Handout IRTG-3, May 26 2009

- Jan Reedijk.
  Leiden Institute of Chemistry

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Bifunctionality in ligands and coordination compounds: application in design of new materials, catalysts and drugs.

IRTG: Spring 2009, Münster

Jan Reedijk
Leiden Institute of Chemistry, Gorlaeus laboratories, Leiden University, The Netherlands.

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Lectures overview

- 1a. Introduction Ligands (general)
- 1b. Introduction Bifunctionality
- 2. Introduction Metal-DNA binding and anticancer drugs, followed by: Bifunctionality in M-DNA binding
- **3. Bifunctionality in Molecular Materials**
- 4. Bifunctionality Homogeneous Catalysis
- Conclusions and Outlook

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Ligands for materials science and molecular materials

Use of ligand as building bricks

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Contents Molecular Materials

- Intro crystal engineering
- Examples with triazine-based ligands
- Examples with anion-pi interations
- Examples with spin-transition compounds
- Examples of rigid coordination polymers (MOFs)

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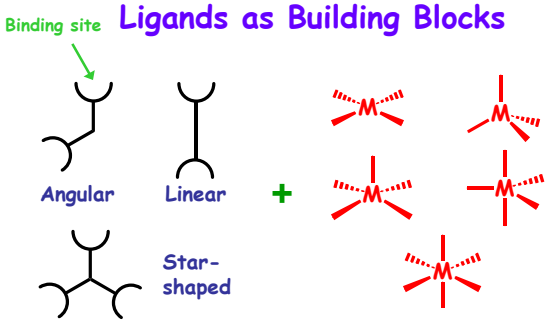
Crystal Engineering: Ligands as Building Blocks



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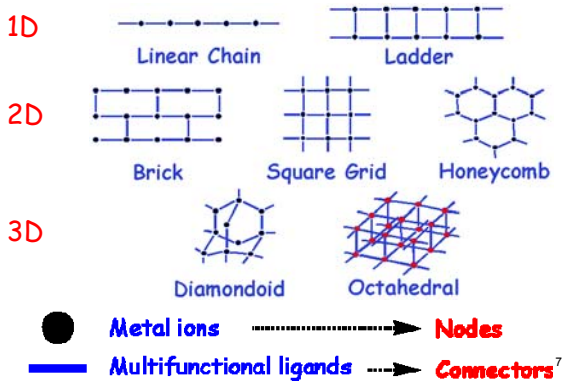
Possible 1D, 2D and 3D Networks



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Materials:
Selection of recent results with triazine-based systems

- Bridging subsystems, symmetric and asymmetric
- Storage materials (cavities)
- **Spin transitions**
- Supramolecular systems with novel anion-π interactions

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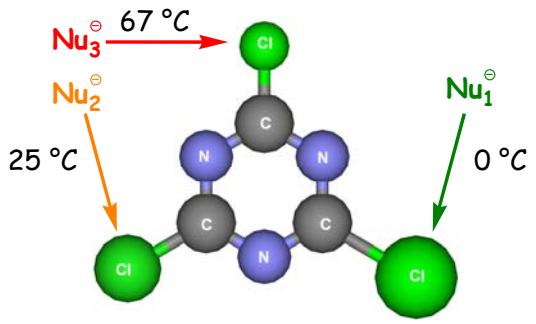
Synthesis of 1,3,5-triazine-derived ligands (Differential reactivity of 1,3,5-triazines)



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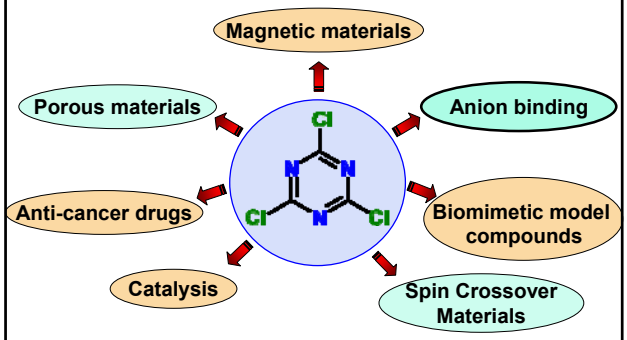
Potential applications



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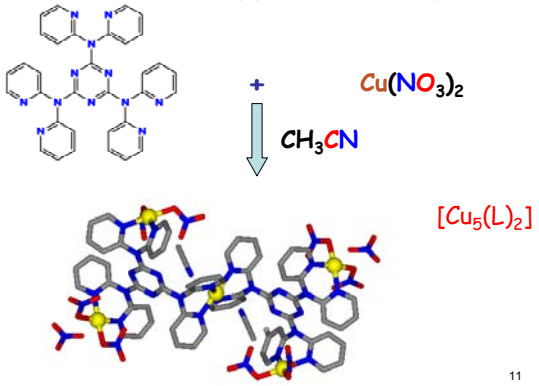
Pentanuclear Copper(II) Complex



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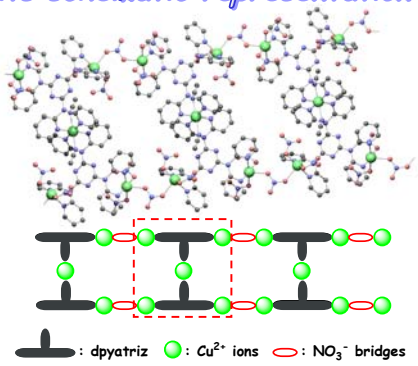
1D ladder and its schematic representation



