SINGLE CRYSTAL TO SINGLE CRYSTAL TRANSFORMATIONS IN Co(II) TRICARBOXYLATE METAL-ORGANIC FRAMEWORKS

Presented
By

Christelle Noëlle Dzesse T.

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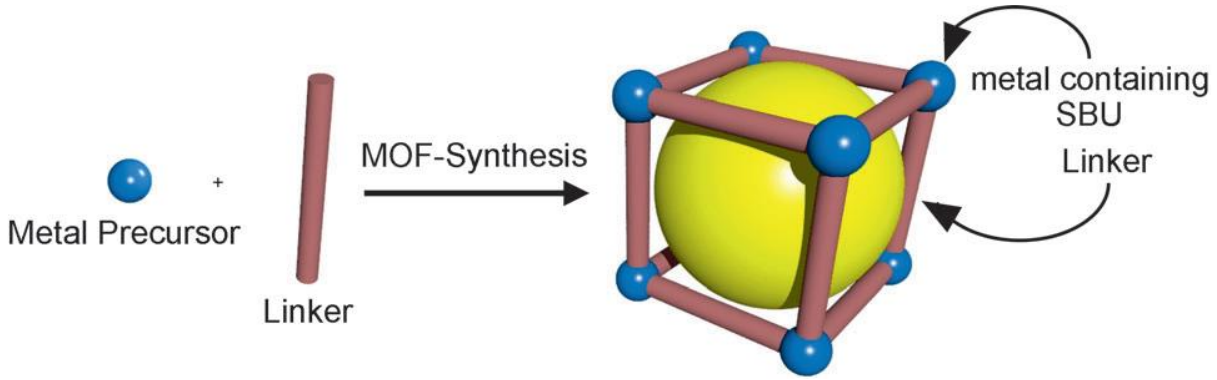
OUTLINE

- ✓INTRODUCTION/LITERATURE REVIEW
- ✓OBJECTIVES
- ✓EXPERIMENTAL
- ✓RESULTS/DISCUSSION
- ✓CONCLUSION/PERSPECTIVE
- ✓ACKNOWLEDGMENTS

INTRODUCTION / LITERATURE REVIEW

Metal-organic frameworks/MOFs are a class of crystalline materials made of metal ions/clusters which are connected to each other by rigid organic linkers to give 1D, 2D or 3D structures.



Their hybrid nature is responsible of their unique properties. Eg: High surface area. Due to their porous nature, they exhibit a lot of potential applications including gas storage and separation, sensing, selectivity, energy, catalysis, drug delivery, photocatalysis, magnetism, …

In liquid phase, molecules move freely, while their movement is confined in the solid state. However, the solid state reactions can also occur with ease if the reactive functional groups are closely and properly oriented. In ST molecules are closely bound to each other with different types of bonding forces, i.e., van der Waals, ionic, covalent, and metallic (Toda, 2002).

Schmidt *et al.* (1971) established the relationship between the structure and reactivity in solid state reactions by exposing the solid materials to light (photochemical reactions) that provided a pathway to the field of solid-state organic photochemistry and crystal engineering.

Single Crystal to Single Crystal (SCSC) transformation is a process where a single crystal is exposed to external stimuli (solvent, heat, or light and sometimes by applying mechanochemical forces) resulting in structurally transformed products (Zhang *et al.*, 2014).

SCSC transformation is fascinating because in many cases it may lead to the formation of products which otherwise cannot be designed by routine synthetic routes which help to directly visualize the change in molecular structure during the transformation process (Huang *et al.,* 2015).

These structural transformations are accompanied by a change in physical properties such as color, magnetism, porosity, luminescence, chirality, etc. as well as a change in coordination number, geometry…

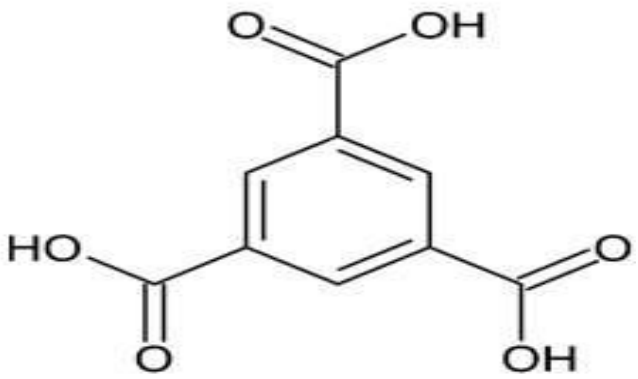
For example, the change in color of the crystals make them a potential candidate for sensor technology.

In most cases, exposing single crystals to external forces results in the loss of crystallinity. Thus, the major challenge in SCSC transformation is to retain crystallinity of the transformed single crystal which can be authenticated by X-ray diffraction techniques (SCXRD, PXRD, and recently by synchrotron facility).

OBJECTIVES

- Synthesis of novel MOFs using tricarboxylic acids and amino acids.
- Elucidate the structures of these MOFs using various instrumental techniques.
- Evaluate their ability to undergo SC/SC transformations.

EXPERIMENTAL

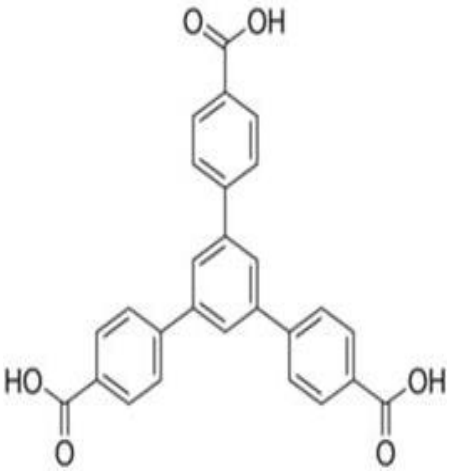


H_3BTC

Amino acid
(Pro, Glu)

