

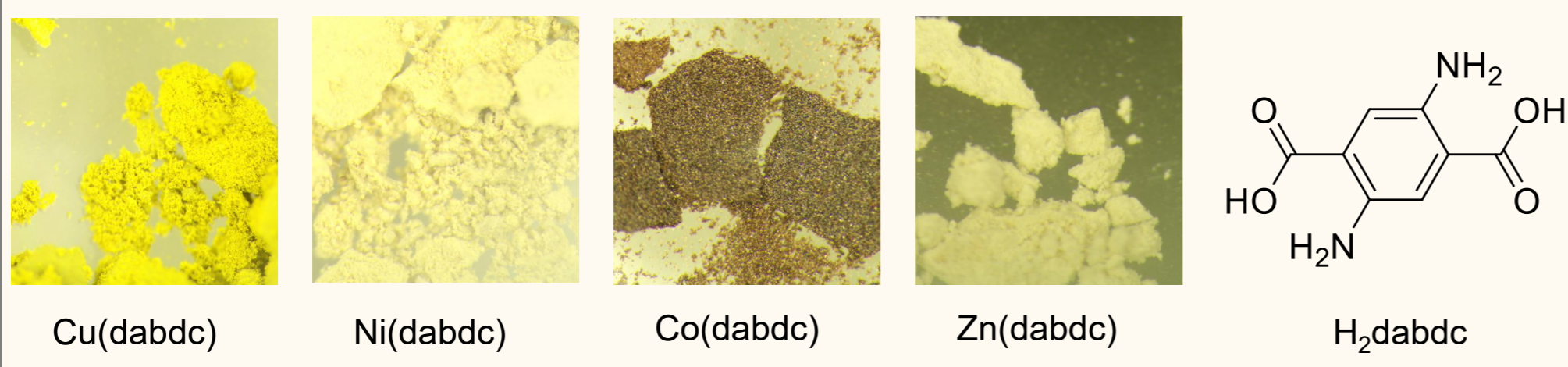
# Nonporous coordination polymers in the search of the porous

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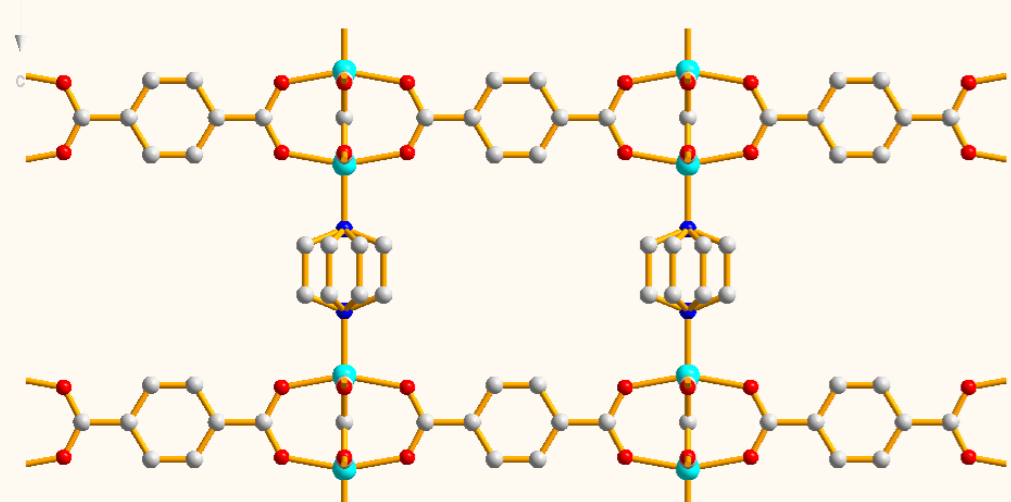
## Abstract

A series of syntheses were carried out with the aim to prepare pillared-layered MOFs isorecticular to  $M_2(bdc)_2(dabco)$ , where the benzene-1,4-dicarboxylate linker is substituted by 2,5-diaminobenzene-1,4-dicarboxylate. While these attempts were unsuccessful to date, a series of non-porous coordination polymers was obtained and identified as  $M(dabdc)$  (with  $M = Co, Cu, Zn, Ni$ ) instead.