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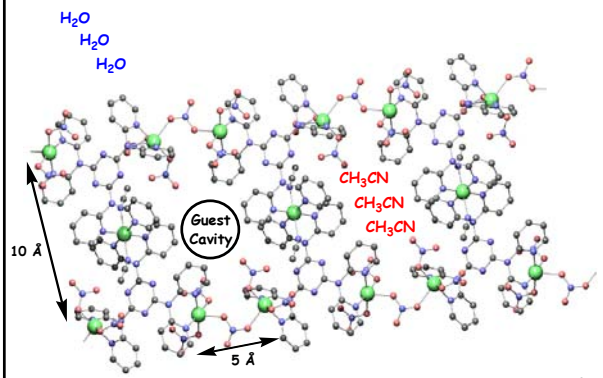
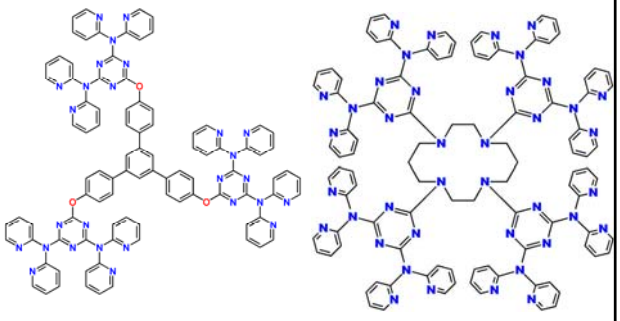
1D Ladder: Host-Guest chemistry



De Hoog et al. Chem Comm.

1,3,5-Triazine-derived ligands prepared (selection of examples)



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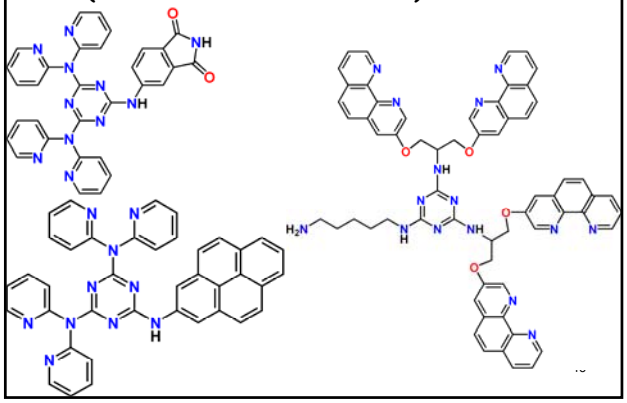
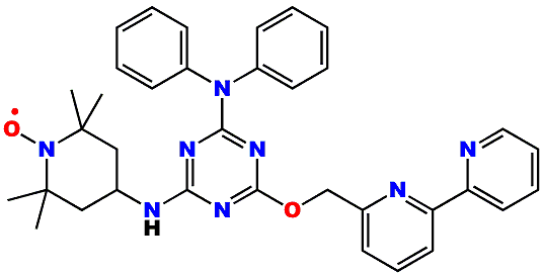
1,3,5-Triazine-derived ligands prepared (2 different substituents)

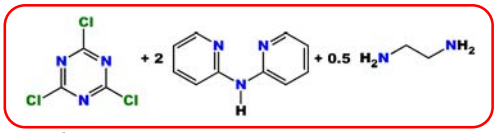


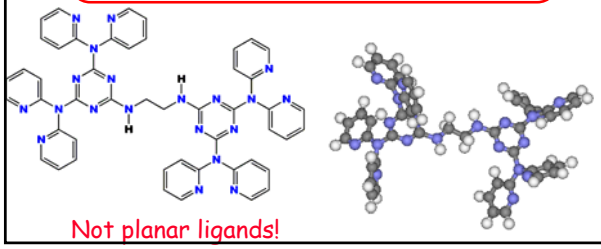
1,3,5-Triazine-derived ligands prepared

(even 3 different substituents!!)



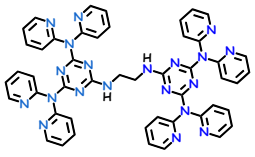
N,N'-{2,4-di[(dipyridin-2-yl)amine]-1,3,5-triazine}ethylenediamine (Opytrizediam)





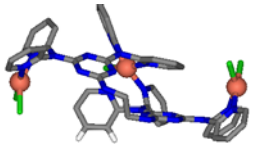
Not planar ligands!