or

+ or + Cobalt nitrate hexahydrate → Solvothermal conditions → 1, 2, 3, 4



4,4-bipyridine

Characterisation / SC/SC studies

H_3BTB = 1,3,5-tris(4-carboxyphenyl)benzene

Compound 1

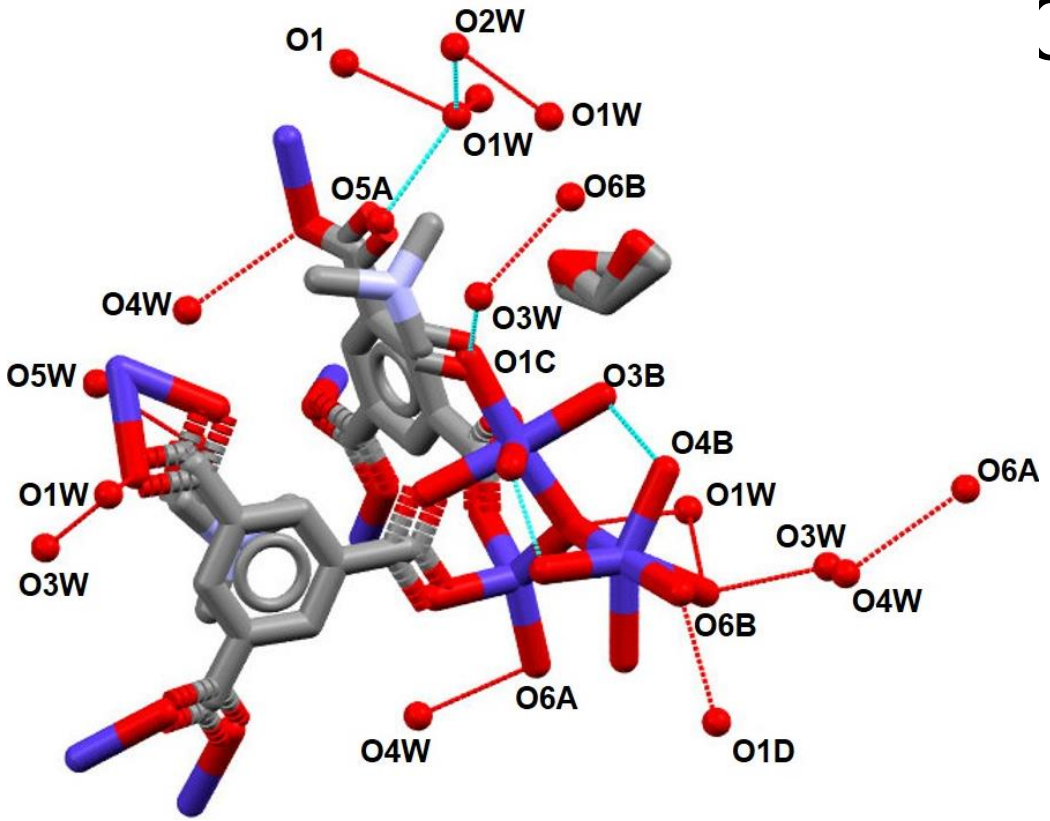


Fig 1 Coordination environment around cobalt ions in **1** with the guest molecules. Ethanol is disordered over two positions, 3 coord mod

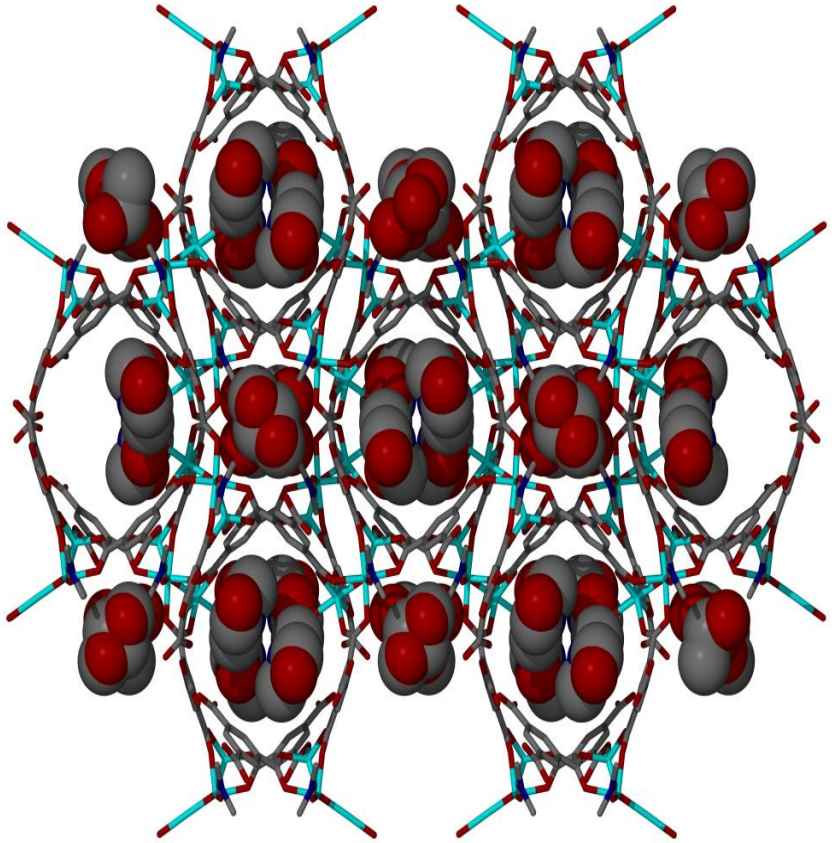


Fig 2 Packing diagram of **1** illustrating different types of pores running parallel to [001]. It has different type of channels of varying sizes which contain DMF and water, or ethanol and water molecules

- **$[Co_3(\mu_3\text{-}O)(BTC)_2(DMF)(OH_2)]_n\,(DMF)(EtOH)_{0.25}(H_2O)_{2.5}]$**
- **Orthorhombic, *Iba*2**
- **a=19.1941(9), b=21.2228(10), c=17.7926(8) Å, V= 7247.9(6) Å^3**
- **R_1= 0.0377, wR_2= 0.1572, 46661 reflections**