## Introduction

In the  $M_2L_2(dabco)$  MOFs, paddle wheels of the metal ions (typically Zn, Cu, Ni, Co) are linked by ditopic linkers, such as benzene-1,4-dicarboxylate (bdc), into layers that are connected in the third dimension (the pillars) through 1,4-diazabicyclo[2.2.2]octane (dabco) at the apex of the square-pyramidal coordination environment of the metal ions.[1]



Composition of the MOF using bdc and dabco.

This structure has already been replicated with 2-aminobenzene-1,4-dicarboxylic acid (abdc) [2] and other bdc derivatives, which imbues the MOFs with different properties for gas adsorption.[3]

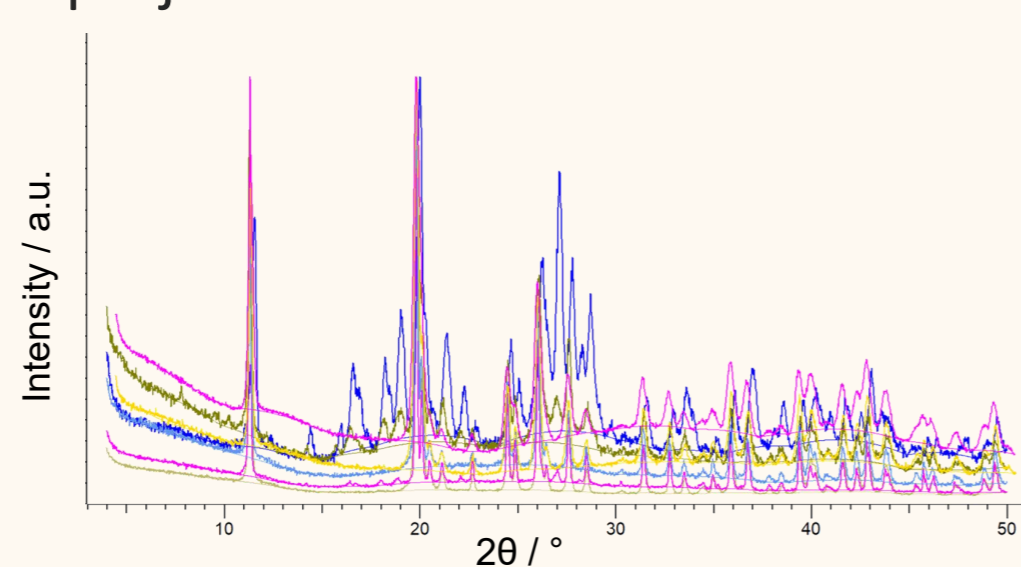
The aim of this project is the preparation of  $M_2L_2(dabco)$  MOFs with 2,5-diamino-functionalized bdc (dabdc), with the expectation that an increase in the number of amino-groups increases the aptitude of the MOF for carbon dioxide capture.



## Method

The syntheses were based on a general procedure for obtaining  $M_2L_2(dabco)$  MOFs, where a 1:1:0.5 ratio of metal salt of Co, Cu, Zn, Ni,  $H_4dabdc$ , and dabco is reacted in DMF for 24 h at 110 °C under solvothermal conditions.

Concentrations of reactants, solvent system, temperature and reaction time were varied throughout the project.



Handful of PXRD patterns from syntheses. Despite the varying peaks, there are some noticeable repeating ones, specifically the ones at 11 and 20°. Wavelength: 1.54060 Å.