Trinuclear Copper(II) Complex with different Cu(II) ions



+ $CuCl_2$

MeOH



$[Cu_3(L)]_n$

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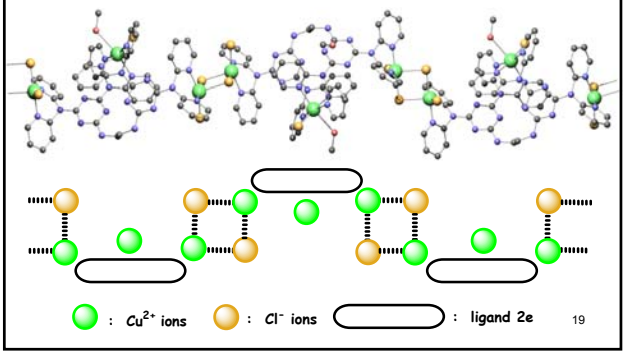
1D zigzag coordination polymer and its schematic representation



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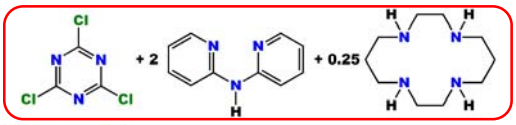
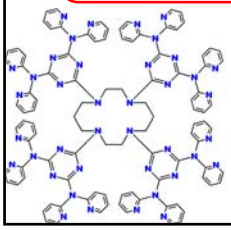
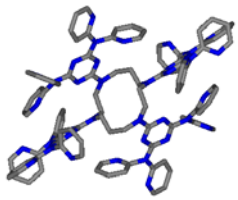
N,N',N'',N'''- {2,4-di[(di-pyridin-2-yl)amine]-1,3,5-triazine }-1,4,8,11-tetraazacyclotetradecane (Azadendtriz)

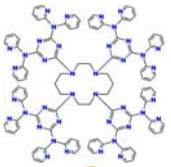




NOT planar



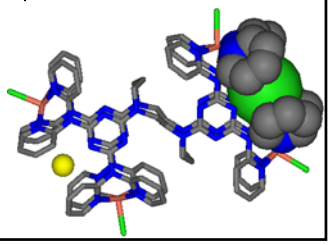
Tetranuclear Copper(II) Complex: as novel Anion Receptor



+ $CuCl_2$

CH_2Cl_2/H_2O

Bromide does not fit



De Hoog et al. Angew Chem Int Ed.

Unusual Coordination Chemistry with triazine-based ligands; inspiration from crystal engineering

Co-supervision: dr. Patrick Gamez

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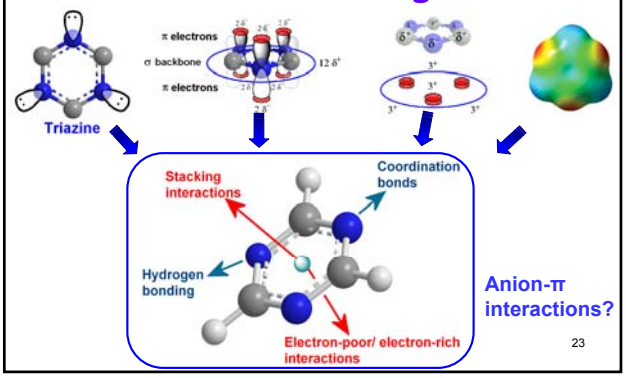
s-Triazine, a particular aromatic ring



Anion-π interactions?

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Potential use: Anion Recognition

- **Anions in biological systems ?**

70 to 75% of enzyme substrates and cofactors are anions:

- phosphate residues (ATP and ADP)
- sulfates
- carboxylates
- chloride anion = major extracellular anion (chloride transport channels)

- **Possible medicinal and biological applications ?**

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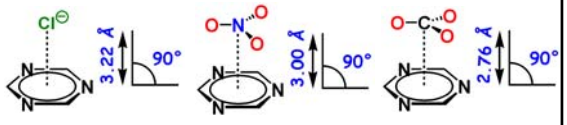
Application: Anion Receptor

Theoretical investigations Anion-pi interactions

➡ Possibility to use electron-poor aromatic rings



Binding Energies (kcal/mol)	$-\Delta E_e$ = 5.23	$-\Delta E_e$ = 5.34	$-\Delta E_e$ = 16.84

M. Mascal, A. Armstrong, M.D. Bartberger, *J. Am. Chem. Soc.* **2002**, *124*, 6274-6276
D. Kim, P. Tarakeshwar, K.S. Kim, *J. Phys. Chem. A* **2004**, *108*, 1250-1258
D. Quinonero, C. Garau, A. Frontera, P. Ballester, A. Costa, P M. Deya, *J. Phys. Chem. A* **2005**, *109*, 4632-4637

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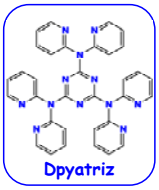
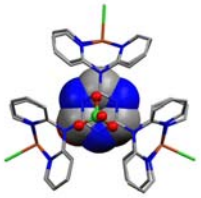
Anion-π Interactions in a Copper(II)-Dpyatriz Complex

1 equiv. $CuCl_2$ + 1 equiv $Cu(ClO_4)_2$ + 1.33 equiv. dpyatriz in DMF/Et_2O





Centroid-centroid : 3.966 Å
Shorter centroid-ClO_4^- : 3.236 Å
Shorter centroid-ClO_4^- : 3.113 Å

➔ Same complex with added $NaClO_4$ in stead of $Cu(ClO_4)_2$

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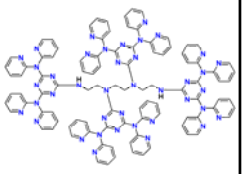
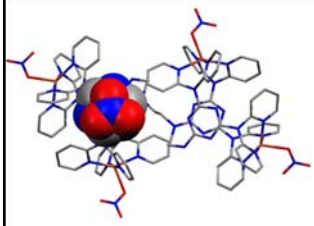
Tetranuclear Copper(II) Complex: Anion-Pi Interactions

4 equiv. $CuNO_3$ + 1equiv. Tetradendtriz in MeOH at 105 °C





Centroid-centroid : 3.445 Å
Shorter centroid-NO_3^- : 3.230 Å

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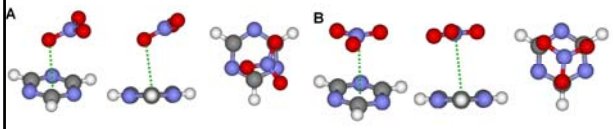
P. Gamez et al., *New J. Chem.* 2006, 30, 1561.