Compound 2

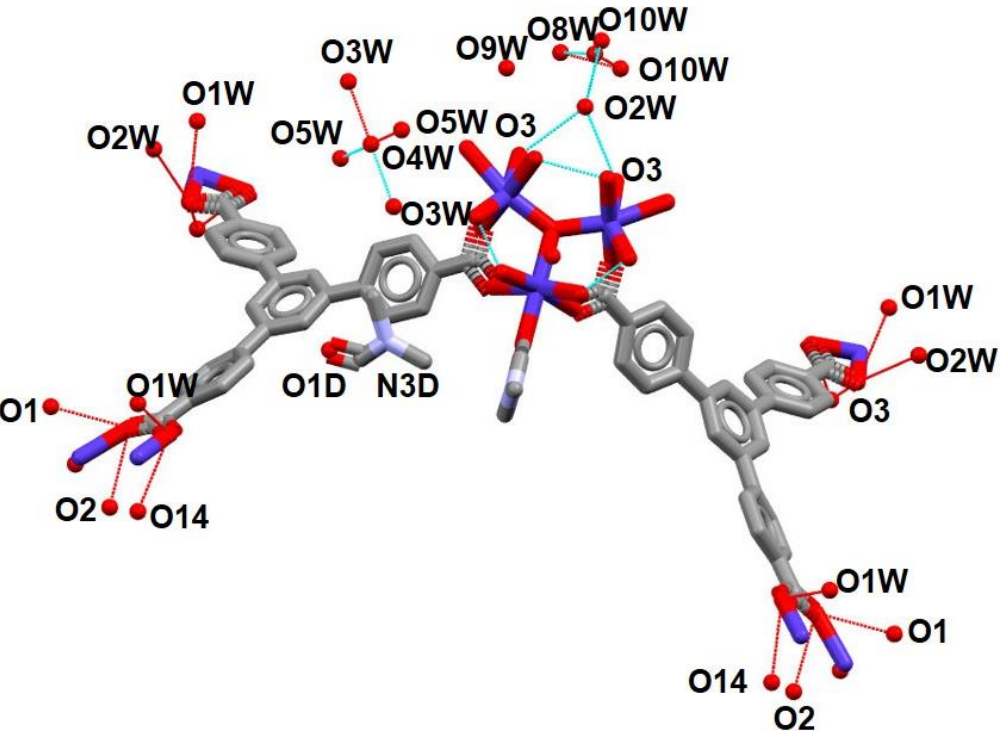


Fig 3 Coordination environment around cobalt ions in **2**, and guests, 2 coord modes.

$[Co_3(\mu_3\text{-}O)(BTB)_2(DMF)(OH_2)_2]_n\,(DMF)_2(H_2O)_{10.2}$

- Orthorhombic, *Pnma*
- a=17.3664(19), b=28.029(3), c=18.260(2) Å, V= 78888.4(17) Å^3
- R_1= 0.0714, wR_2= 0.1926; 53407 reflections

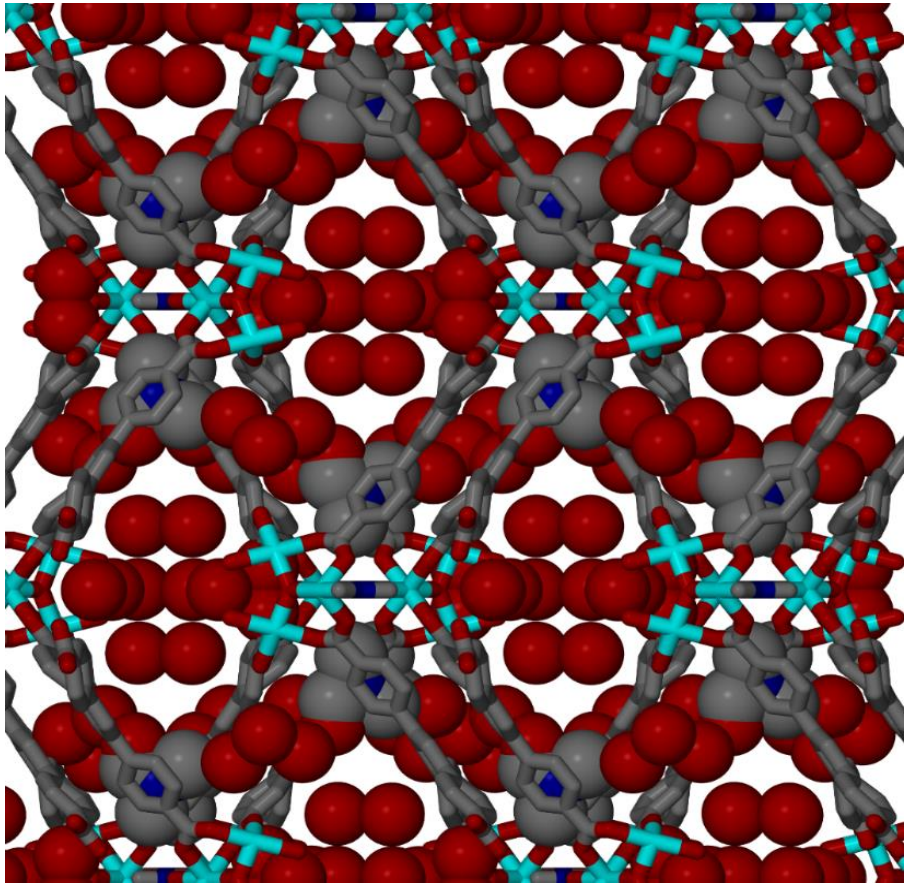


Fig 4 Packing of **2** showing large channels running parallel to [100] which contain water molecules. DMF is contained in pores and close to the metal centre.

