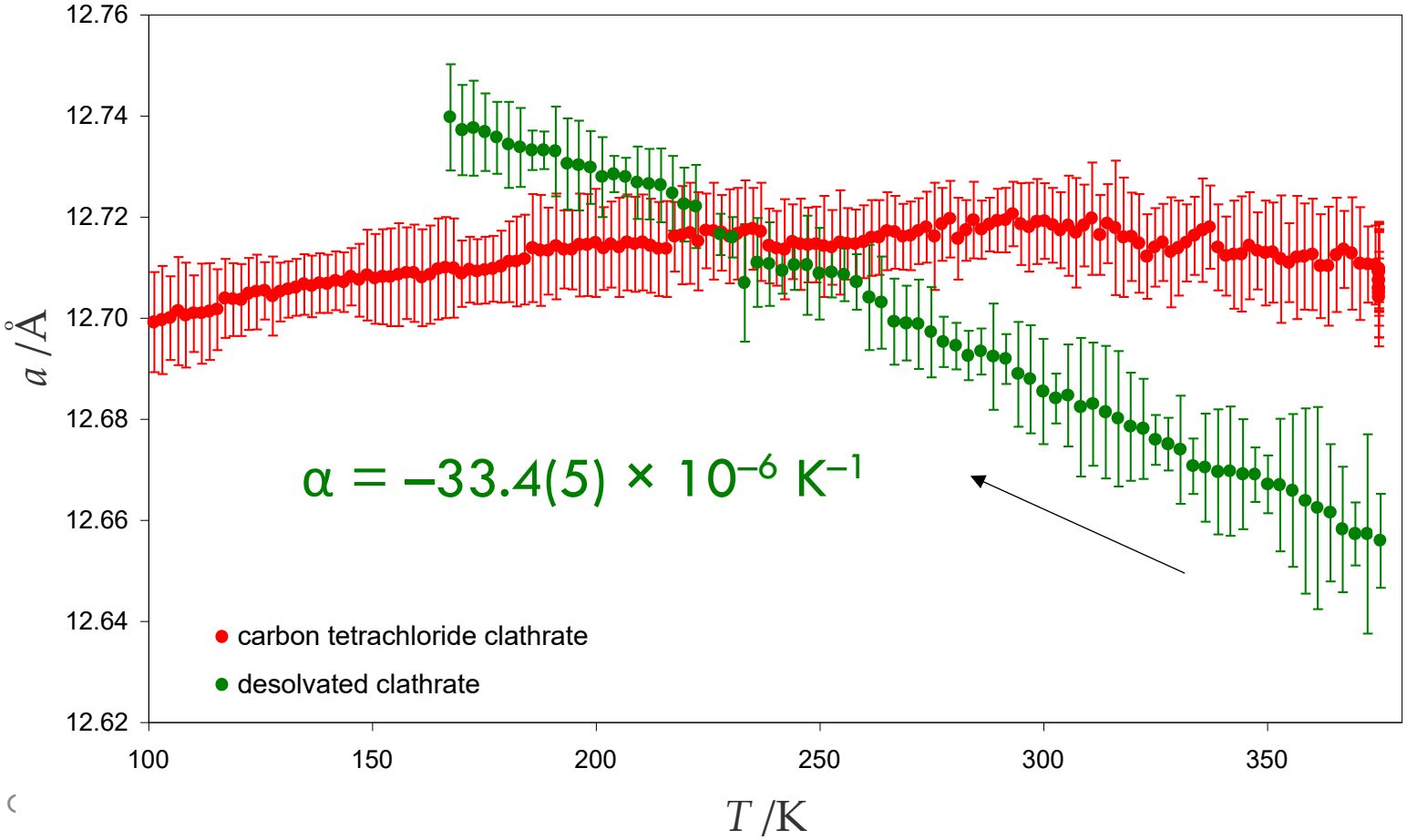


$Cd(CN)_2$

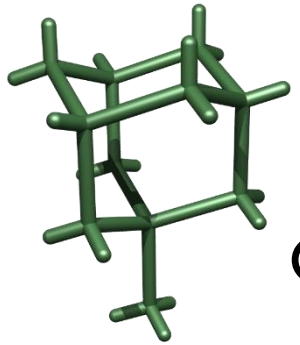
Angew. Chem. Int. Ed., **47**, 1396 (2008).

NTE in MOFs: the $M(CN)_2$ family

Example 2: Cadmium cyanide with a carbon tetrachloride clathrate guest molecule in the cavity



On cooling, the lattice parameter of the desolvated material expands, exhibiting NTE behaviour.