Copper(II) nitrato Complex: Anion-Pi Interactions



Optimization (DFT-BLYP) based on the crystal structure of the complex obtained.

Experimental
centroid-$O_{nitrate}$: 3.47 Å

Calculated
Centroid-$O_{nitrate}$: 3.151 Å

P. Gamez et al., *New J. Chem.* 2006 30, 1561. Acc. Chem. Res. 2007, *40*, 435-44.

DFT-BLYP calculation on the model proposed by Kim et al.

centroid-$N_{nitrate}$: 3.4 Å (3.0 Å with MP2)

D. Kim et al., *J. Phys. Chem. A* 2004, *108*, 1250-1258

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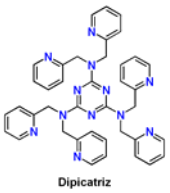
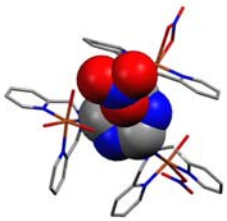
Trinuclear Copper(II) Complex: Anion-Pi-Anion Interactions

3 equiv. $CuNO_3$ + 1equiv. dipicatriz in acetonitrile.





centroid-$O_{nitrate}$ distances: 3.202 Å and 3.502 Å.

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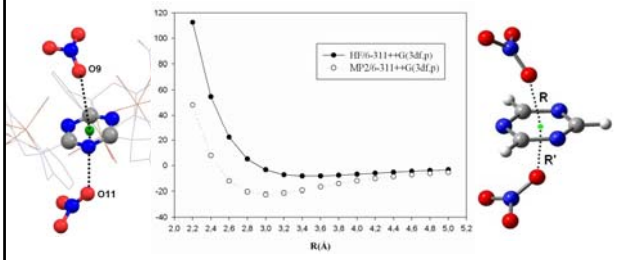
P. Gamez et al., *Inorg. Chem.* 2006, 45, 6637

Trinuclear Copper(II) Complex: Anion-Pi-Anion Interactions



centroid-O9: 3.202 Å.
Centroid-O11: 3.502 Å.

R = R' = 3.2 Å for a 2/1 nitrate/triazine system.

R = 3.0 Å for a 1/1 system.

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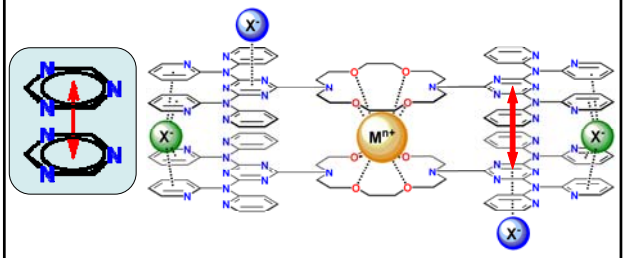
P. Gamez et al., *Inorg. Chem.* 2006, 45, 6637; Acc. Chem. Res. 2007, 40, 435.

Recent extensions: Formation of the coordination compounds driven by anion-π Stacks: M = K



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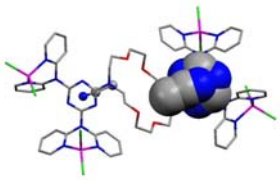
NOT only ANIONS: (Electron rich) neutral molecule-π Interactions in a Zinc(II)-Oxodendtriz Complex

4 equiv. $ZnCl_2$ + 1 equiv. Oxodendtriz in acetonitrile/methanol 1/1



Short experimental N_{MeCN}-triazine distance : 3.087 Å

Short calculated N_{MeCN}-triazine distance: 3.116 Å

P. Gamez et al., *Cryst. Growth Des.* 2006, *6*, 1569.
C. Massera et al., *CrystEngComm* 2005, *7*, 121.

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Concluding remarks anion-π interactions

- Non-coordinating anions may be more important than just charge compensation
- Many cases known in databases, but only recently realized and recognized as such *(review: Gamez at al, Acc. Chem. Res, 40 (2007), 435;*
  New data: Cryst. Growth Des., 8, (2008), 1082-1093.
- **Early paper:** R. Ahuja and A. G. Samuelson, CrystEngComm, 2003, 5(69), 395–399
- Relevant for selective anion-binding?
- Outlook to: Lone pair-p interactions: a new supramolecular bond?
  See Mooibroek et al., *Crystengcomm*, *10*, (2008), 1501-1515.