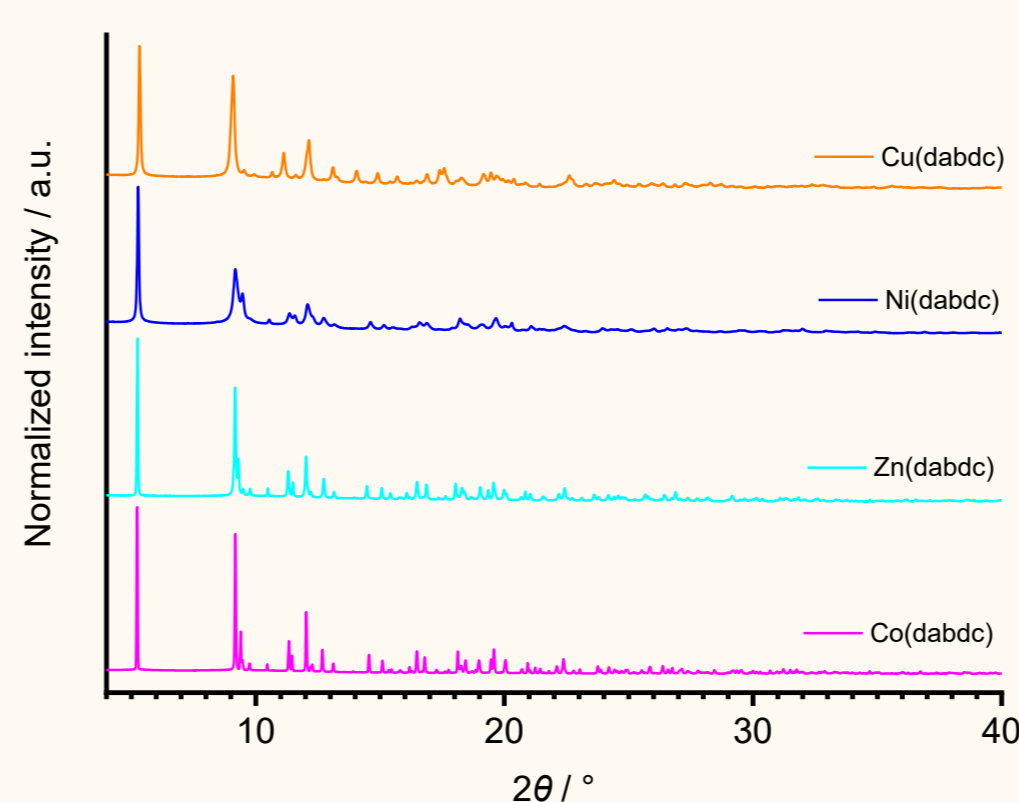
After over 50 syntheses no product corresponding to the target system had been produced. However, some possibly non-porous compounds (based on the appearance of the powder X-ray diffraction data) repeatedly formed, so it was decided to prepare phase pure samples of these for analysis. These were measured with home-lab PXRD to check for phase-purity and subsequently measured at the ESRF synchrotron facility to get high resolution information for solving the structure.

The used reactants in preparing nonporous  $M(dabdc)$ .

Metal	Additional Reactant	Solvent	Temp.
Co	dabco (×0.5)	DMF, H <sub>2</sub> O, HBF <sub>4</sub> (10:0.4:0.4 mL)	120
Cu	NaOH (×2)	EtOH, H <sub>2</sub> O (8:2 mL)	110
Zn	dabco (×2)	DMF (10 mL)	160
Ni	dabco (×2)	DMF (10 mL)	160

## Results

The powder X-ray diffraction patterns observed matched with the pattern of a non-porous structure of  $Mg(dabdc)$ , previously observed by another member of the research group. Following this, the various non-porous samples from these syntheses were identified as  $Co(dabdc)$ ,  $Cu(dabdc)$ ,  $Zn(dabdc)$ , and  $Ni(dabdc)$ .