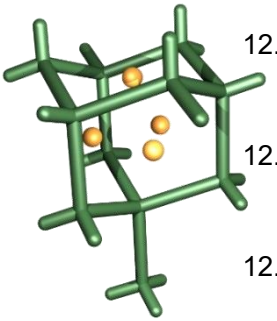


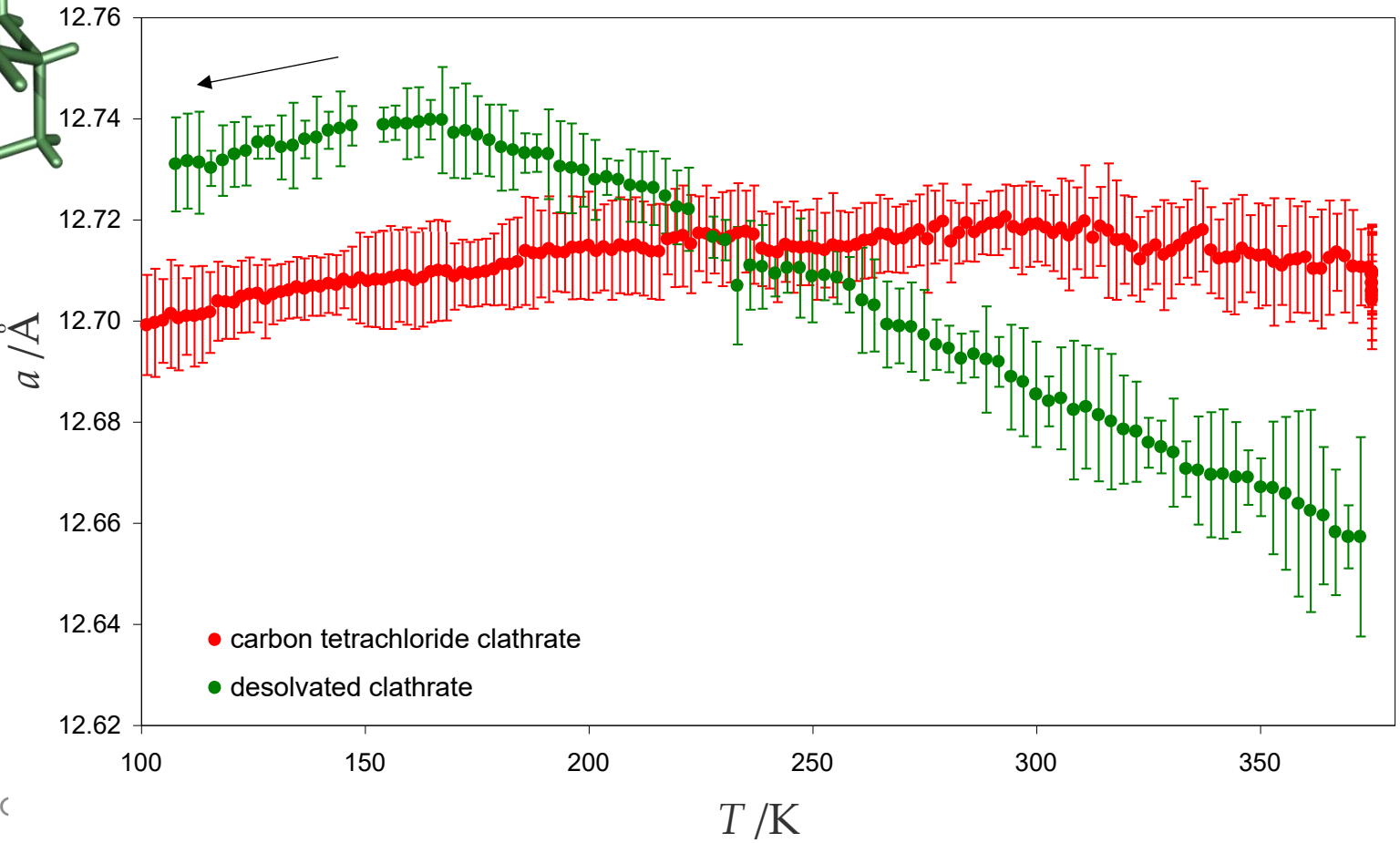
$Cd(CN)_2$

Angew. Chem. Int. Ed., **47**, 1396 (2008).

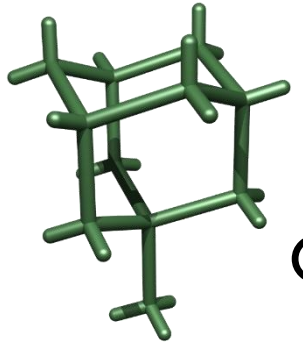
NTE in MOFs: the $M(CN)_2$ family

Example 2: Cadmium cyanide with a carbon tetrachloride clathrate guest molecule in the cavity





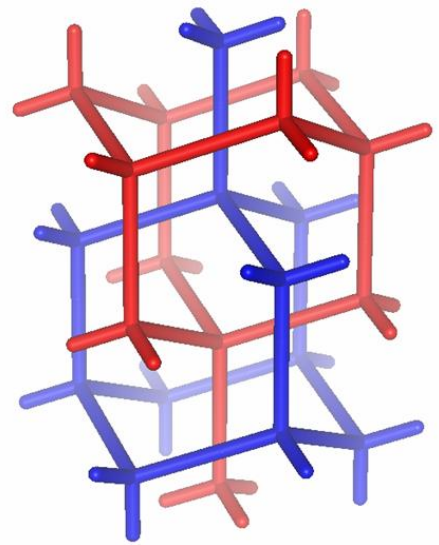
At low temperatures, air molecules condense in the pores, and the material again exhibits thermal expansion behaviour.



$Cd(CN)_2$

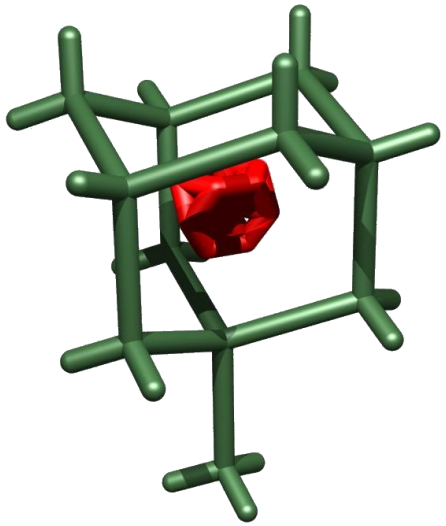
Negative Thermal Expansion (NTE) in MOFs

$M(CN)_2$ family



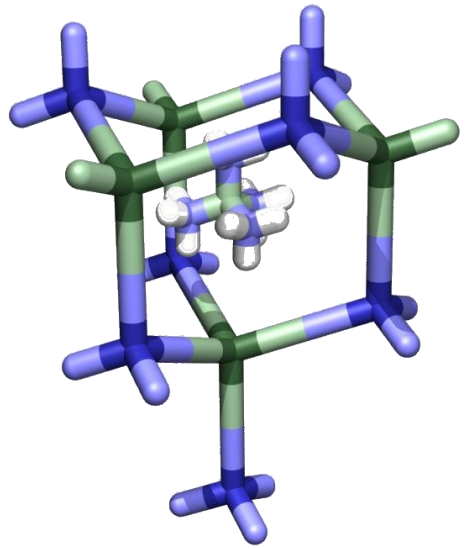
$M^{II}(CN)_2$

– two networks
– neutral framework
– no guests



$Cd^{II}(CN)_2 \cdot G$

– single porous network
– neutral framework
– guest molecules



$N(CH_3)_4Cu^{I}Zn^{II}(CN)_4$

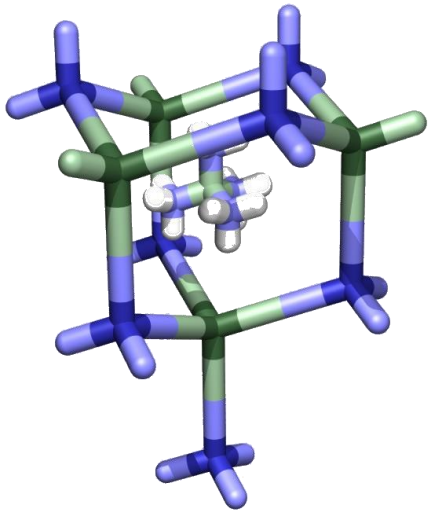
– single network
– anionic framework
– $N(CH_3)_4^+$ cations in pores