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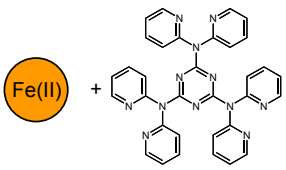
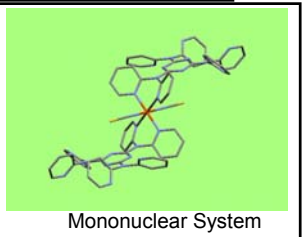
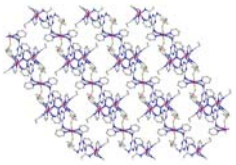
Triazine ligands in spin-transition materials



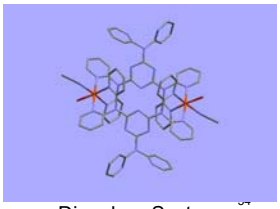
Spin transition systems!



Mononuclear System



Polymeric System



Dinuclear System

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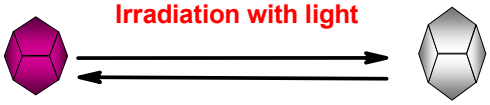
- **Spin transition compounds INTRO:**
- **Switchable bistable iron(II) materials**

Temperature
Pressure
Irradiation with light



Iron(II) spin-crossover

Change in optical and magnetic properties

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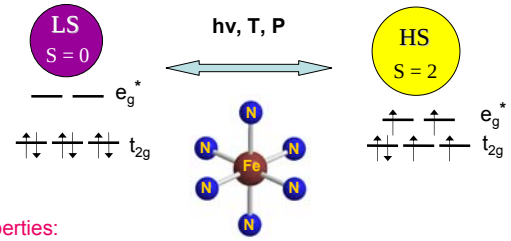
Fe^{2+} possible electronic configurations



Properties:

Purple/Red	Yellow / White
Diamagnetic	Paramagnetic
Fe-N distance ~ 2 Å	Fe-N distance ~ 2.2 Å

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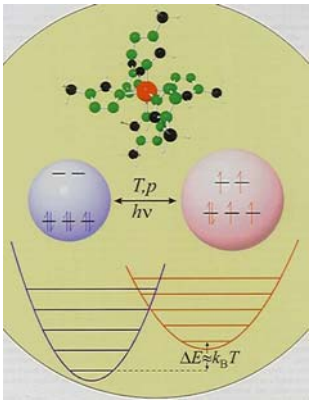
Spin Transition possibilities in Fe(II) species of octahedral geometry.
Left: low spin;
Right: high spin

Differences in: magnetism, optical properties, ligand exchange, redox, electron exchange

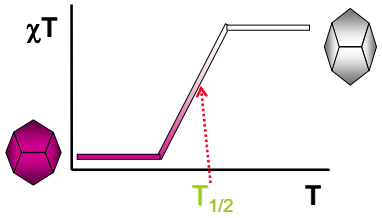


Magnetic susceptibility (χ) measurements

Magnetisation M = χ H

$\chi = \chi_{diamagnetic} + \chi_{paramagnetic}$

all electrons — unpaired electrons



Low-spin Fe(II) ion:
No unpaired electrons
S = 0
Diamagnetic

High-spin Fe(II) ion:
Four unpaired electrons
S = 2
Paramagnetic

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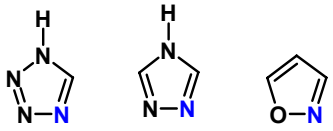
Simplest $Fe^{II}N_6$ spin-crossover chromophores in

$[Fe(ligand)_6]^{2+}$



tetrazole **1,2,4-triazole** **isoxazole**

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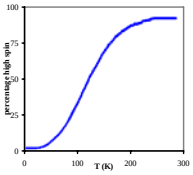
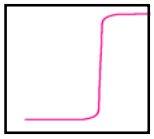
Cooperativity and the ideal ST curve

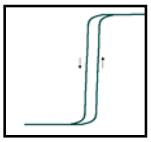
• In solution or in diluted matrices.



• Strictly a molecular process



Cooperativity



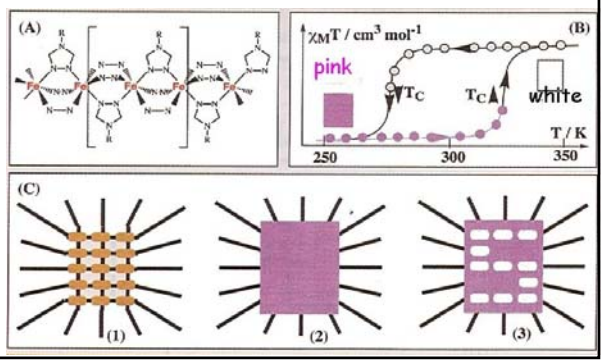
T — RT

Steep Transitions
Temperature sensors.

Hysteresis
Memory-storage devices.

40

Application of the spin transition in a display, using Joule or Peltier effect



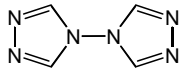
Problems on the way to applications

1. Transtion near room temperature is difficult to reach
2. Sensitivity to traces of solvent

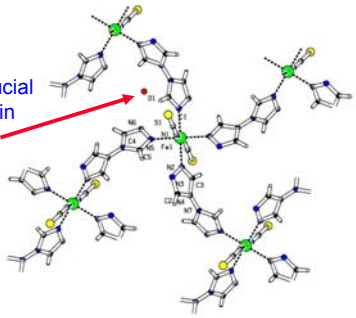
42

Structure of the 2D magnet $[Fe(btr)_2](NCS)_2$

btr =bistriazole

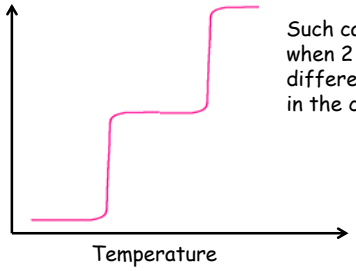


Water crucial for the spin transition



43

Two-step transitions: rare



Such cases may occur when 2 slightly different sites occur in the crystal lattice