Compound 3

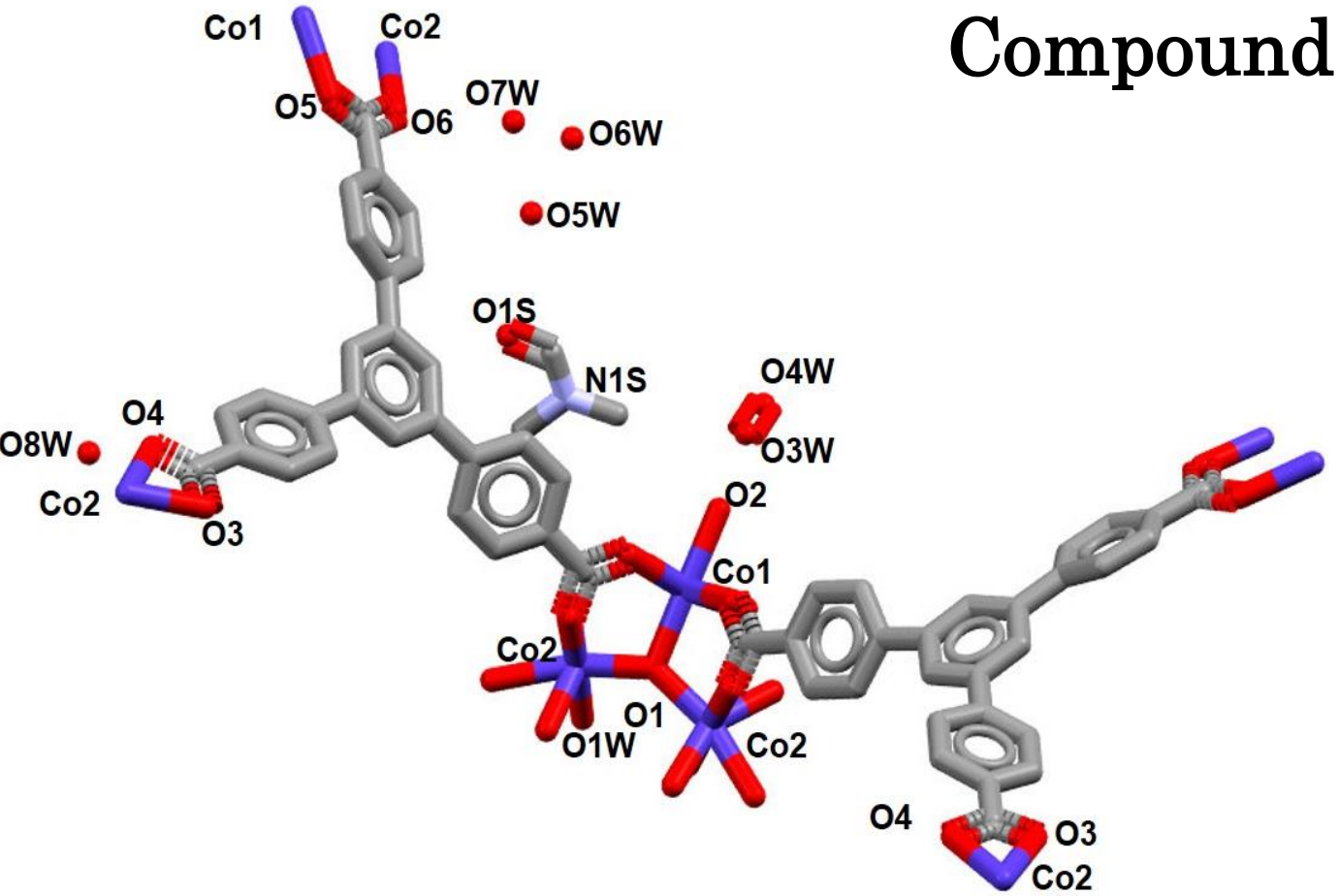


Fig 5 Coordination environment around cobalt ions in **3,** with the guests, 2 coord modes.

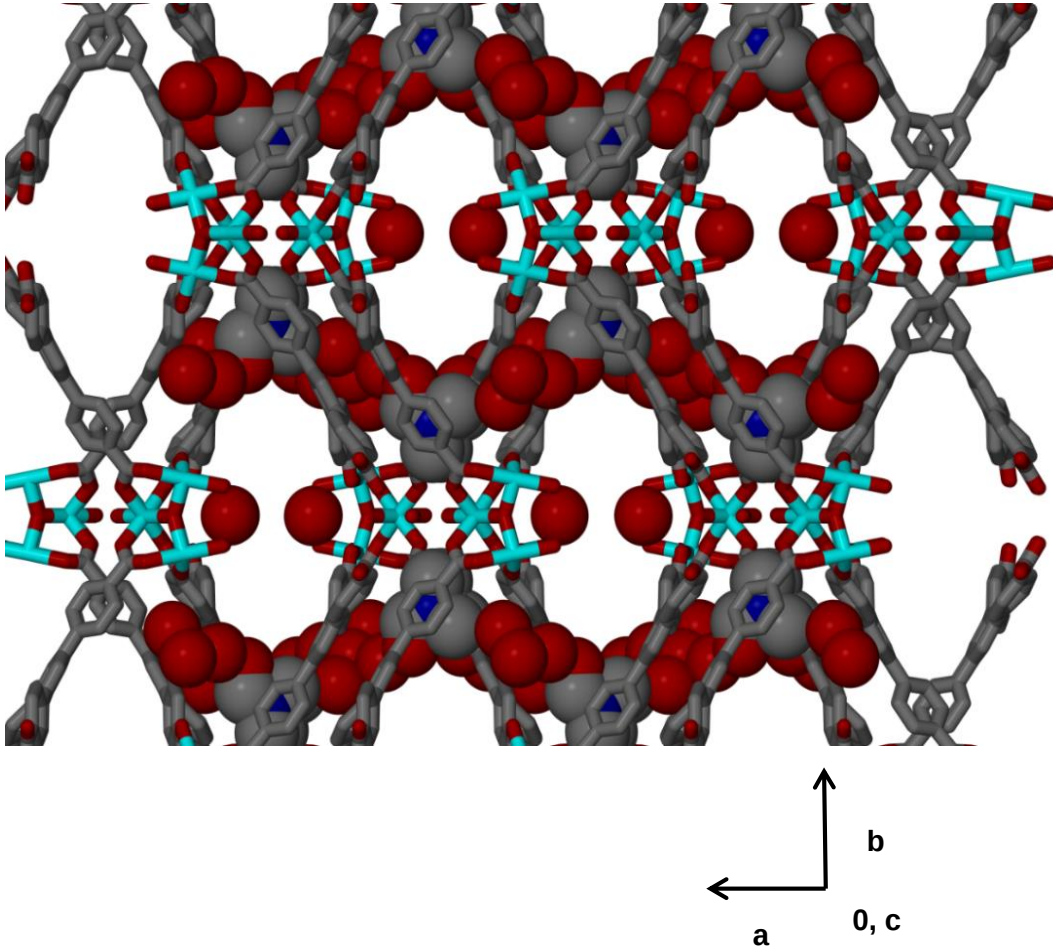


Fig 6 Packing of **3** showing large channels running parallel to [100] which contain water molecules.

- $[Co_3(\mu_3\text{-}O)(BTC)_2(DMF)(OH_2)]_n\,(DMF)(EtOH)_{0.25}(H_2O)_{2.5}]$
- Orthorhombic, *Pnma*
- a=17.360(7), b=28.618(11), c=17.303(7) Å, V= 8596(6) Å^3
- R_1= 0.0347, wR_2= 00.1133; 140529 reflections

Compounds 4 & 4’