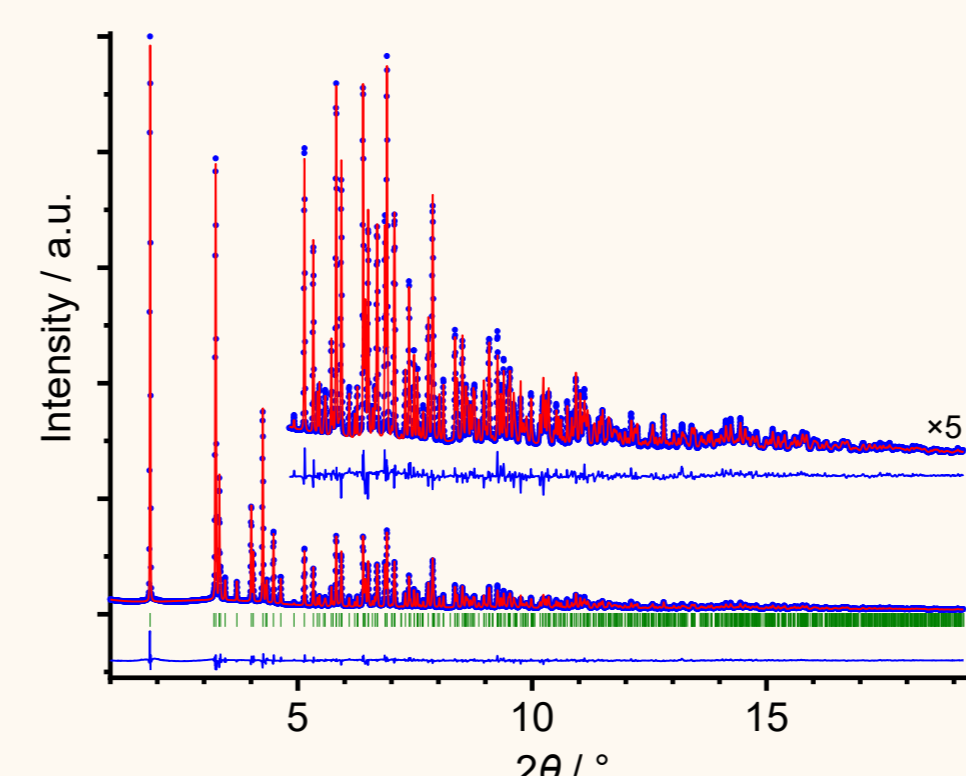
PXRD patterns of Co, Zn, Ni, Cu (dabdc) measured in synchrotron radiation, wavelength 0.718220 Å.

The slight difference in angle and intensity can be explained by respectively a slight variation in composition and lattice parameters.

Lattice parameters of the compounds, all of which are monoclinic with space group P12/c