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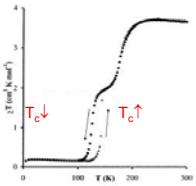
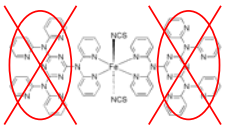
Spin transition in two or more steps

- Two steps: several examples known from literature; ratio is 1:1
- Two steps with different ratio like 1/3 vs. 2/3: a very rare case
- A special SCO compound $[Fe(babpbpy)(SCN)_2]$

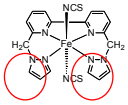


45

Design of the ligand babpbpy



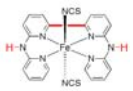
Quesada *J. Mat. Chem.* **2006**



Sanchez Costa *Inorg Chem.* **2007**

Inspired by above earlier work in our group:

S. Bonnet, P. Gamez and J. Reedijk; *Chem. Comm.*, (2008), 5619-5621.



$[Fe(babpbpy)(SCN)_2]$

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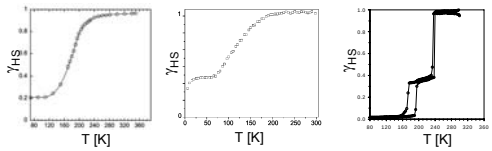
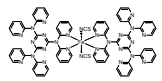
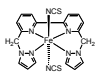
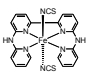
Synthesis and magnetic properties









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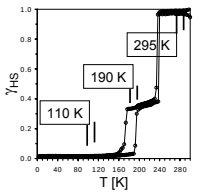
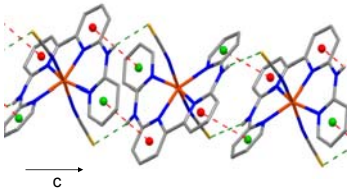
X-ray structures: 110, 190 & 295 K



T [K]	295	190	110
Fe-N (Å, HS)	2.146	2.135	-
	2.135	2.131	-
	2.148	2.149	-
Fe-N (Å, LS)	-	1.980	1.980
	-	1.942	1.942
	-	1.932	1.933
	-	1.942	1.944
	-	1.983	1.987
	-	1.936	1.942

In all 3 phases: 1D supra-molecular chains along **c**



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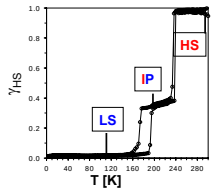
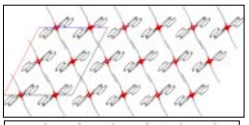
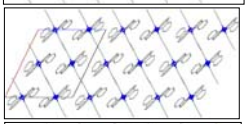
A peculiar intermediate phase

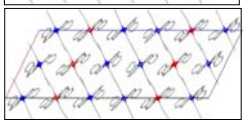


[HS]



[LS]





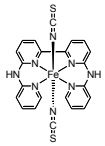
The intermediate phase [HS-LS-LS]

- **c** is 42.4 Å instead of 14.2 Å
- long-range order
- unprecedented 1:2 HS:LS ratio

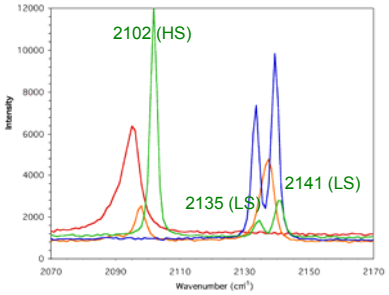
-S. Bonnet; *Chem. Comm.*, (2008), 5619-5621.

Vibrational spectroscopy

IR:
ν_{SCN} = 2094 cm^{-1}
at 298 K (HS)

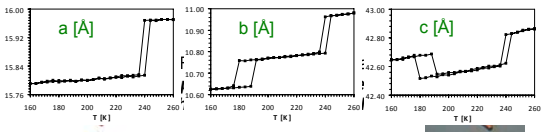


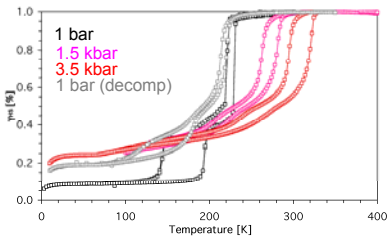
Raman: at 303 K, 210 K, 130 K, 77 K



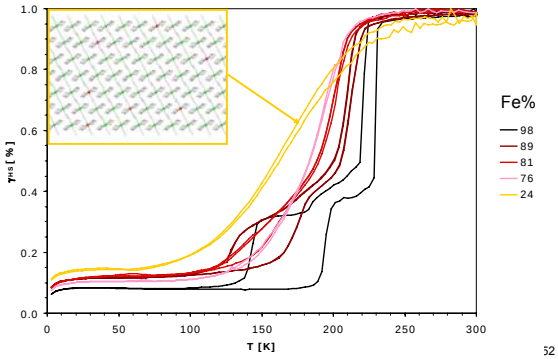
⇒ Specific Raman signature of the intermediate phase!

