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N-Donor Functionalized Acetylacetones for Heterobimetallic MOFs – The Next Episode: Trimethylpyrazoles

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Abstract: While metal-organic frameworks (MOFs) have been investigated intensively throughout the last decades, only a fraction of the published articles on MOFs feature heterobimetallic structures. Combining two metallic centers in a rigid framework could lead to interesting effects, such as magnetic coupling, collaborating fluorescence or catalytic properties; however, its synthesis is more sophisticated than for monometallic MOFs. We utilize ditopic ligands whose coordination sites differ in their Pearson hardness (HSAB). This enables a stepwise selective formation of heterobimetallic MOFs: first, a monometallic building block is synthesized. In a second step the framework can be constructed by crosslinking with a second metal ion.
In this work we present our most recent ligand candidate: 3-(1,3,5-trimethyl-1*H*-pyrazol-4-yl)acetylacetone. Its synthesis is straightforward and inexpensive. The O,O' coordination was accomplished with a variety of hard cations like Fe^{III} or Ga^{III}. First crosslinking attempts with N coordination of the Fe^{III} building block to Ag^{I} leads to a one-dimensional coordination polymer with high porosity.

Keywords: MOFs; coordination chemistry; crystal engineering

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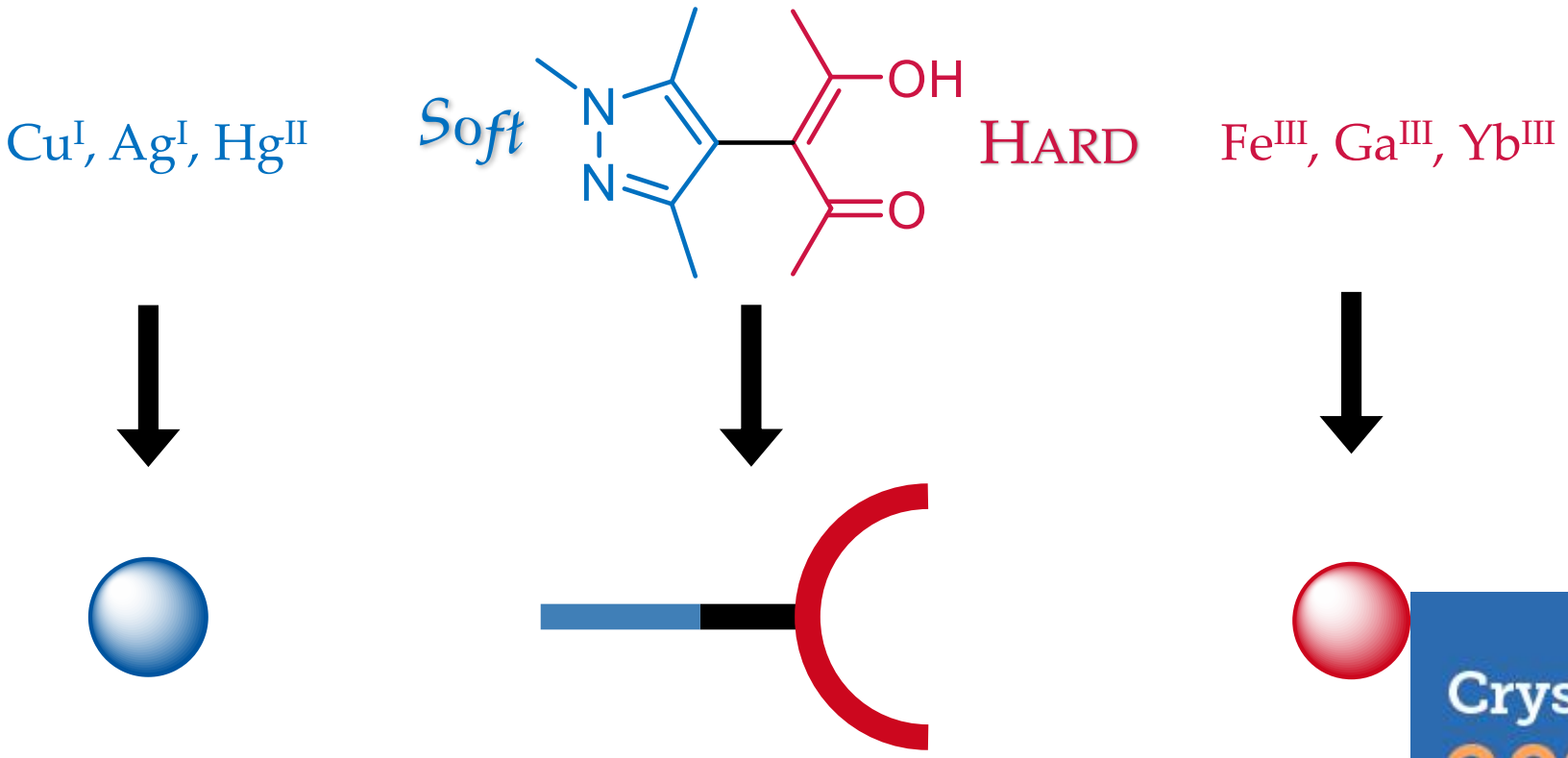
Introduction