J. Am. Chem. Soc., **132**, 10 (2010).

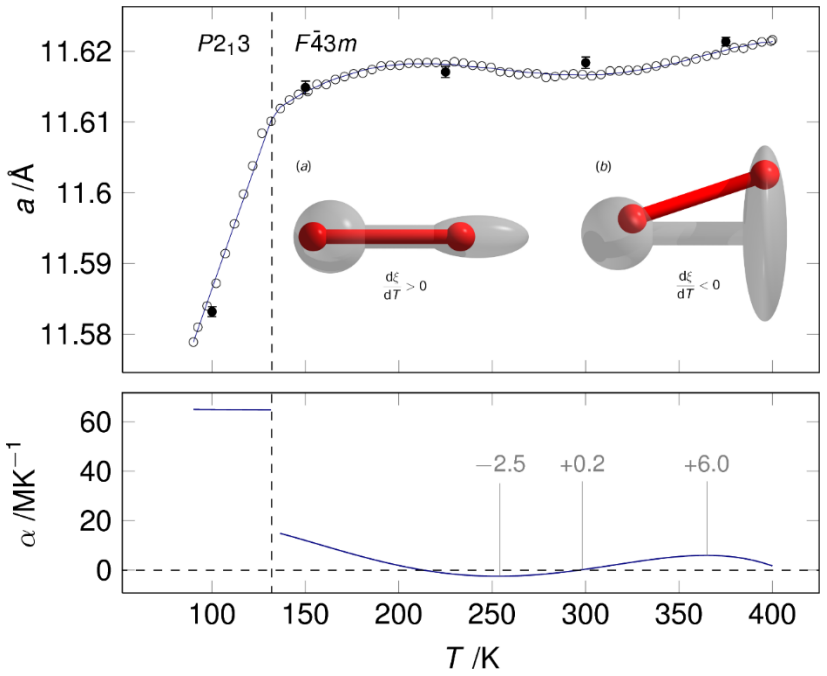
NTE in MOFs: the $M(CN)_2$ family

Example 3: Tetramethylammonium copper(I) zinc(II) cyanide

Between 200–400 K, this material shows an almost constant lattice parameter, termed zero thermal expansion, due to two competing effects.



$N(CH_3)_4CuZn(CN)_4$



As temperature increases:

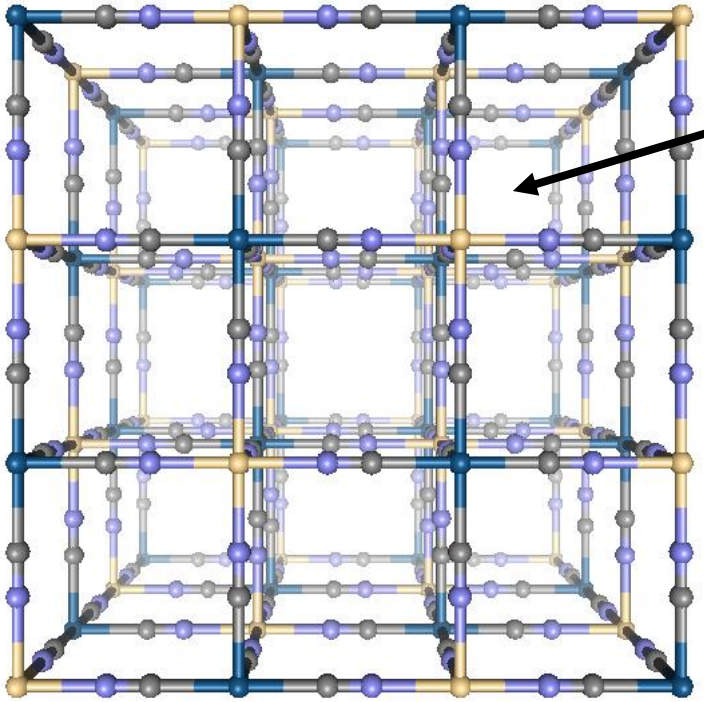
- The framework undergoes the transverse vibrational modes that (typically) lead to contraction.
- The cation vibrates and rotates more, occupying more space, and expanding the framework.

J. Am. Chem. Soc., 127, 17980 (2005); J. Am. Chem. Soc., 128, 7009 (2006).

Negative Thermal Expansion (NTE) in MOFs

$M^{II}Pt^{IV}(CN)_6$ family

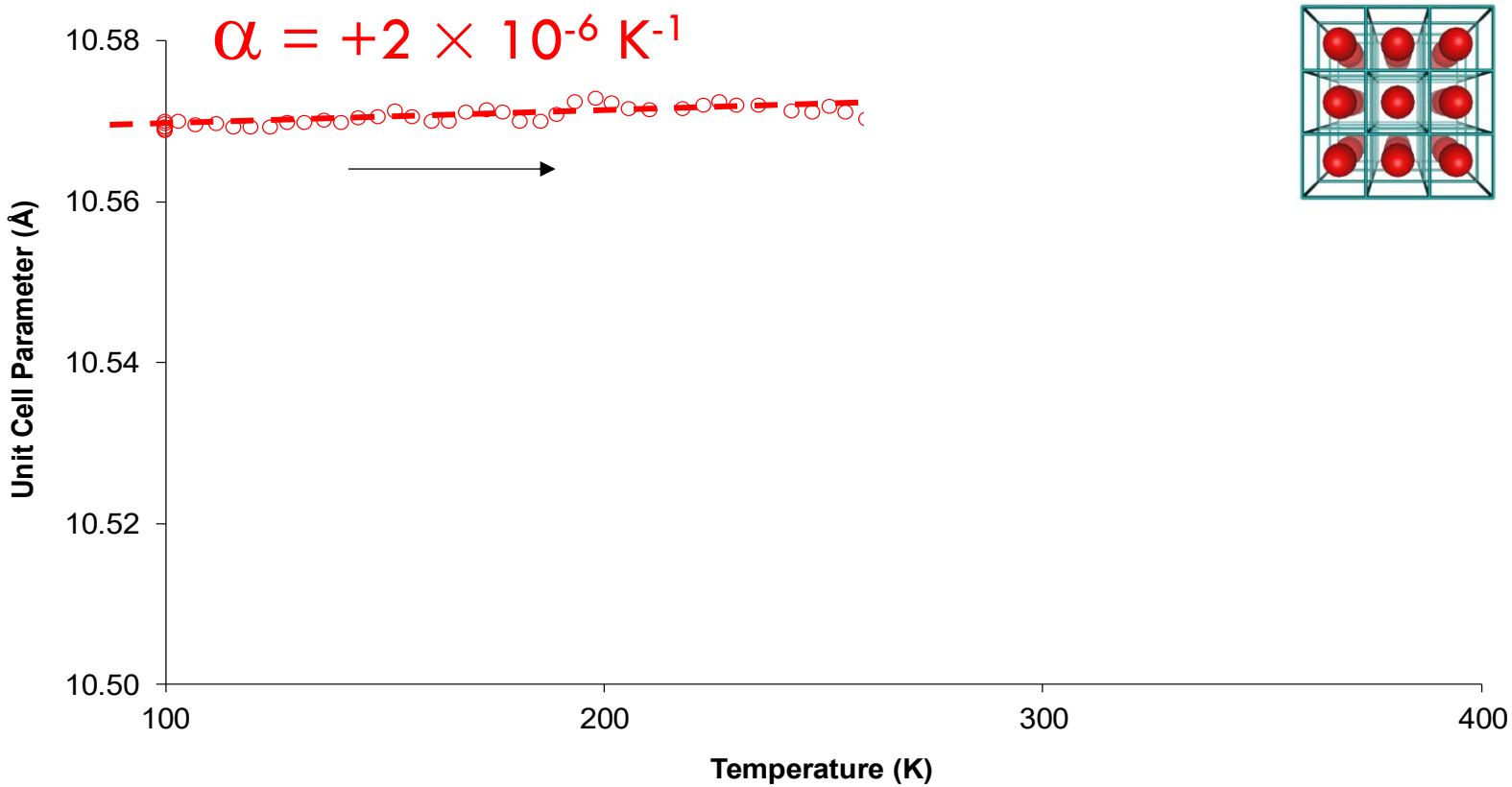
Prussian blue type compounds with octahedral metal centres with linear cyanide linkers