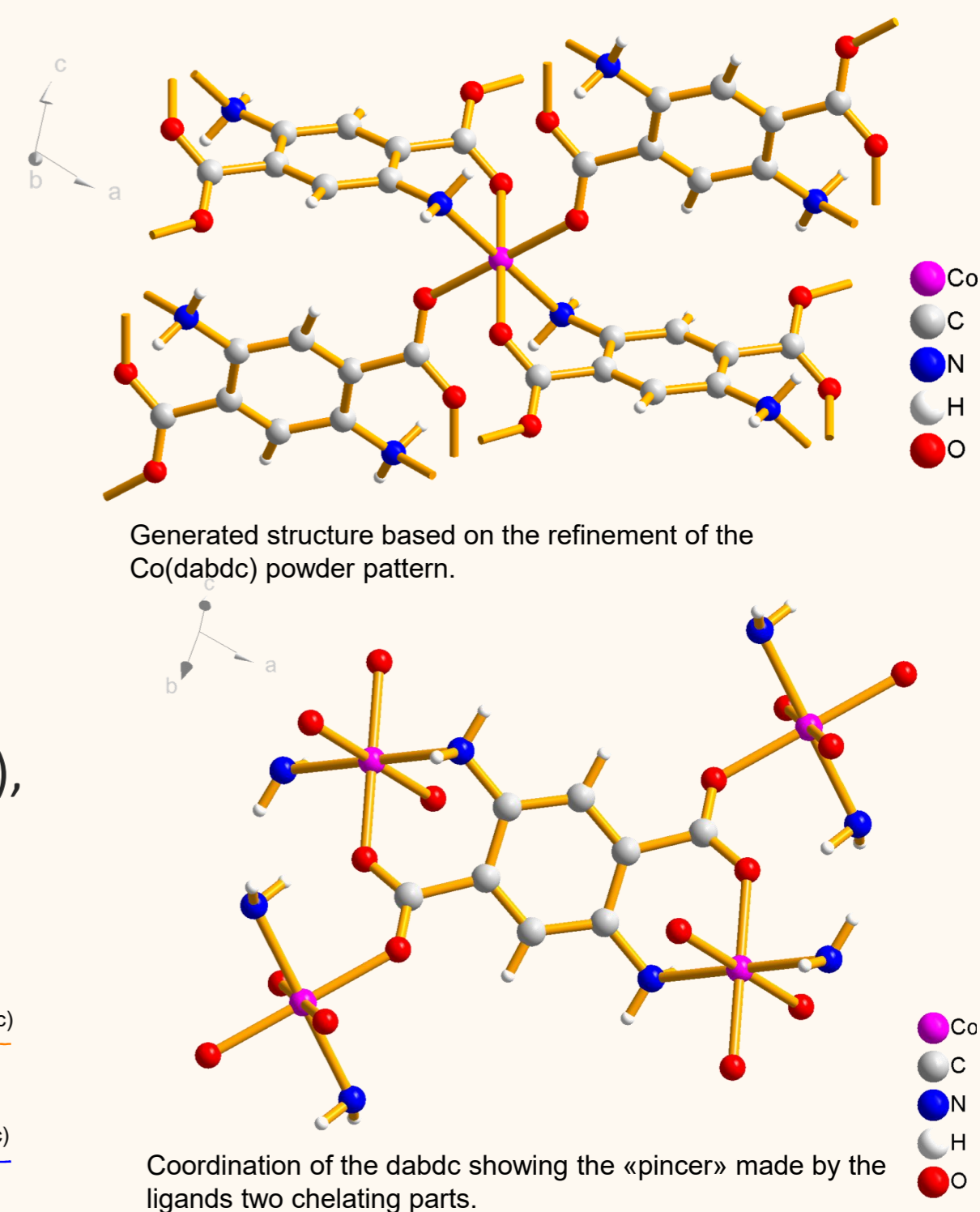
Compound	a / Å	b / Å	c / Å	$\beta$ / °	Cell volume / Å <sup>3</sup>
Cu(dabdc)	8.008	5.212	9.467	105.08	381.852
Ni(dabdc)	8.290	5.219	9.142	109.61	376.708
Zn(dabdc)	8.312	5.210	9.383	109.29	384.039
Co(dabdc)	8.349	5.226	9.305	109.79	382.145

$Co(dabdc)$  had the best resolved diffraction pattern. A structural model was obtained by simulated annealing and the crystal structure confirmed by subsequent Rietveld refinement.