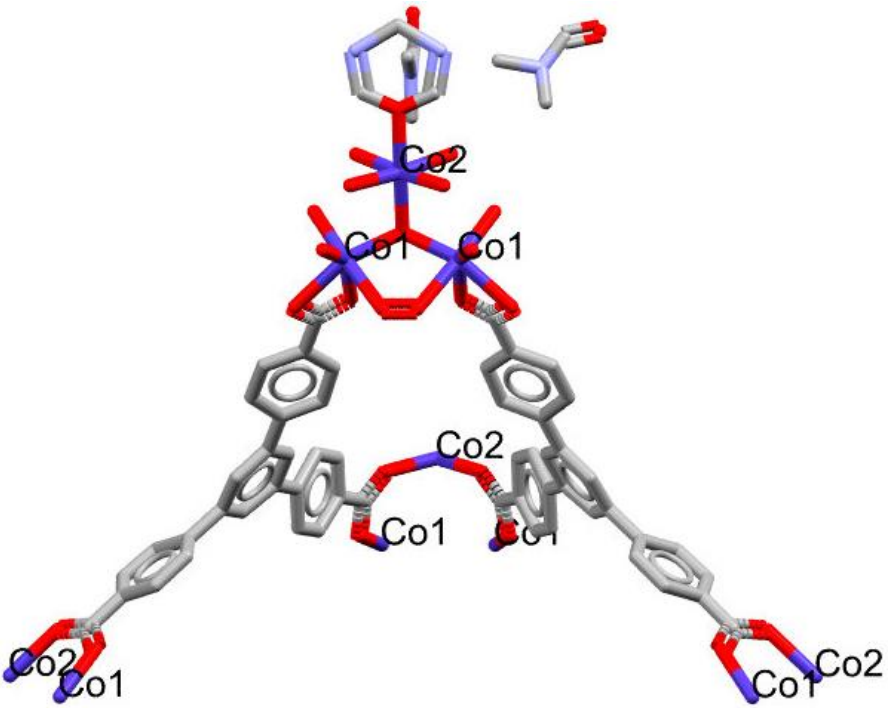


Fig 7 Coordination environment around cobalt ions in **4**

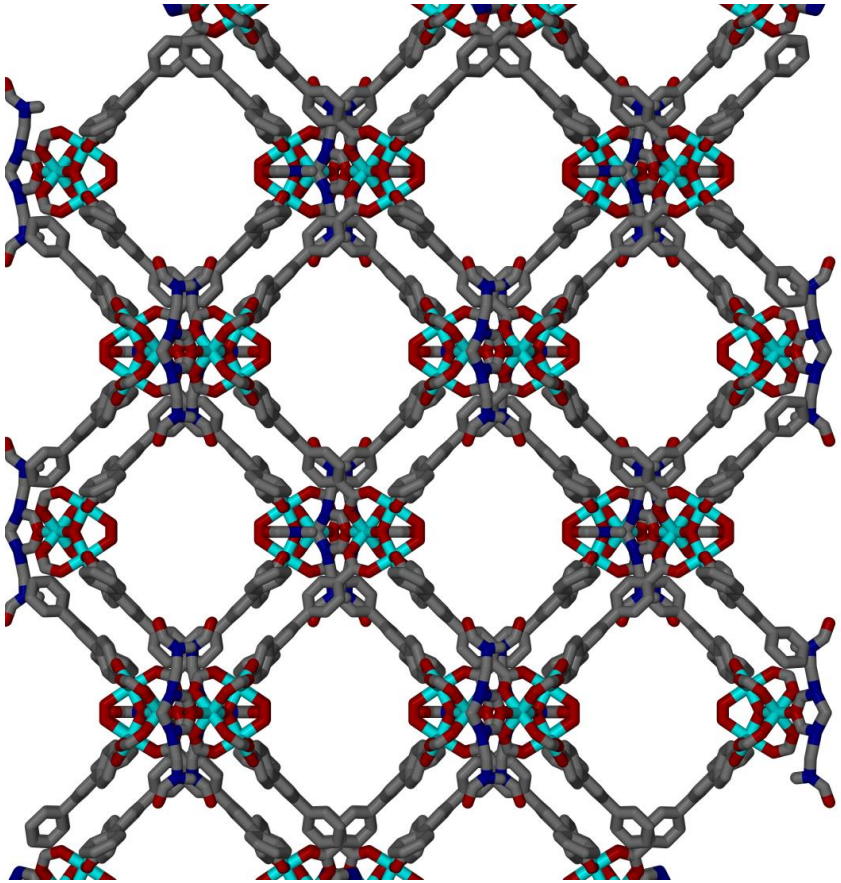
- $[[Co_{1.5}(\mu_3\text{-}O)_{0.5}BTB(OH_2)(DMF)_{0.5}](DMF)_{0.5}(H_2O)_{5.8}$
- Orthorhombic, *Pnma*
- a=17.39(6), b=21.92(7), c=25.03(9) Å,

V= 9657(5) Å^3

- R_1=0.0917 , wR_2= 0.2947; 118723 reflections

Compound 4’ , reported, Yao *et al.,* 2012:

- $Co_{0.25}C_{6.75}H_{4.5}N_{0.25}O$
- Cubic, *Pm*-3*n*
- a= b=c=27.65(6) Å, V= 21144.32 Å^3



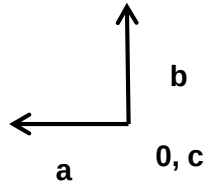
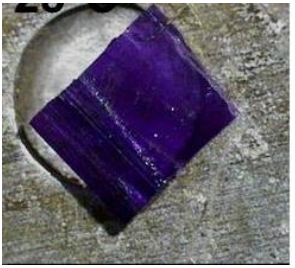


Fig 8 Packing of 4 showing large channels running parallel to [100] which contain water molecules. The cooordinated DMF is close to the metal centre and connected to the other uncoordinated DMF which is disordered over two positions.

SC/SC transformation studies

1

or



2

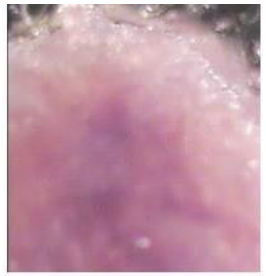
Soaked in DMF
or EtOH solution of Cu,
Zn or Ni salt

?