J. Am. Chem. Soc., 127, 17980 (2005).

NTE in MOFs: $Zn^{II}Pt^{IV}(CN)_6 \cdot xH_2O$

These materials are synthesised with water in the cubic holes. Below room temperature, this material shows near "zero thermal expansion" due to two competing effects.



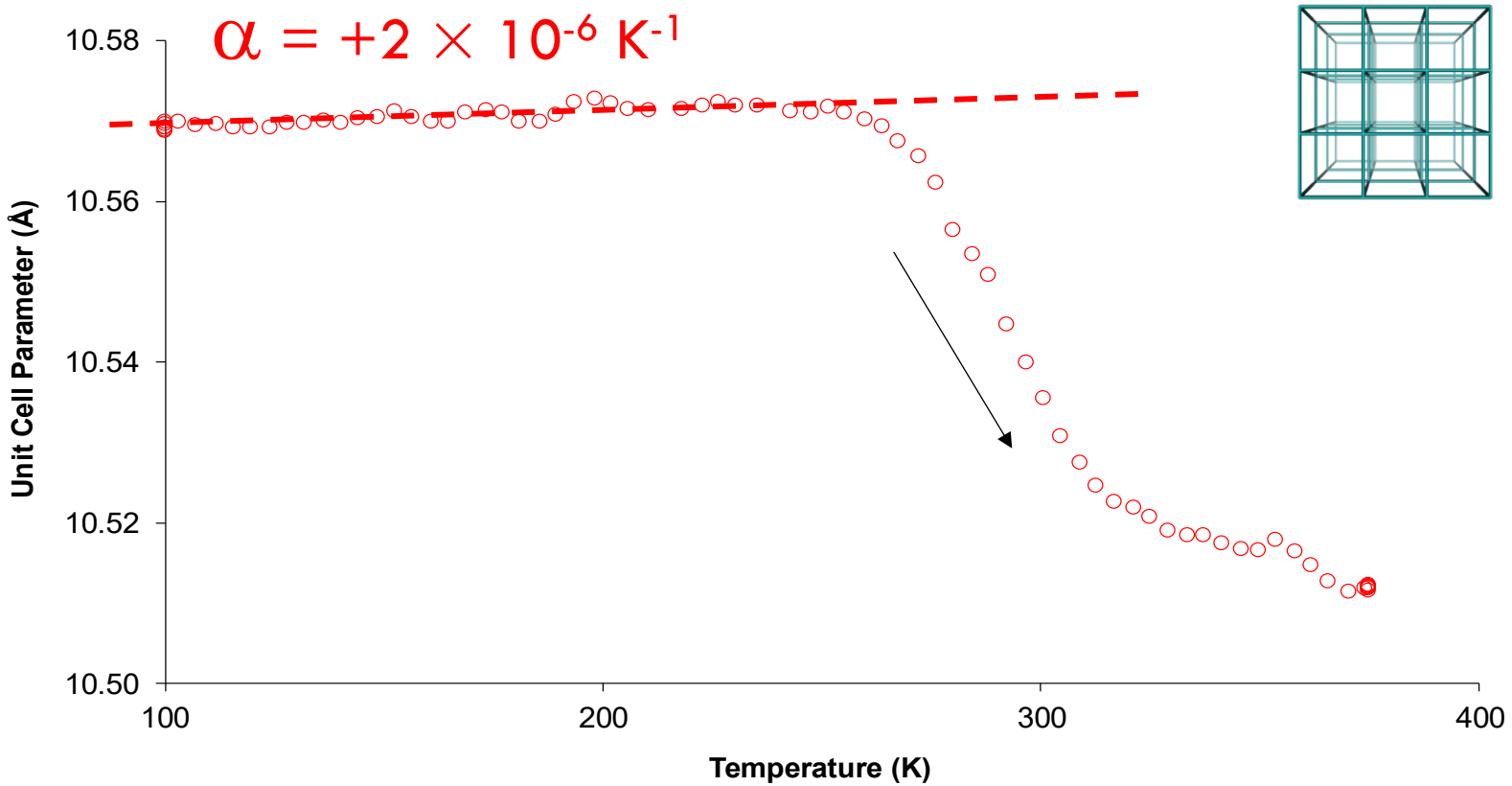
As temperature increases:

- The framework undergoes the transverse vibrational modes that (typically) lead to contraction.
- The water vibrates and rotates more, occupying more space, and expanding the framework.