We aim for the stepwise and selective synthesis of heterobimetallic metal-organic frameworks (MOFs). For that purpose we utilize ditopic ligands which donor sites differ in Pearson hardness [1]. Here we present a trimethylpyrazolyl substituted acetylacetone to construct a heterobimetallic coordination polymer.



[1] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

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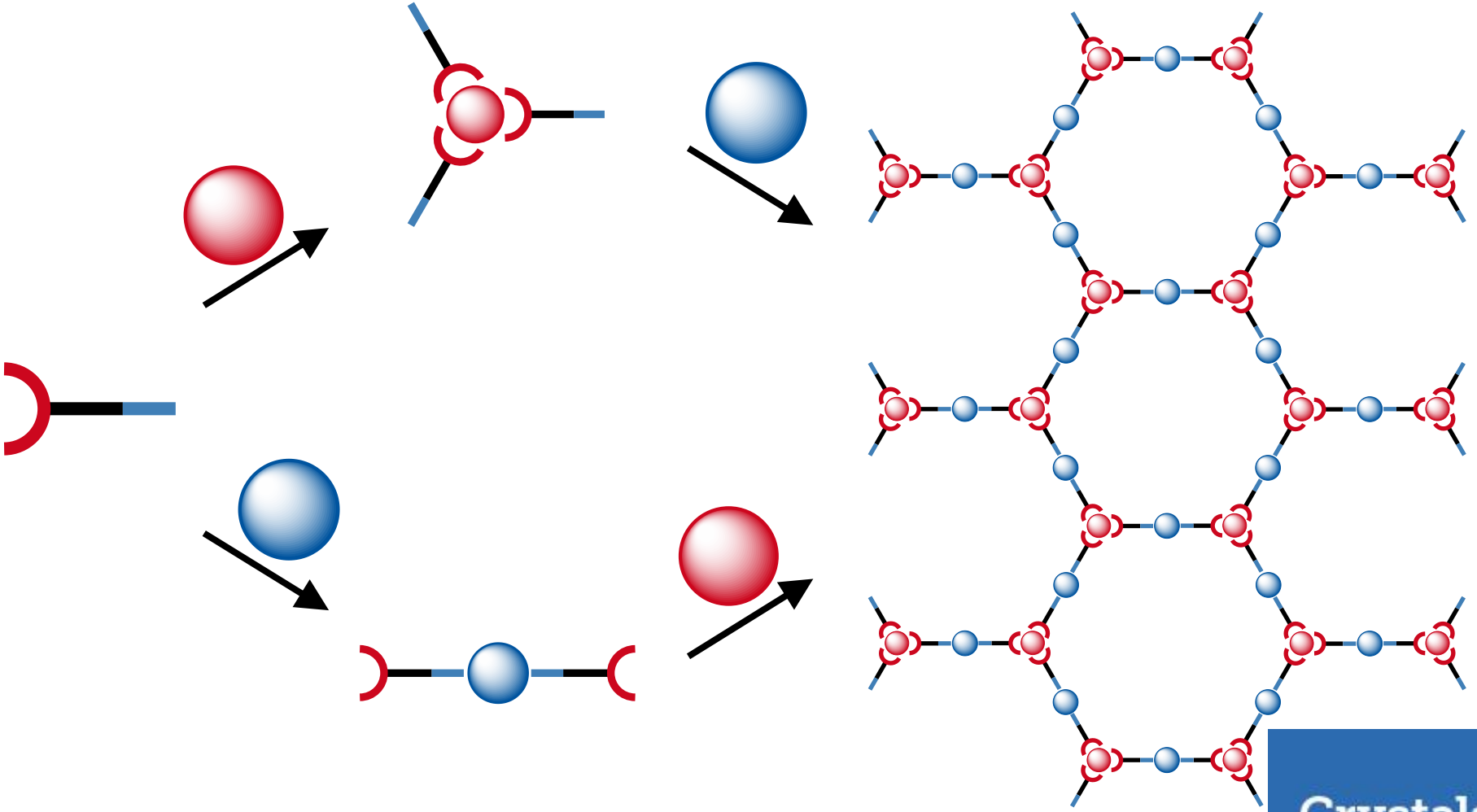
Motivation