or

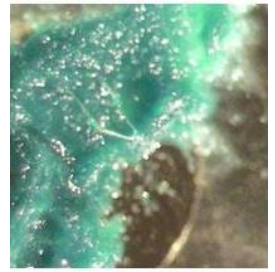
4

Compound 1

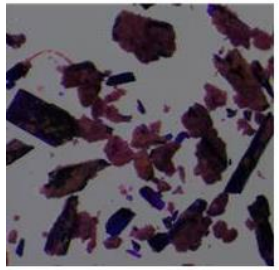


1-Zn

1



1-Cu



1-Ni

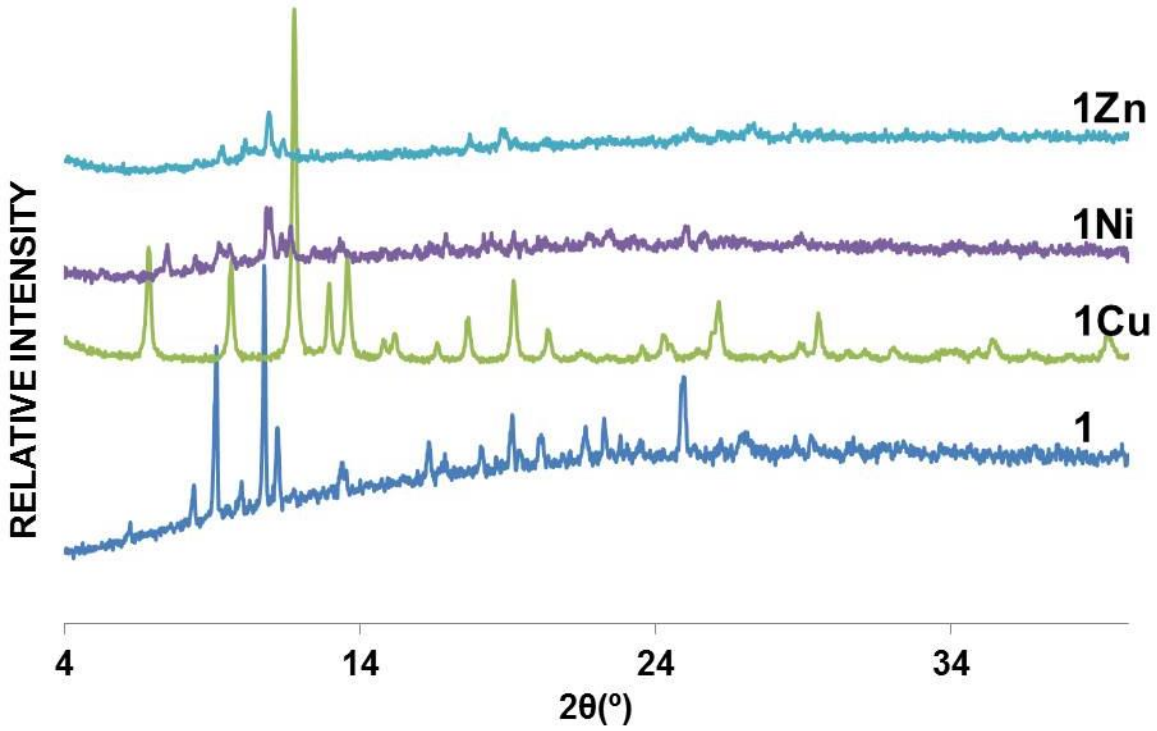


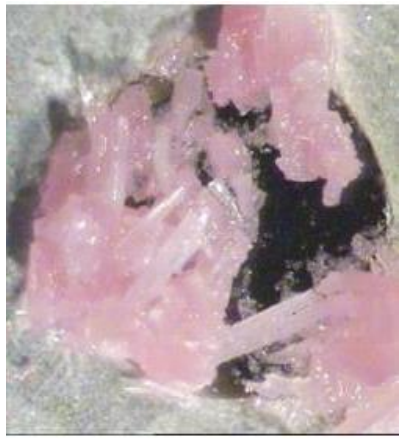
Fig 9 PXRD profile of **1** and its metalated samples.

Table 1 Metal ion ration in **1** after analysis by ICP-AES.

Samples	Elements / Metal molar ratio (%)			
	Co	Cu	Zn	Ni
1 crystals in EtOH solution of $Cu(NO_3)_2.3H_2O$	0	100	/	/
1 crystals in EtOH solution of $Zn(NO_3)_2.6H_2O$	0	/	100	/
1 crystals in EtOH solution of $Ni(NO_3)_2.6H_2O$	63	/	/	37
1 crystals in DMF solution of $Cu(NO_3)_2.3H_2O$	80	20	/	/
1 crystals in DMF solution of $Zn(NO_3)_2.6H_2O$	73	/	27	/
1 crystals in DMF solution of $Ni(NO_3)_2.6H_2O$	99	/	/	1