J. Am. Chem. Soc., 127, 17980 (2005).

NTE in MOFs: $Zn^{II}Pt^{IV}(CN)_6 \cdot xH_2O$

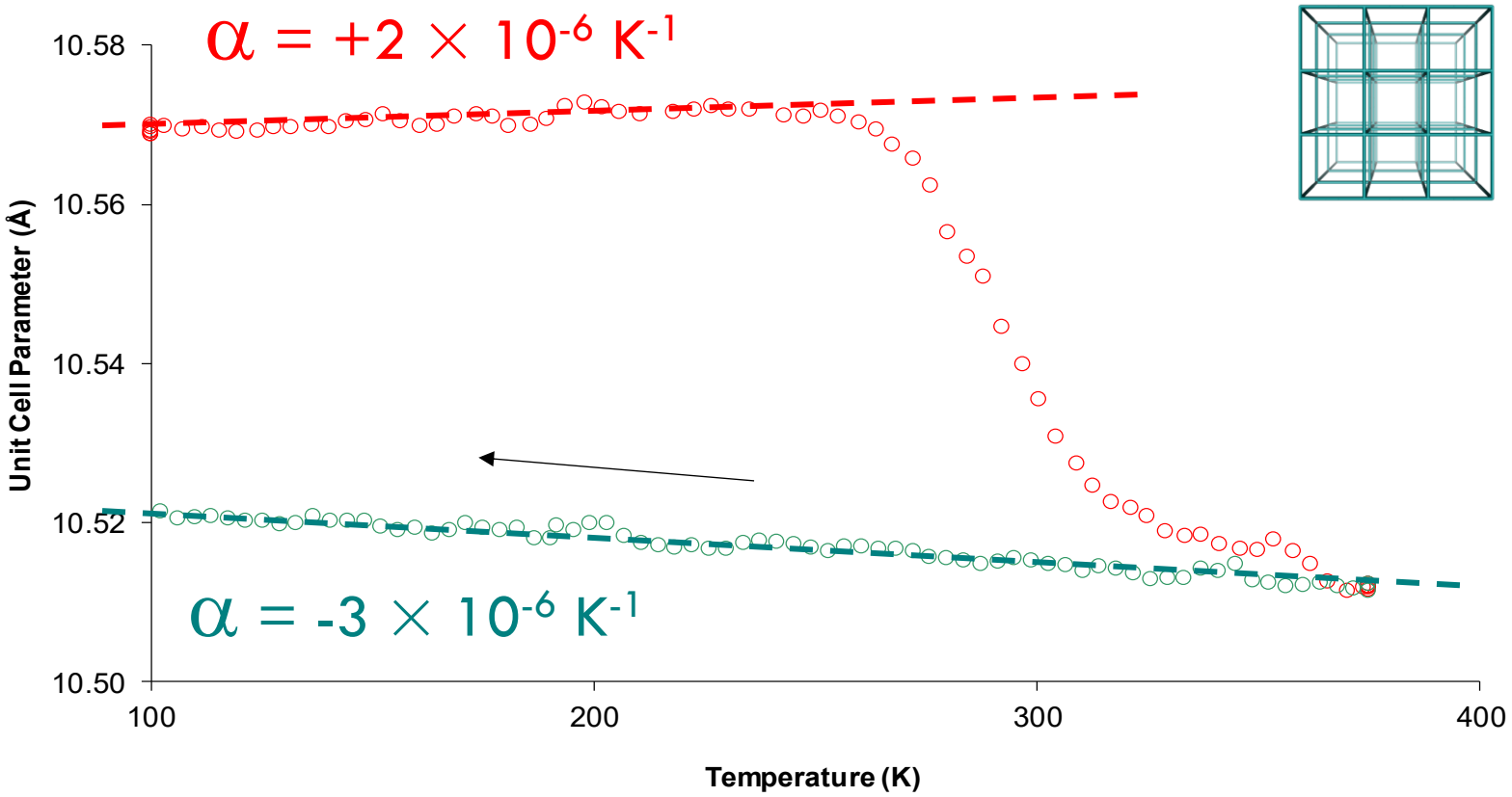
Above room temperature, the water molecules are removed, and the lattice parameter decreases.



J. Am. Chem. Soc., 127, 17980 (2005).

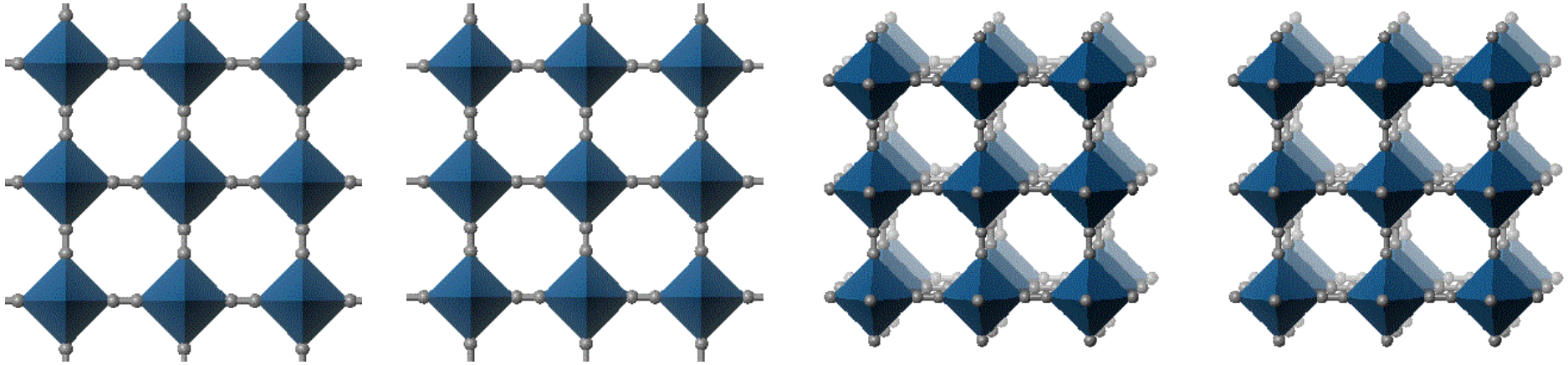
NTE in MOFs: $Zn^{II}Pt^{IV}(CN)_6 \cdot xH_2O$

The materials then show NTE behvaiour due to the transverse vibrations of the framework.