Stepwise synthesis of a heterobimetallic MOF achieved with a ditopic ligand:

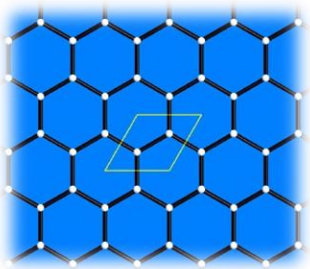


Ligand building unit heterobimetallic MOF

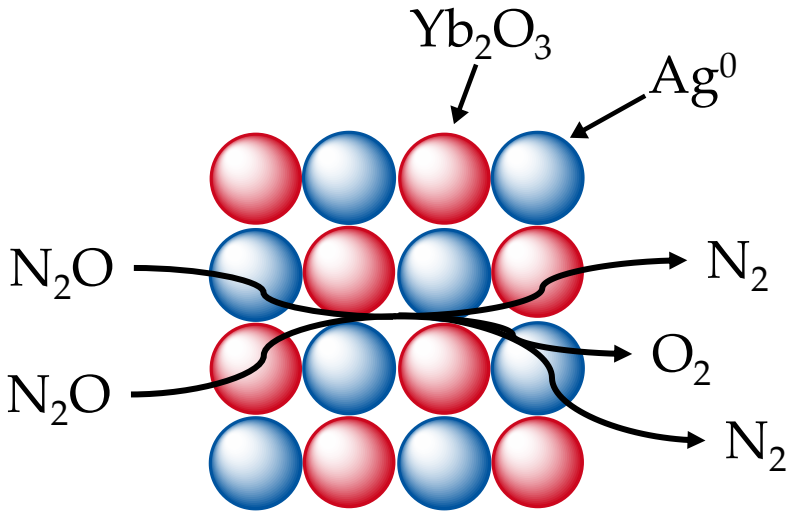
Motivation

There are various properties of these MOF's which are worth investigating (bottom left). Post-modification and/or thermal decomposition can also lead to complex systems with interesting features, e.g. one example of our group shows catalytic properties for the N_2O conversion to the elements after thermal decomposition of an Yb^{III}/Ag^{I} MOF (bottom right) [3]:

Analysis of the MOF's:



- topology[2]
- catalytic properties[3]
- luminescence
- gas storage properties
- magnetism



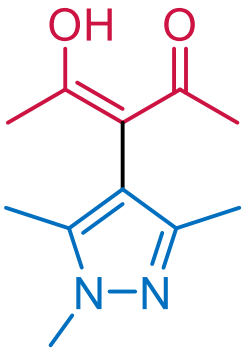
heterogeneous solid[3]

$$2\,N_2O \xrightarrow{Ag^0} 2\,N_2 + O_2$$

[2] M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Accts. Chem. Res.* **2008**, *41*, 1782-1789.
[3] M. Konkol, M. Kondracka, P. Kowalik, W. Próchniak, K. Michalska, A. Schwedt, C. Merkens, U. Englert, *Appl. Catal., B* **2016**, *190*, 85-92.