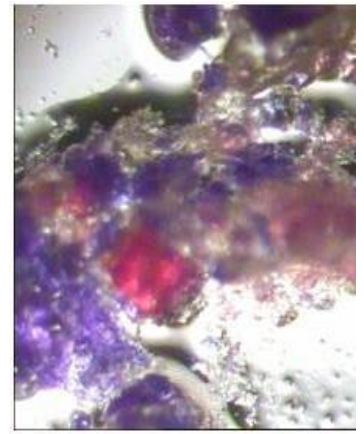
Compound 2

2- Cu



2- Zn

2



2- Ni

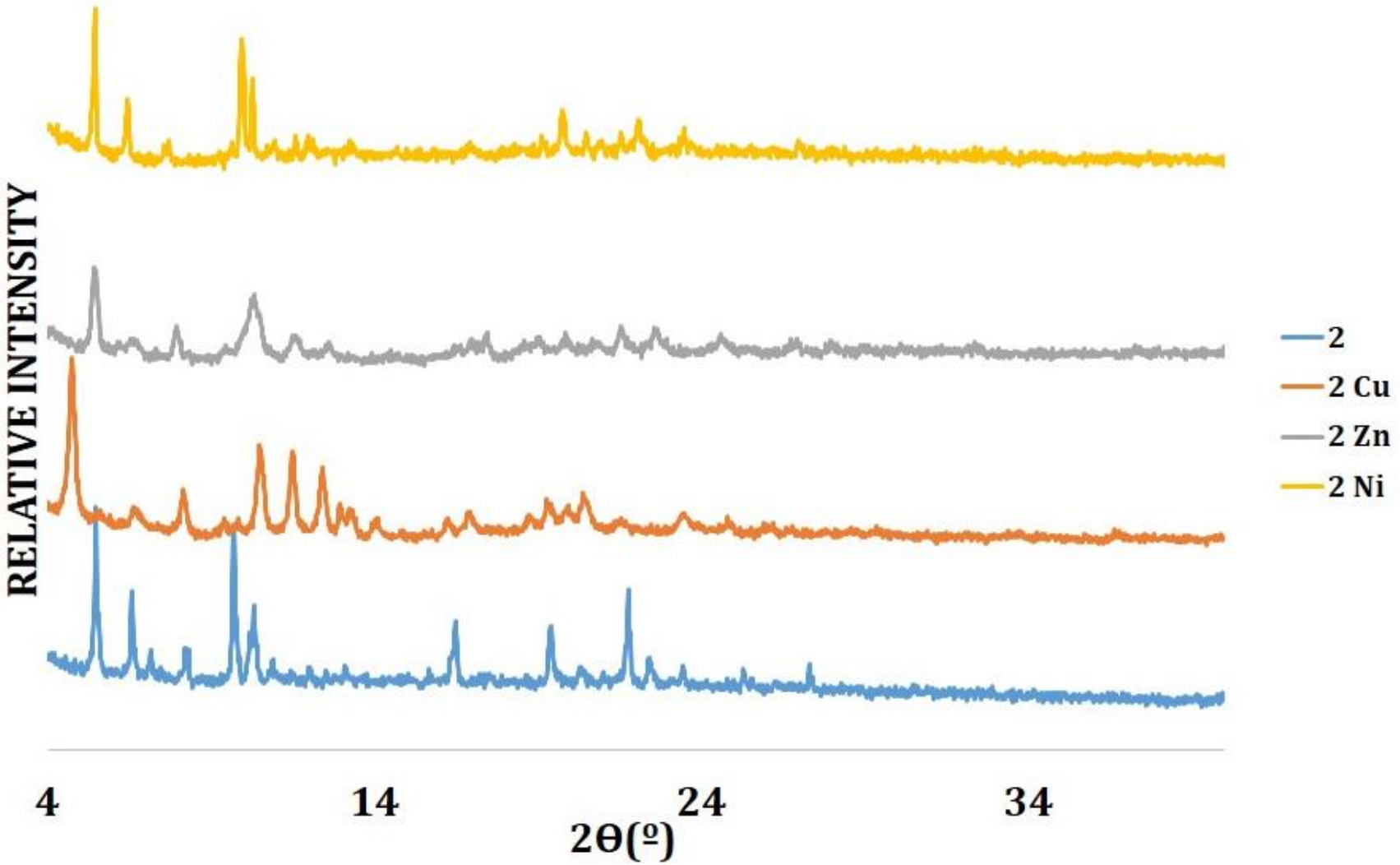
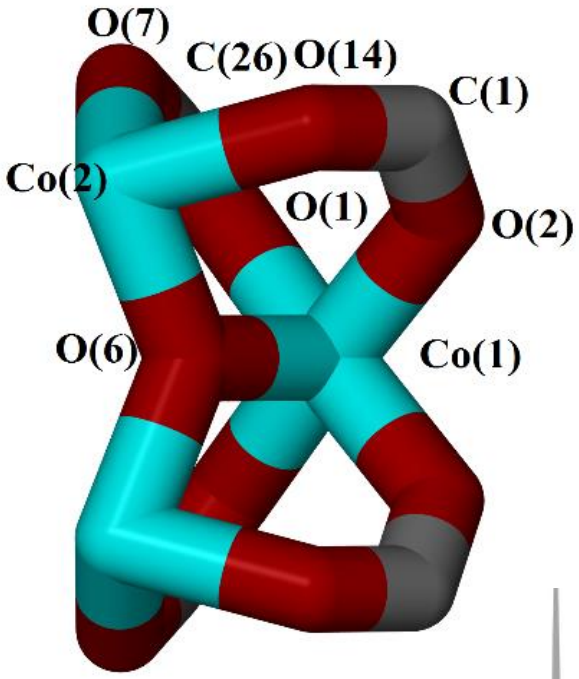
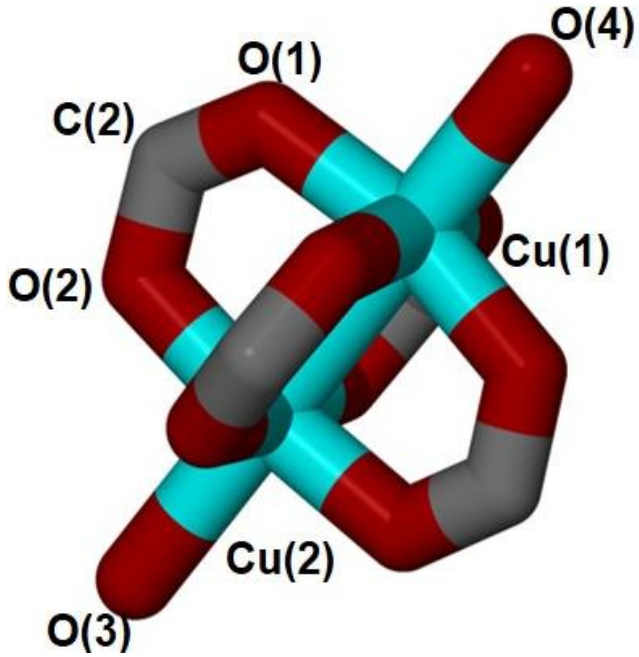


Fig 11 Photographs of **2** (purple) and its metalated samples.