Effect of bond strength on vibration modes

Low energy phonon (lattice vibration) modes



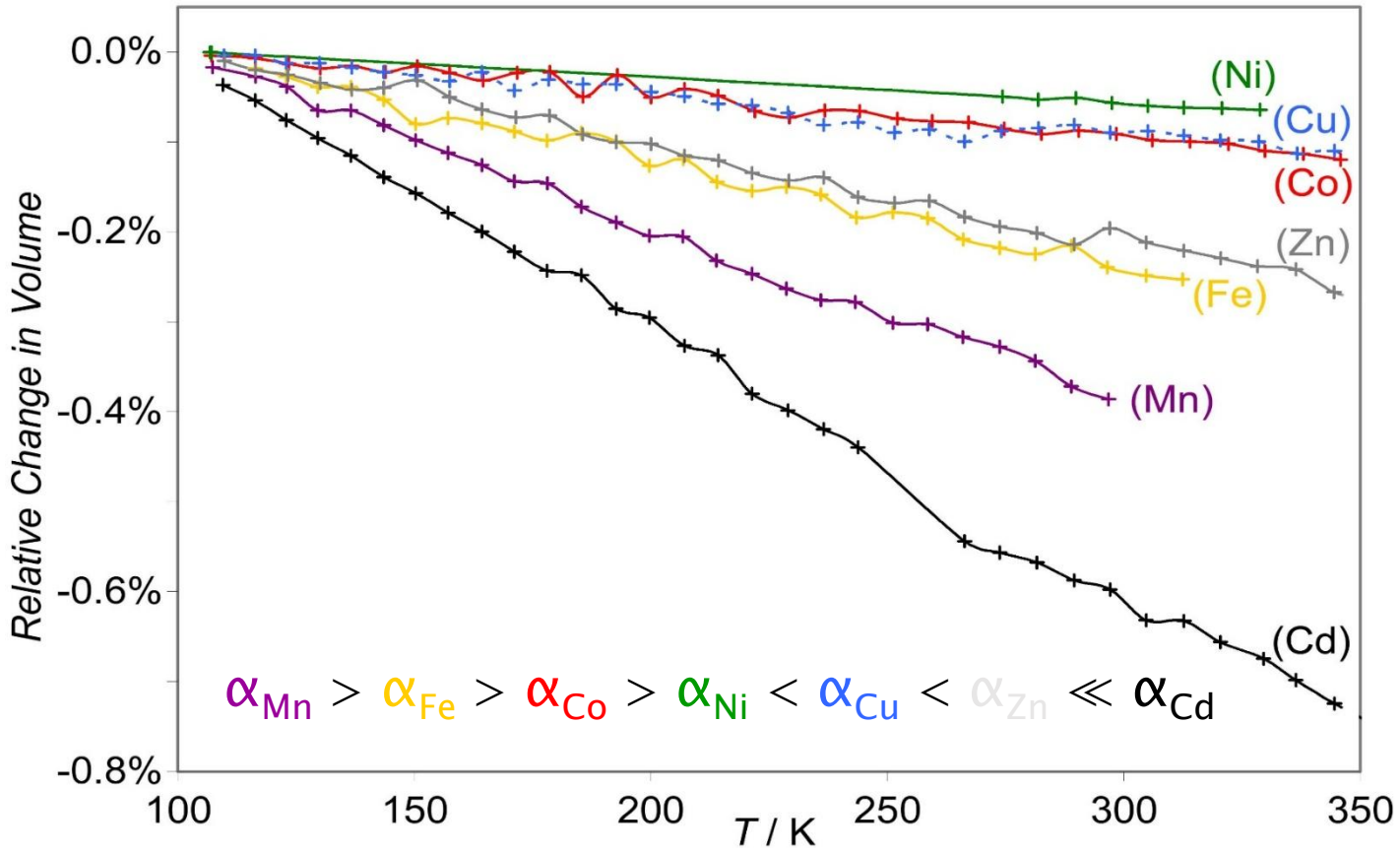
The energies of these phonons, and therefore their amplitudes, depends on the strength of the M(1)–C≡N–M(2) bonding:

- *tightly* bound cyanides gives small amplitudes so *small* NTE
- *loosely* bound cyanides gives large amplitudes so *large* NTE

J. Am. Chem. Soc., 128, 7009 (2006).

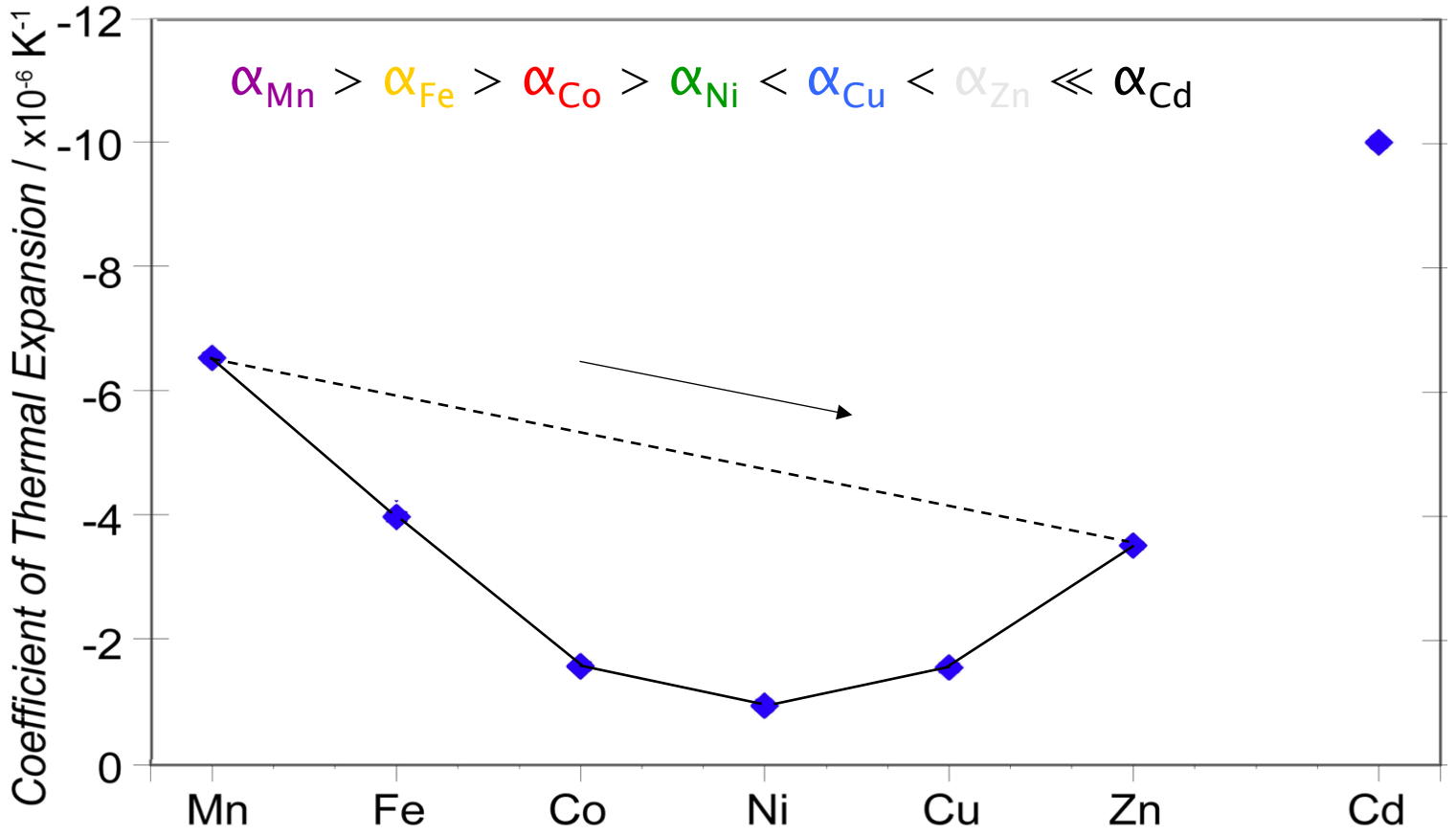
NTE in MOFs: The effect of M in $M^{II}Pt^{IV}(CN)_6$