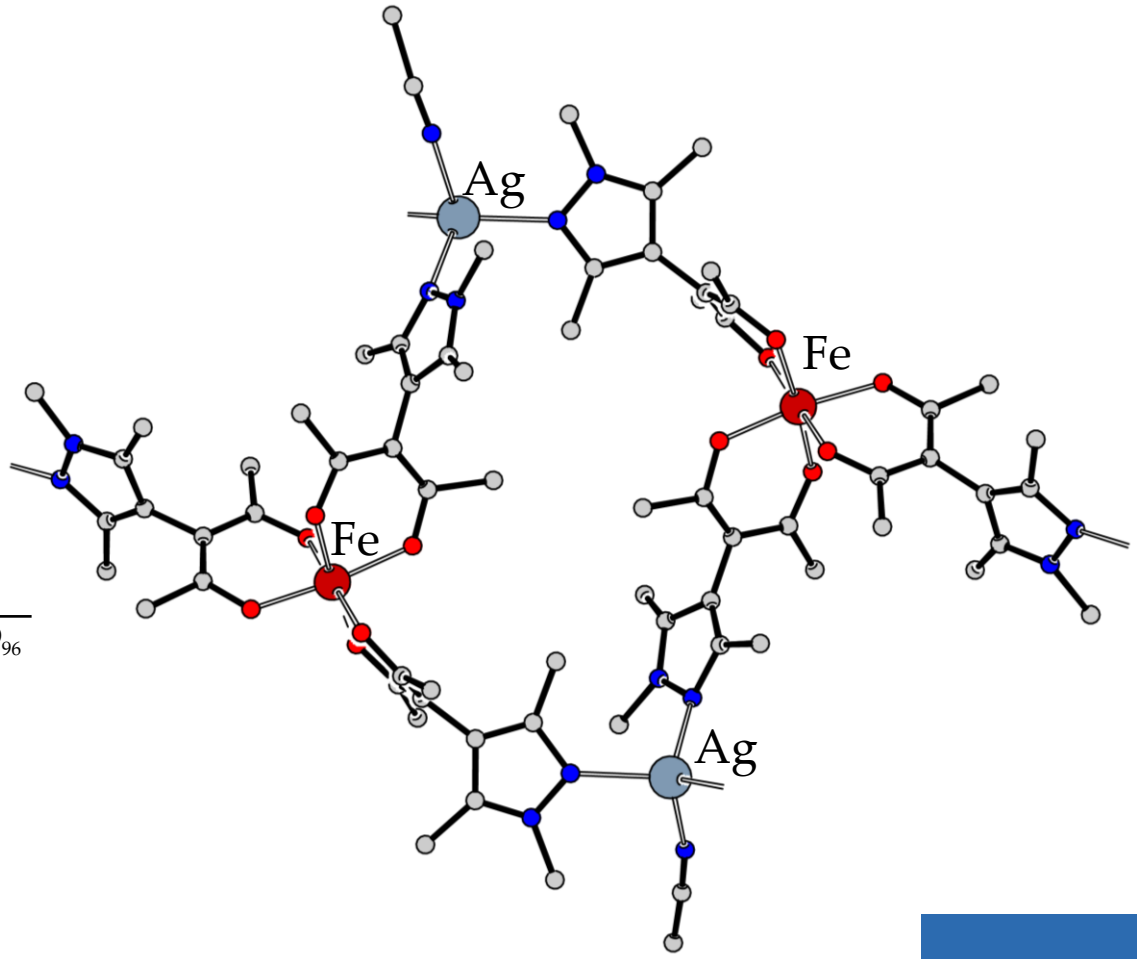
Results – Synthesis

Crosslinking with Fe^{III}/Ag^{I} leads to a 1D polymer **1**:



1. $Fe(NO_3)_3$
2. $AgClO_4$

MeCN



1

composition	$C_{560}H_{768}Ag_{16}Fe_{16}N_{112}O_{96}$
Crystal system	orthorhombic
Space Group	*Fdd*2
a / Å	53.3047(8)
b / Å	70.5917(12)
c / Å	15.1465(3)
V / Å	56994.3(17)
Z	2
$\theta_{min/max}$(Cu-K_α)	2.08/58.2
total/unique/observed refl.	144676/19245/10675
$R_1[I > 2\sigma(I)]$	12.92 %
wR_2[all data]	22.75 %
S	0.962