Effect of high pressures

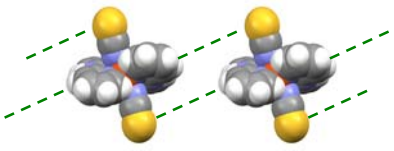




Effect of dilution into Zn(II)



Conclusions 2-step SCO



- [Fe(bapbpy)(SCN)$_2$] is two-step SCO with strong cooperativity
- X-ray of HS, IP and LS phases: supramolecular interactions
- peculiar Intermediate phase (IP): long-range order, [HS-LS-LS] motif, 1:2 HS:LS ratio
- DMF in the crystal quenches the cooperativity
- influence of light, pressure and dilution on SCO was studied

Conclusions Fe complexes and solvents

- The spin transition properties can be fine-tuned with the solvent.
-Solvent-dependant property depends on the ligands.
-Often compounds go through a hydrated phase.
-A structural reversibility accompanies the magnetism.
-It is possible to observe the transition by means of X-ray powder diffraction experiments.
-Lattice solvent molecules are desorbed/substituted.
-Coordinated solvent molecules may also be responsible for the changes observed in the spectra.

Other uses of ligands

- Ligand in MOFs and bifunctionality
- Ligands in catalysis and bifunctionality (last class: May 27)

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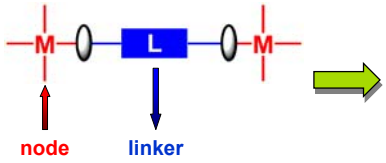
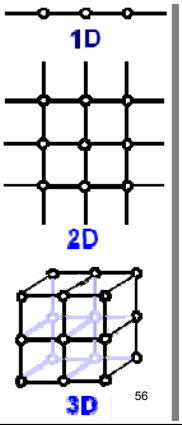
MOFs = Rigid (porous) coordination polymers





Different topologies can be obtained by:

- varying the coordination geometry of the **node** (**transition metal**);
- varying the organic **linker**.

In principle, a judicious selection of the molecular **Building Blocks** allows a (partial) control on the self-assembled structure.

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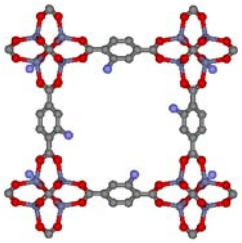
Introduction Coordination Polymers

- Metal-Organic Frameworks – MOFs
  - Crystalline Materials
  - Facile synthesis
- **Applications**:
  - Gas Storage
  - Catalysis
  - Sensor Technology
  - Chiral Discrimination



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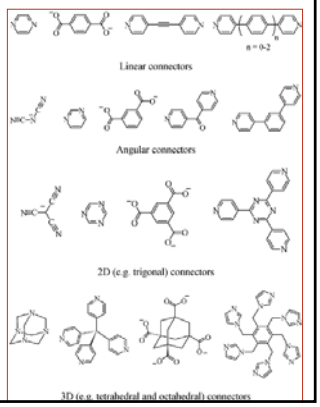
Yaghi et al. *Science* **2002**, 469

Rigid Coordination networks

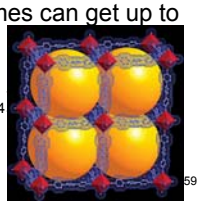
Tectons and synthons

- (Rigid) ligands capable of bridging two or more metals



Metal-Organic Frameworks (MOFs)

- Porous crystalline compounds based on zeolites
  - metal ions coordinated to organic molecules creating holes (cavities) in the structure.
- Cavities can get as large as 29 Å
- Very low densities for a crystalline compound (as low as 0.2 gcm^{-3}) – Pore volumes can get up to 91 %
- Applications
  - Gas Storage (e.g. H_2, CO_2, CH_4
  - Heterogeneous Catalysis
  - Chiral Discrimination



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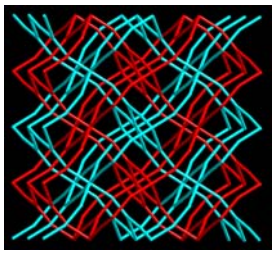
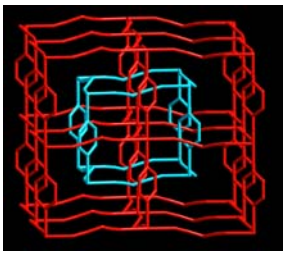
Porosity





Interpenetration: vacant space can be occupied by copies of the same network

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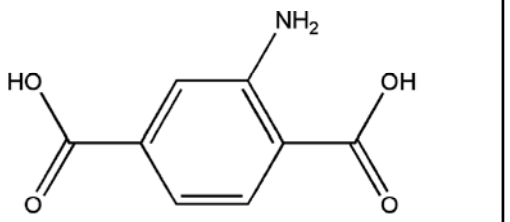
3-D Lanthanide Metal-Organic Frameworks: Structure, Photoluminescence, and Magnetism

Inorg. Chem., 2009, 48, 1062–1068



2-amino-1,4-benzene dicarboxylic acid - N-H_2BDC

Post-modification of a Bridging Ligand Inside A Metal-Organic Framework (= Rigid Coordination Polymers)

A simple and versatile method to prepare custom-made functional MOFs in a straightforward manner.