25	26	27	28	29	30
MANGANESE	IRON	COBALT	NICKEL	COPPER	ZINC
Mn	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
54.94	55.85	58.93	58.69	63.55	65.39



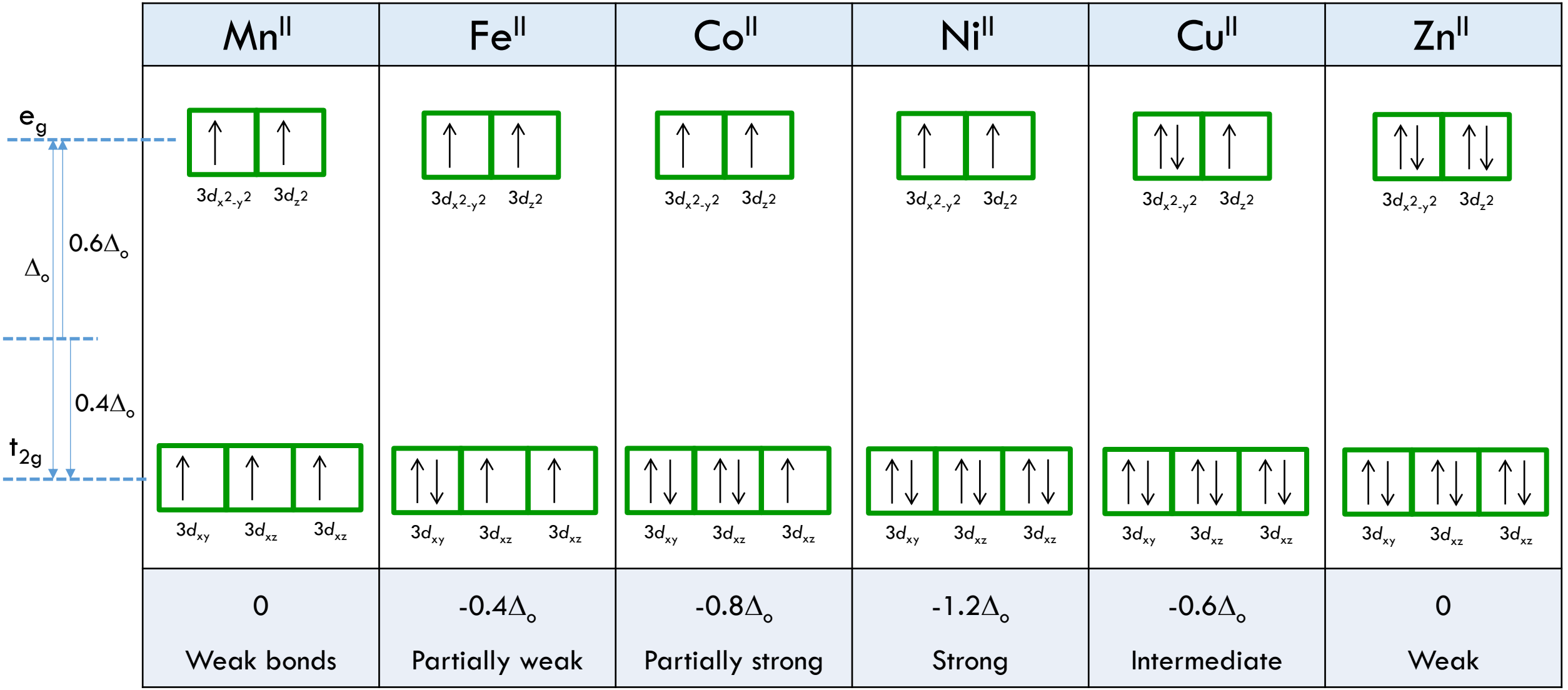
J. Am. Chem. Soc., 128, 7009 (2006).