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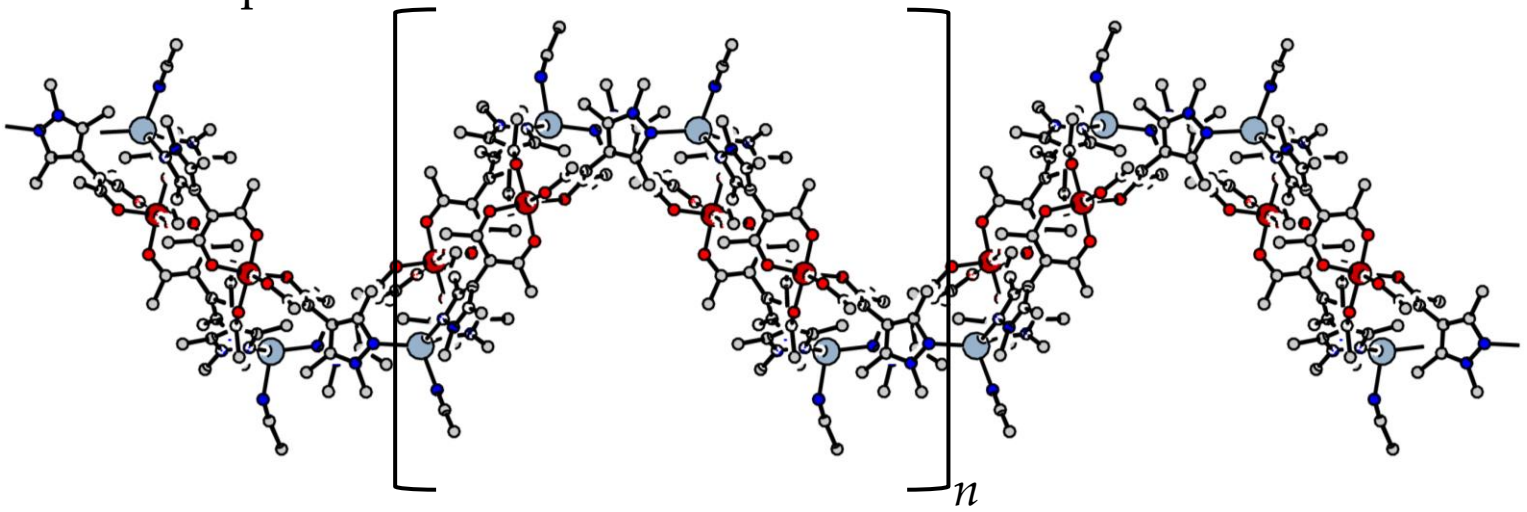
Results – Topology

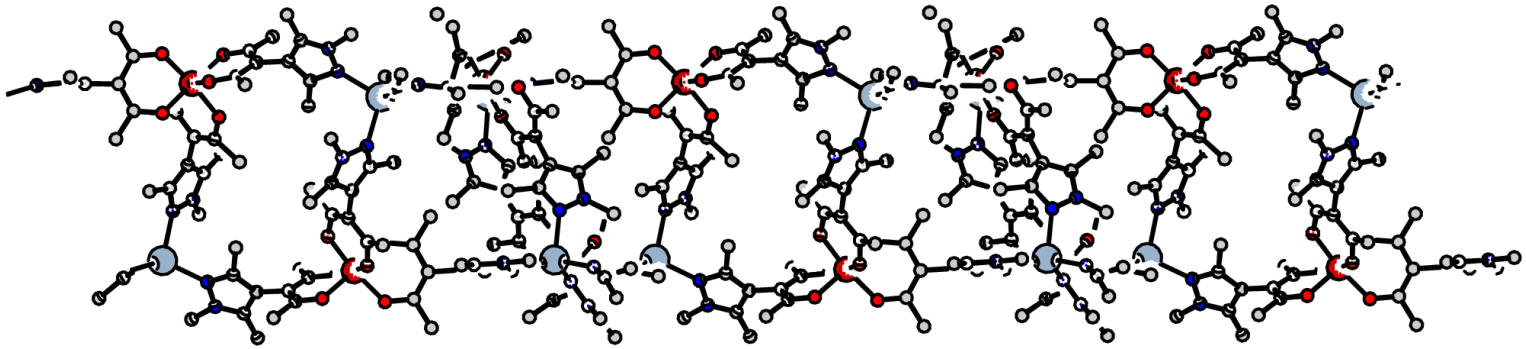
The chain polymer propagates in a wave-like fashion:

View from the *ab* plane:

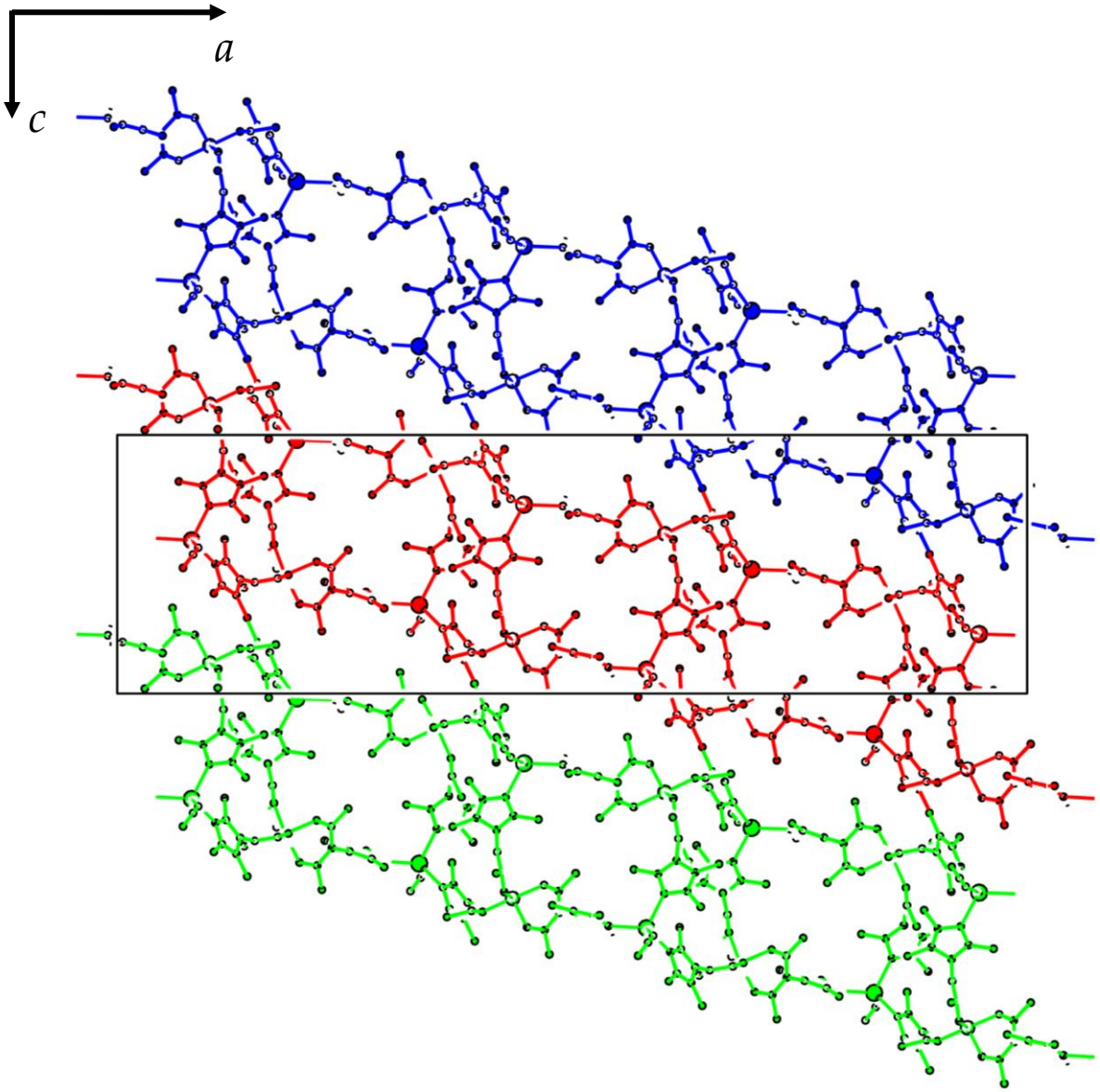


The chains exhibit ligands as crosslinkers between two strands, forming a ladder-like chain:

View from the *ac* plane:



Results – Topology



The polymer propagates in [1 0 1] direction. Three different strands are depicted on the right.

The point symbol for this coordination polymer is $4^1.4^1.6^1$.