2



2-Cu/QOWRAV02

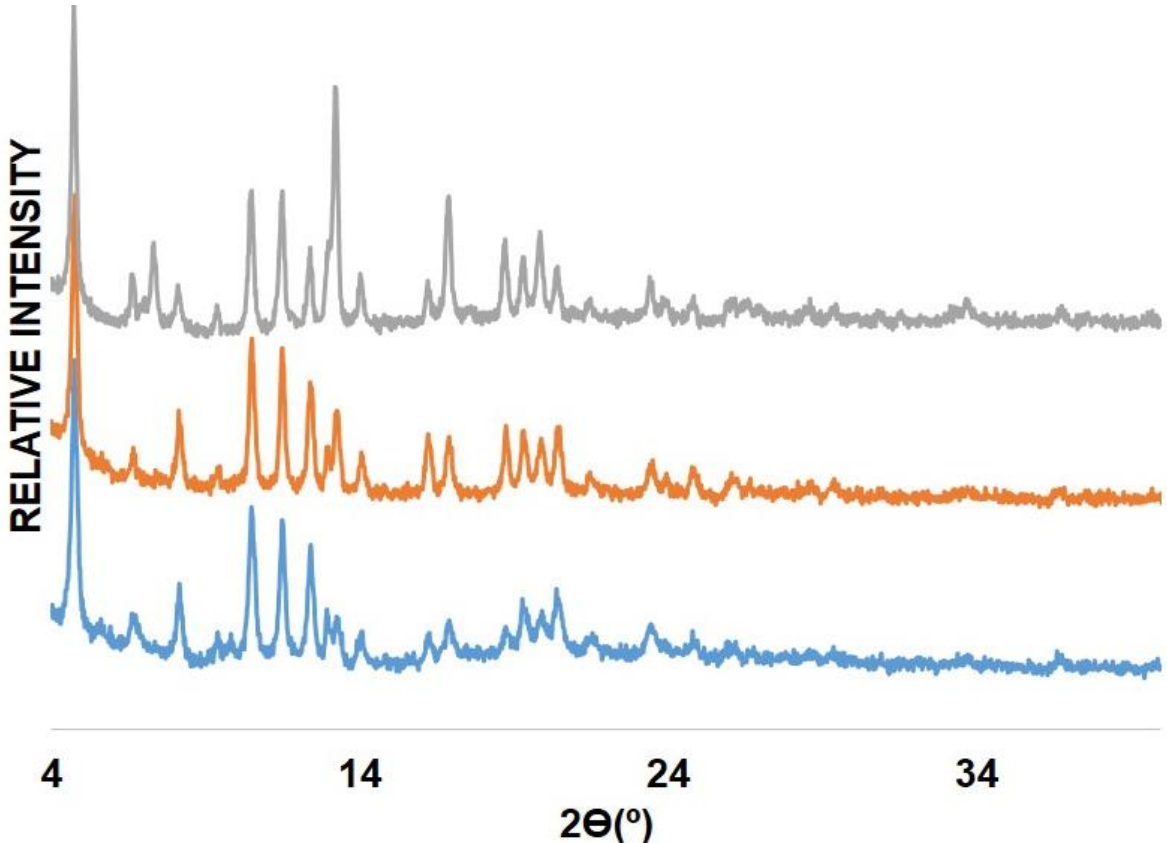


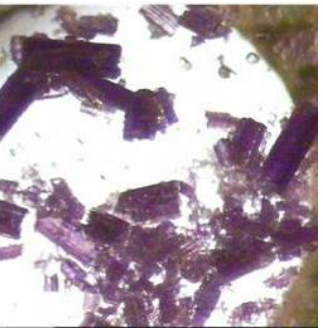
Fig 12 PXRD of **2-Cu** (blue),

2-Cu in hydrated Cobalt nitrate salt

for a month (orange) and after two and half months (grey).

Compounds 4 & 4’

4-Cu



4-Ni

4

4-Zn

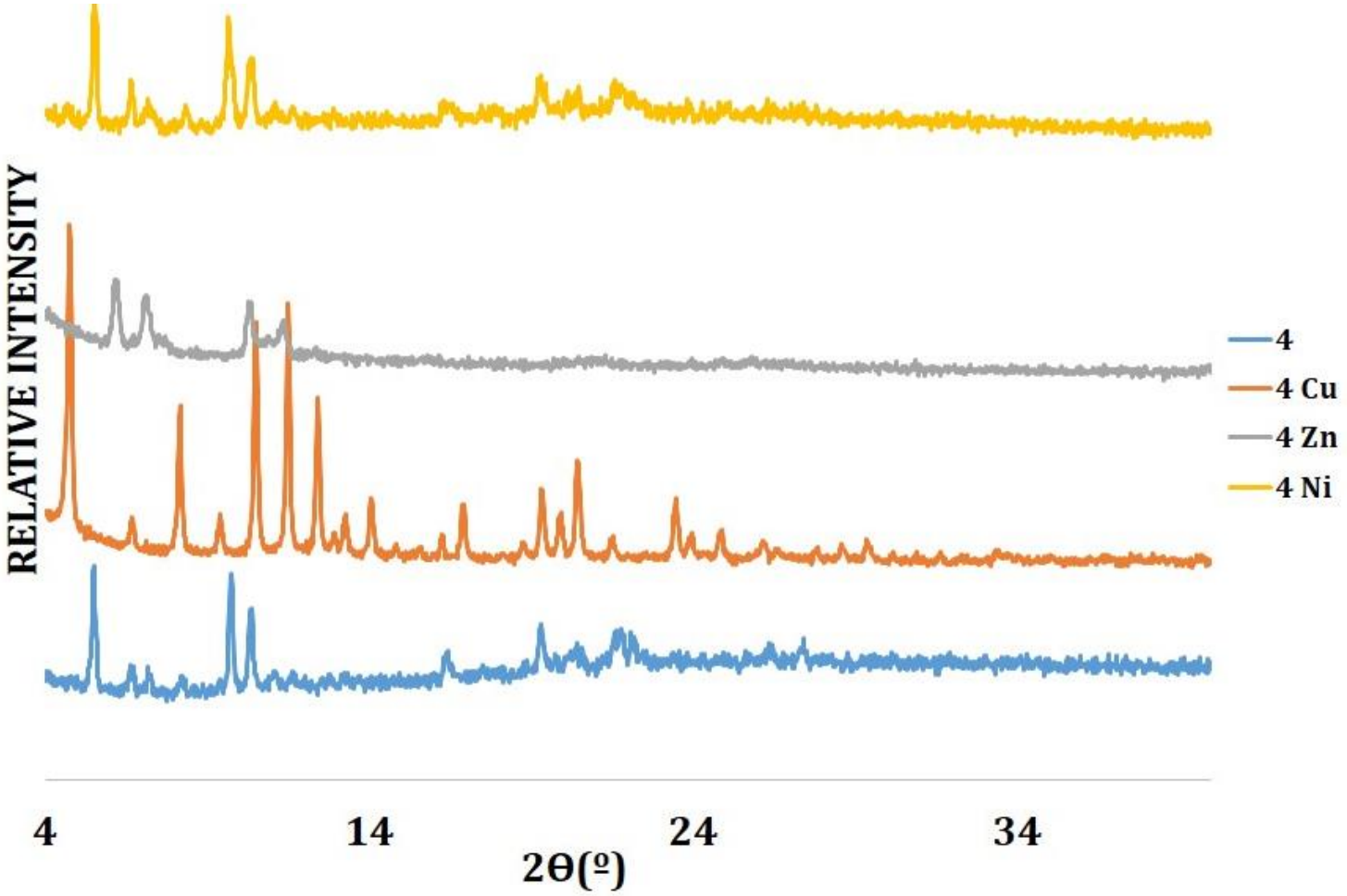


Fig13 PXRD profile of **4** and its metalated analogues

Conclusion/perspective

- Four novel compounds were synthesized and fully characterised by various techniques.
- Compounds **1**, **2** and **4** were used for single crystal solid state studies, where new structures were obtained, no study done on **3**.
- Use Rietveld refinement to rebuild the structures of all the new compounds obtained, so as to undertand the mechanism of interaction of both guests and frameworks.
- Investigate magnetic behaviour and other properties of the both parents and daughter MOFs.
- The use of different synthetic methods to grow crystals of structures that were found new. allow to analyse them using SCXRD diffraction and get the exact structure of the compounds.

Acknowledgements

THANKS FOR YOUR KIND ATTENTION