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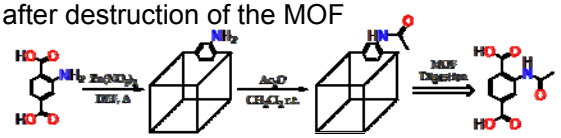
Post-Synthetic Modification

- 1990 – Robson: Reactive molecules can access pores no structures
- 2000 – Kim: Converted pyridyl groups to *N*–methyl pyridinium ions (NMR study only)
- 2007/2008 – Cohen: ESI-MS, NMR and only: after destruction of the MOF



Robson et al. *J. Am. Chem. Soc.* **1990**, 1546
Kim et al. *Nature* **2000**, 982
Cohen et al. *J. Am. Chem. Soc.* **2007**, 12368; *Angew. Chem. Int. Ed.* **2008**, 4777

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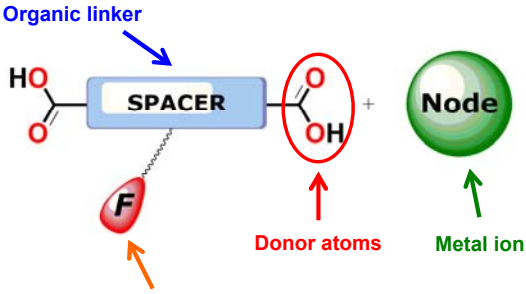
Preparation of Functional MOFs: a novel *Post-synthetic Approach*



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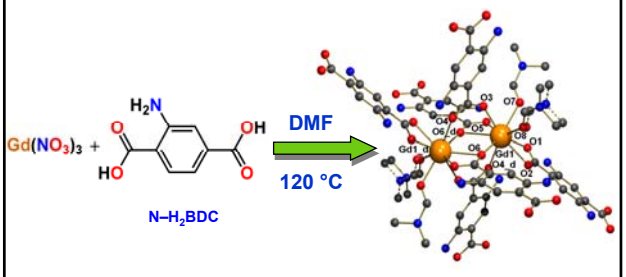
Preparation of the MOF-LIC-1



Gd(III) can be varied to any lanthanoid

Y = 74%

65

Post-synthetic modification of a MOF

FG = Functionalizable Group
R = Functional group

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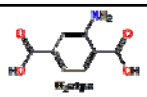
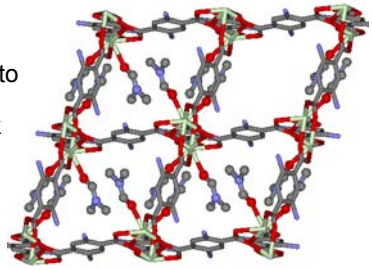
Pore Modification



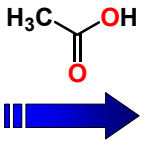
- Catalysis/Gas Sorption
- Normally build functionality into the structure pre-framework formation
- Our MOF
  - Gd^{III}
  - Amino–Terephthalic acid



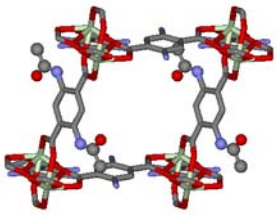
Reedijk et al. *Eur. J. Inorg. Chem.* **2008**, 1551

Highlight Article: Cronin et al. *Angew. Chem. Int. Ed.* **2008**, 4635

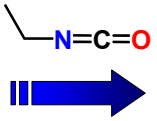
Acetamide Formation



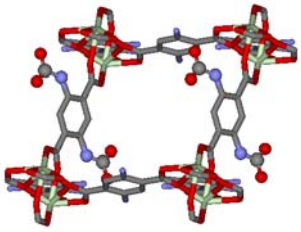
- 40% Conversion of Amino Groups



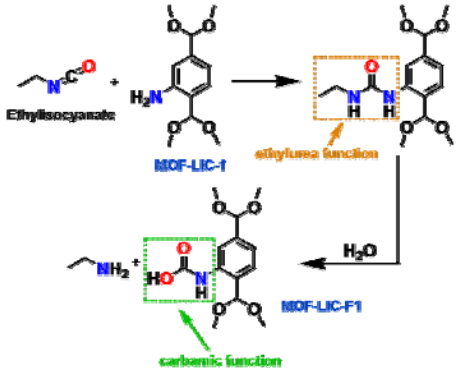
Carbamate Formation



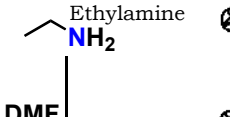
- Expected ethylurea function is hydrolysed



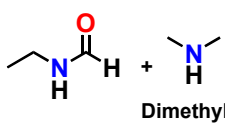
Carbamate Formation



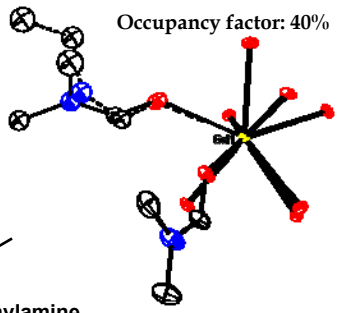
Ethylformamide Formation



DMF



Dimethylamine



Concluding Remarks and Outlook

- Ligands are THE tool for the coordination chemist in making materials
- Fine tuning applications of coordination compounds, requires always also DESIGN & FINETUNING of the ligands