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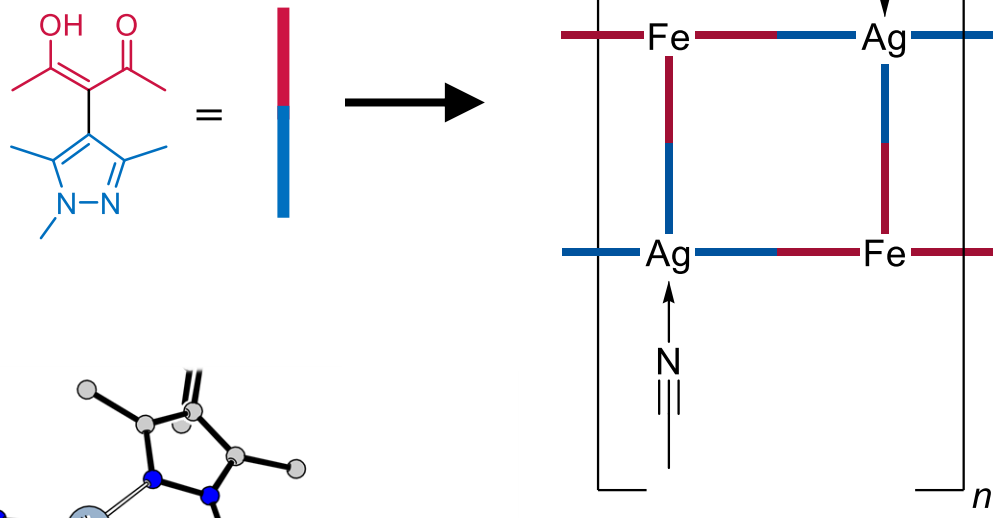
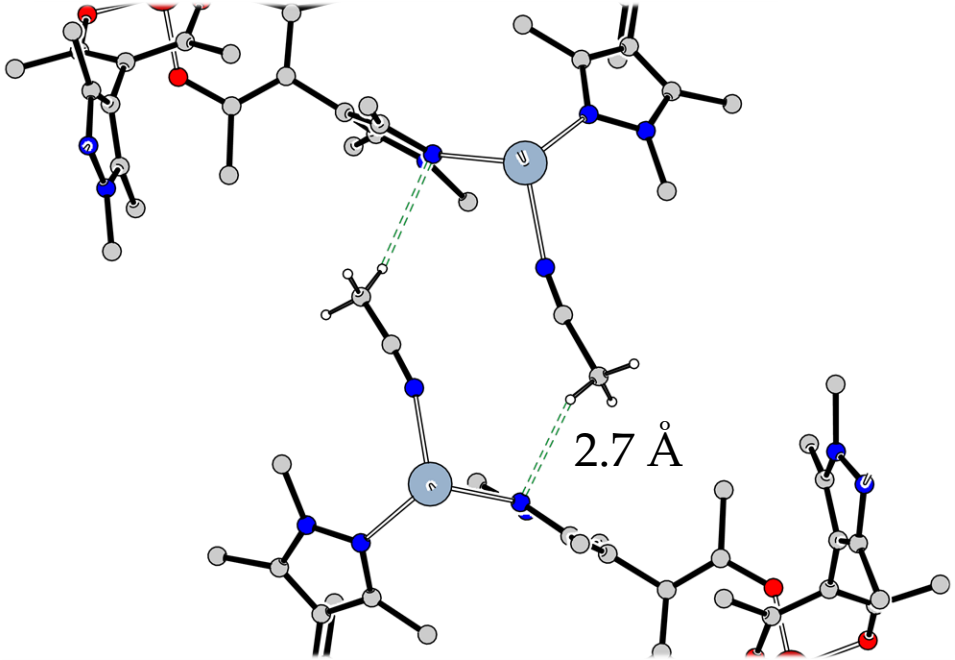
Results – Topology

simplified representation of the 1D polymer:



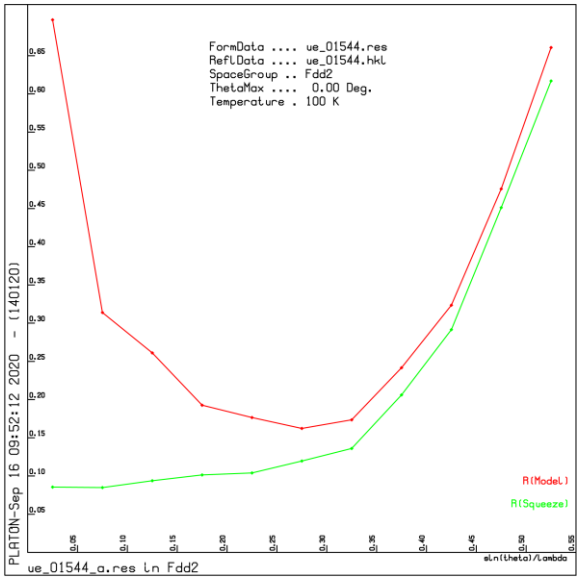
There are no meaningful interactions between two of the ladder-like chains. The shortest distance between them amounts to 2.7 Å:

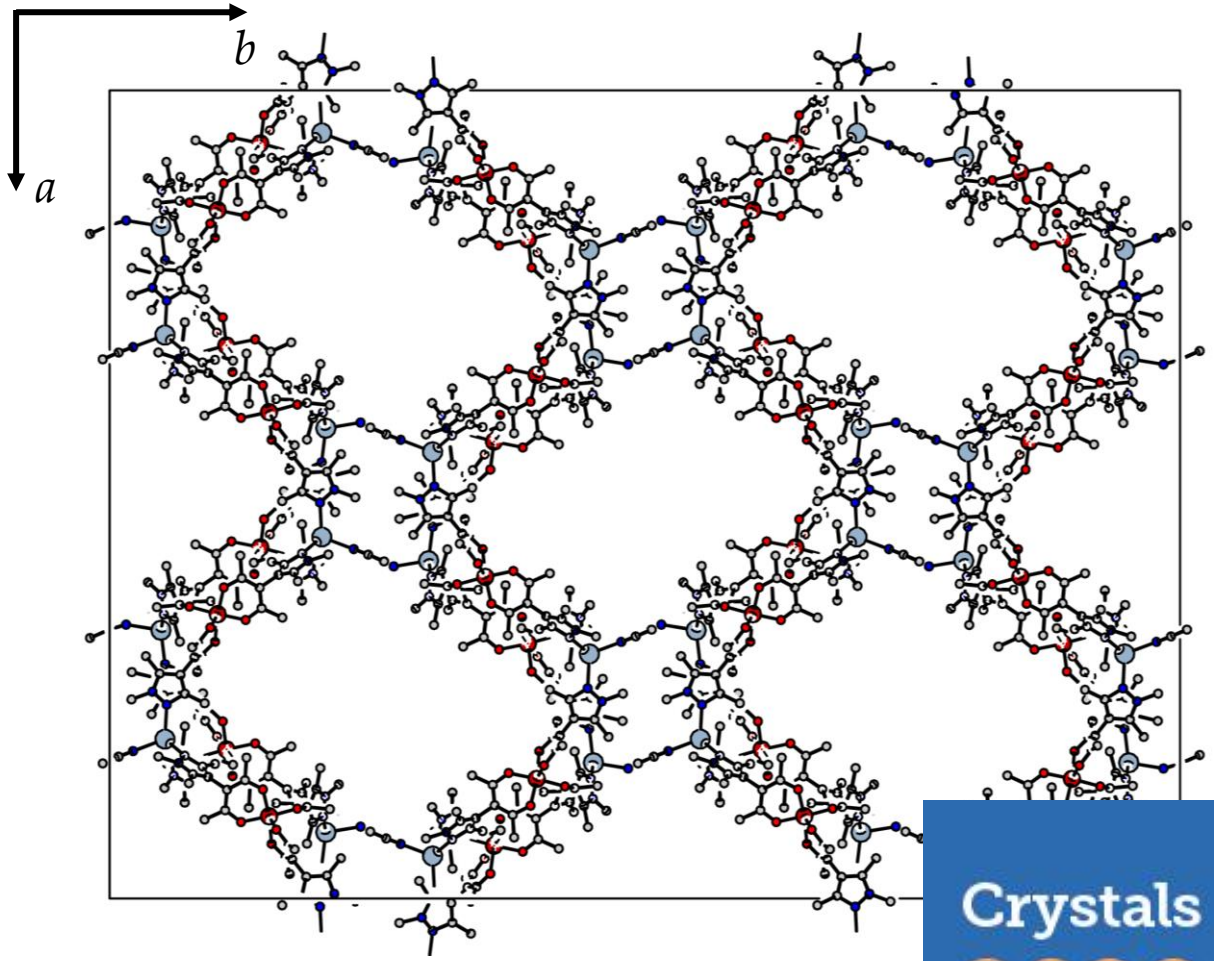


Results – Topology

There are huge solvent accessible voids in the structure. The PLATON SQUEEZE [4,5] procedure was used to determine size and electron count of the voids:

Cell volume / Å^3	56994.3(17)
Void volume / Å^3	30200
percent void of cell	53.1 %
electron count	9600
packing index	67.4 %
electron count – 32 ClO_4^-	8250
amount* of MeCN/H_2O	260
Volume* per Atom / Å^3	25





[4] A. L. Spek, *Acta Crystallogr.* **2009**, *D65*, 148–155.
[5] A. L. Spek, *Acta Crystallogr.* **2015**, *C71*, 9–18.

* assuming 32 e$^-$ and 80 Å^3 per MeCN/H_2O pair

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Conclusions

The potential of the novel ligand featuring a pyrazolyl group shows promising results for the stepwise synthesis of heterobimetallic MOFs. The coordination polymer with Fe^{III}/Ag^{I} shows large solvent-filled voids, created by the wave-like propagation of the one-dimensional chains in [1 0 1] direction.

Further investigation of the properties is planned. Thermal decomposition and, afterwards, screening for catalytic properties will be performed. The anion of the Ag^{I} salt will be altered, to investigate ist effects on the related structure. Also, the choice of different metals, e.g. Cu^{II}, could lead to interesting effects and different topologies.
If you have any questions please do not hesitate to write me an e-mail:
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