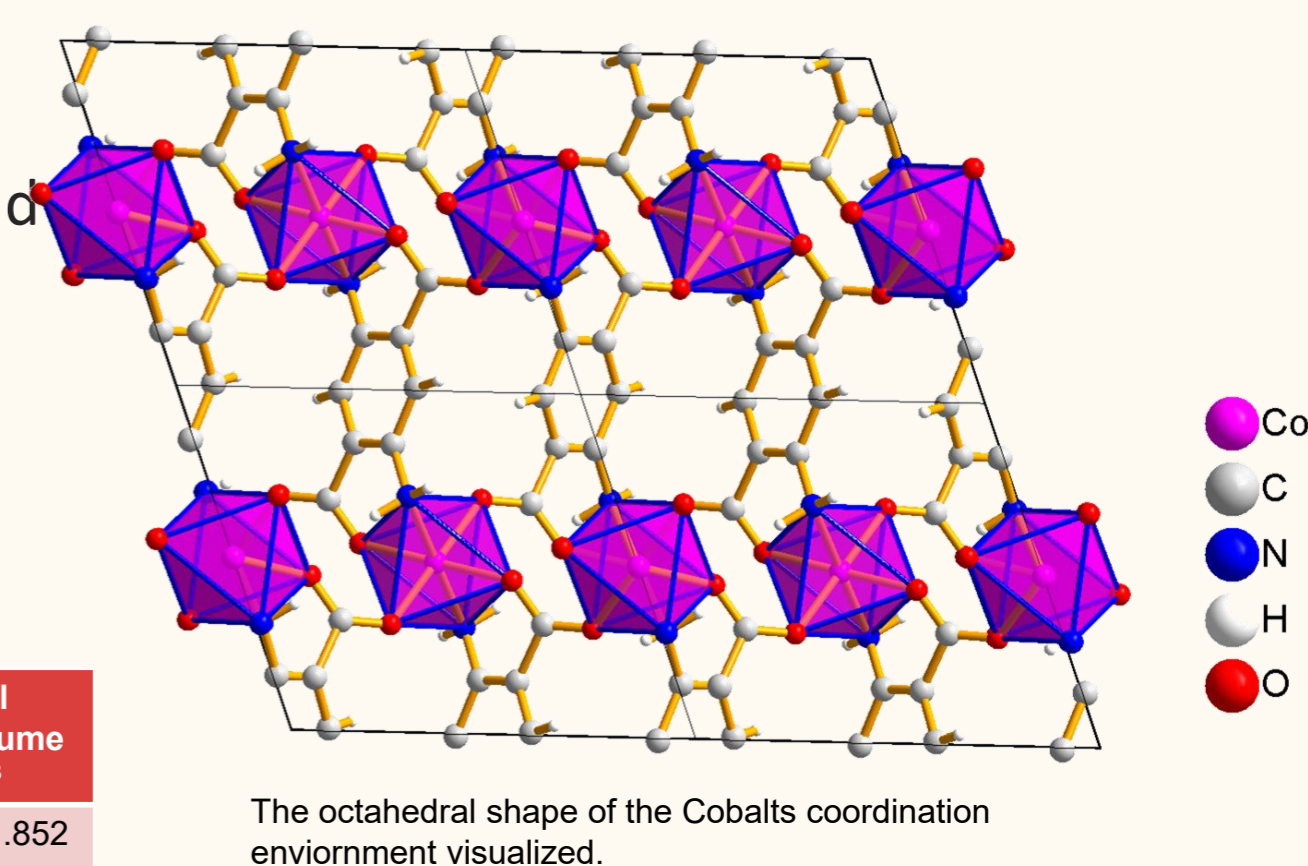


Rietveld refinement plot of  $Co(dabdc)$  measured in synchrotron radiation, wavelength 0.25402 Å.

The cobalt atom is 6-coordinate, with an octahedral coordination environment. Two ligands chelate the metal through a carboxylate oxygen atom and the nitrogen atom of an amino group, and two ligands only coordinate to it with a single carboxylate oxygen.



The octahedron can be visualized, and one can see that the octahedra are "layered" in an alternating fashion.



## Conclusion

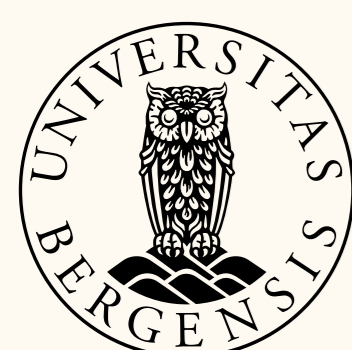
These results provide a landmark for the dabdc linker, making it easier to determine the composition of further syntheses, should the same products show up in the results. These results show that the amino groups on the linker participate in coordination of the central atom, thus enabling the formation of a densely packed structure that favorably competes with the original target structure under the explored reaction conditions.

## REFERENCES

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- [2] X. Hu, F. Liu, H. Wang, C. Quin, C. Sun, Z. Su, F. Liu, *J. Mater. Chem. A.* 2014 **2**, 14827
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## ACKNOWLEDGEMENTS

The author acknowledge the assistance from the staff at the Swiss-Norwegian Beamlines for their support in performing the experiments at the ESRF, Ruplekha Bordoloi for assisting the synthesis of the dabdc ligand, and the invaluable support the rest of the Dietzel Research group.



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