NTE in MOFs: The effect of M in $M^{II}Pt^{IV}(CN)_6$



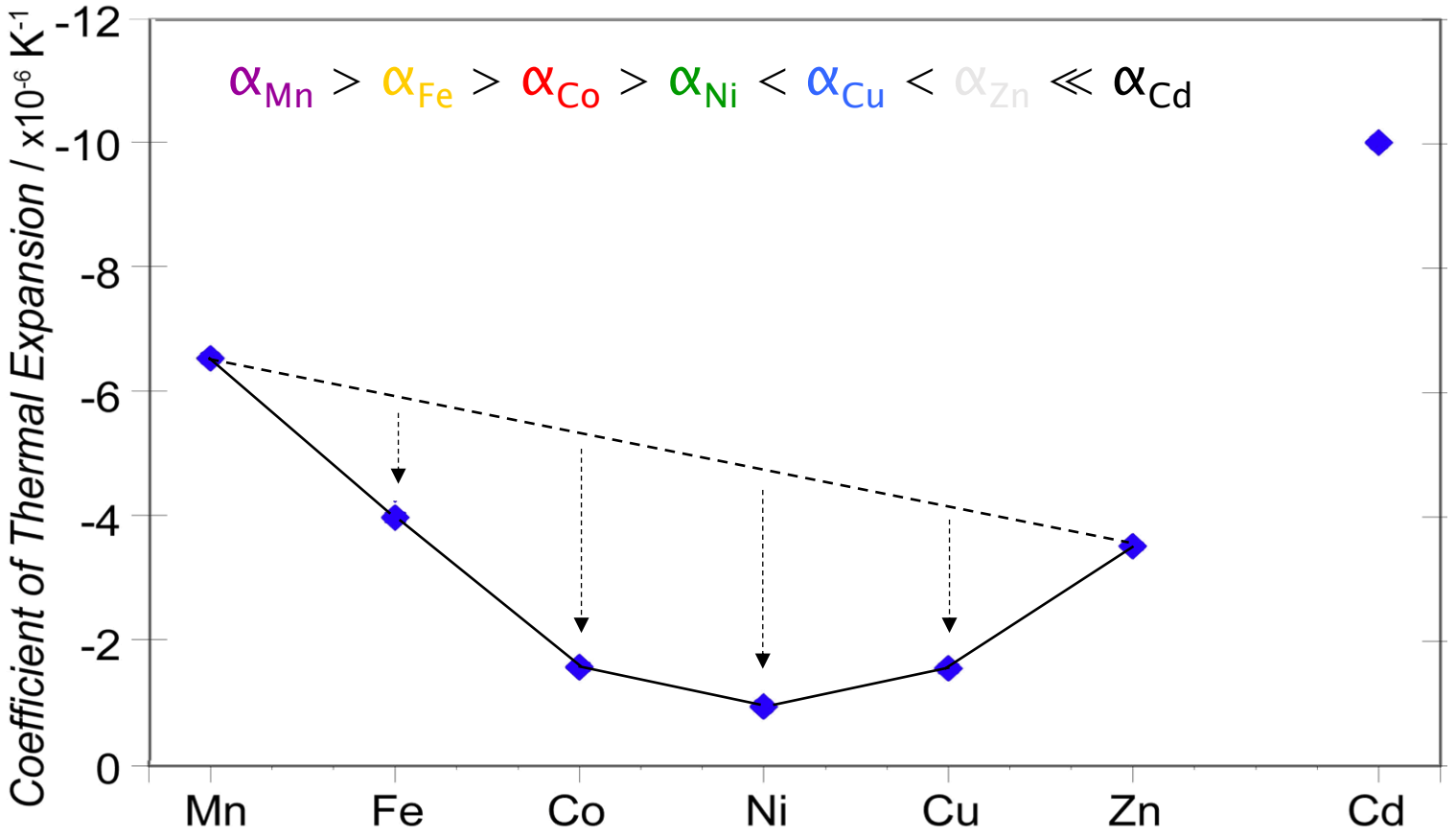
- Ionic radius decreases across the period due to the increasing effective nuclear charge.
- Smaller metal ions form stronger metal–ligand bonds due to greater electrostatic attraction.
- Stronger bonds leads to smaller NTE.
- Hence, the downward trend from Mn to Zn.

Bond strength and crystal field stabilisation energies



J. Am. Chem. Soc., 128, 7009 (2006).

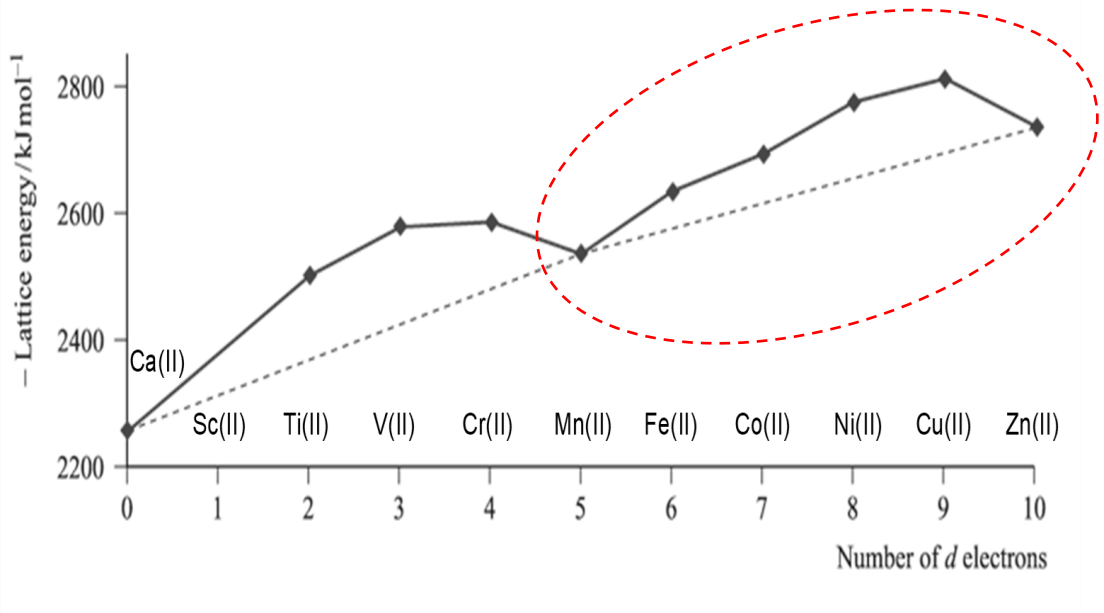
NTE in MOFs: The effect of M in $M^{II}Pt^{IV}(CN)_6$



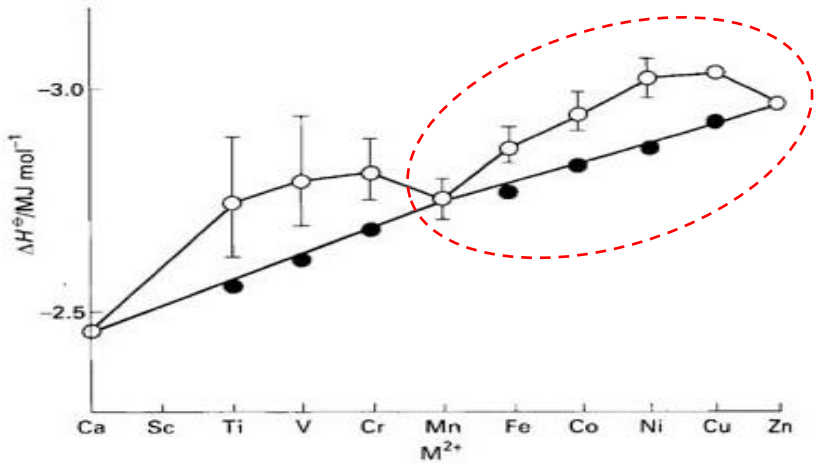
- The contribution from the crystal field stabilization energy (CFSE) creates the overlayed trough shape.
- Ni(II) has the largest CFSE and hence the strongest bonds.
- Stronger bonds leads to smaller NTE.

Other properties where CFSE has an impact

$M^{II}Cl_2$ lattice energies



M^{II} hydration enthalpies



Beyond the Born-Mayer equation: When unpaired electrons are present the CFSE also contributes to the lattice enthalpy.

Learning outcomes

After this lecture you should be able to

- Appreciate the basic design principles of MOF synthesis
- Explain how longitudinal vibrations lead to the expansion of matter on warming
- Explain how transverse vibrations can lead to contraction on warming (NTE)
- Describe the underlying mechanism of NTE in metal-cyanide frameworks
- Explain ways in which the thermal expansion behaviour of materials can be varied