Mechanochemical Synthesis of Zinc and Cadmium Metal-Organic Frameworks – The Story of Dimensionality and Solid-State Reactivity

V. Štrukil,[a] *L. Fábián,*[b] *D. G. Reid,*[c] *M. J. Duer,*[c] *G. J. Jackson,*[d] *M. Eckert-Maksić*[a] *and T. Friščić*[c]

[a] Ruđer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia
[b] University College Cork, Cork, Ireland
[c] University of Cambridge, Lensfield Road CB21EW, Cambridge,United Kingdom
[d] University of Cape Town, Rondebosch 7700, Cape Town, South Africa

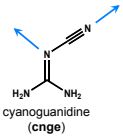
Solvent-free paradigm in a research laboratory

- direct application of the "green concepts" in metal-organic chemistry – **mechanochemical synthetic methodology**
- *completely solvent-free procedure* for the synthesis and full structural characterisation of new materials – **solid-state analytical tools**

INTRODUCTION

- **cyanoguanidine metal complexes** ⇒ the study of metal binding at two different positions:
  1. bonding through the cyano group **– monodentate ligand**
  2. both the cyano and imino groups coordinate the metal centre **– heteroditopic bridging ligand**

  ⇒ ***rational construction of MOFs with different topologies!***



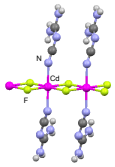
cyanoguanidine (**cnge**)

- solid-state synthesis of cadmium chloride cyanoguanidine complexes *via* mechanochemistry – ***the possibility to control the stoichiometry and dimensionality of simple MOFs??***

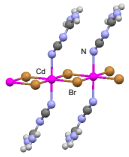
?

$CdCl_2$-**cnge** complexes

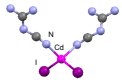
Cambridge Structural Database search:



Cd(**cnge**)$_2$F$_2$ (1-D polymer)



Cd(**cnge**)$_2$Br$_2$ (1-D polymer)



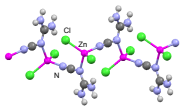
Cd(**cnge**)$_2$I$_2$ (0-D discrete)

- cadmium halide complexes – a **1 : 2** metal-to-ligand ratio
  fluoride and **bromide** ⇒ 1-D polymeric structures
  iodide ⇒ 0-D discrete assemblies

RESULTS

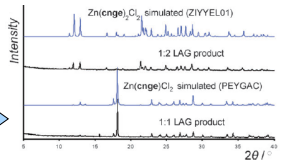
Zinc chloride complexes

- **mechanosynthesis** of known zinc chloride – cyanoguanidine 1 : 1 and 1 : 2 complexes previously obtained by crystallisation from a solution ⇒ testing the **solid-state reactivity** of **cnge** towards metal halides
- **neat** or **liquid-assisted grinding** (**LAG**) using MeCN, EtOH or $MeNO_2$

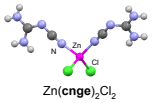


Zn(**cnge**)Cl$_2$ (1-D polymer)

1 : 1



1 : 2

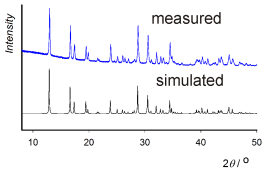


Zn(**cnge**)$_2$Cl$_2$ (0-D discrete)

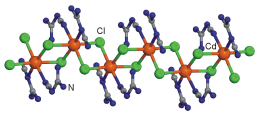
- the expected zinc coordination compounds have been prepared and identified employing the **powder X-ray diffraction** (**PXRD**) and **IR spectroscopy**
- the control of stoichiometry was achieved through the composition of the reaction mixture
- topological properties: **higher metal-to-ligand ratio ⇒ higher dimensionality MOFs**

Cadmium chloride complexes

- **neat grinding** or **LAG** of an equimolar mixture of **$CdCl_2$** and **cnge** yielded the 1 : 1 complex quantitatively in 30 minutes
- the product was obtained using either **two 7 mm diameter stainless steel balls** or **one 10 mm ball**
- **structure solution from PXRD data** revealed a **3-D framework based on octahedral Cd ions and bridging cyanoguanidine ligand**

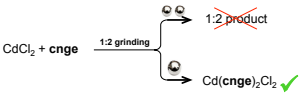


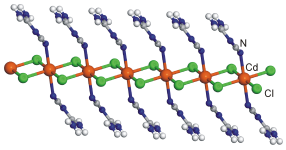
1 : 1



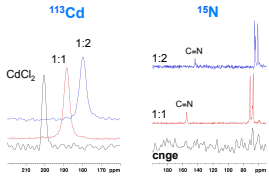
Cd(**cnge**)Cl$_2$ (3-D framework)

- an attempt to prepare the corresponding **1 : 2 complex with lower dimensionality** (lower metal-to-ligand ratio) by neat grinding or LAG:





Cd(**cnge**)$_2$Cl$_2$ (1-D polymer)

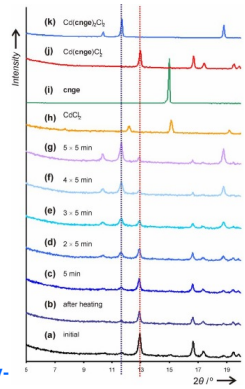


Solid-state NMR

- **harsher reaction conditions using 10 mm ball are necessary** to transform the intermediate 1 : 1 complex into the final 1 : 2 complex quantitatively
- **structure solution from PXRD data** ⇒ **monodentate binding of cyanoguanidine in a 1-D coordination polymer** (analogous to CdF_2 and $CdBr_2$)
- FTIR-ATR and solid-state ^{113}Cd, ^{13}C and ^{15}N NMR analyses of **$CdCl_2$-cnge** complexes – **exclusively solid-state analytical methods**

What influences the synthesis of $CdCl_2$-cnge 1 : 2 complex?

thermodynamic (meta)stability? **thermal effect?** **higher impact force?**



- a 1 : 2 synthesis in **a series of 5 min. grinding cycles using one 10 mm ball** ⇒ **minimisation of the thermal effect** (a)
- the major product is the 1 : 1 complex!

Impact force alone is not enough!!

- **ageing of** manually or mechanically ground **$CdCl_2$-cnge mixtures at 85 °C** ⇒ **minimisation of the mechanical effect** (b)
- the major product is again the 1 : 1 complex!

Temperature alone is not enough!!

- **pre-heating of the grinding jars at 85 °C before each 5 min. grinding cycle** (c-g)
- gradual transformation of the intermediate 1 : 1 into 1 : 2 **$CdCl_2$-cnge** complex

Combined mechanical and thermal effects!!

CONCLUSION

- **mechanosynthesis** – screening for different stoichiometries of MOFs *via* **neat** or **LAG methodologies**
- the use of a heteroditopic ligand to control the topology of MOFs
- dismantling higher dimensionality metal-organic structures requires harsher mechanochemical conditions (grinding ball size)
- an interplay of mechanical and thermal effects – the control over reactivity
- **a complete implementation of the "solvent-free paradigm" in an environmentally-friendly MOF synthesis**