

Abstract

Metal-Organic Frameworks (MOFs) have emerged as a promising technology in recent years, with a huge variety of applications due to their tunability, large surface area, and rigid structure. However, they can be challenging to synthesize with certain metal and ligand combinations. One type of method used to allow greater flexibility in metal-ligand combinations is post-synthetic modification. In particular, cation exchange allows a MOF to exchange metal ions without losing structure. This can be useful in synthesizing MOFs with metals which would not normally be able to be used to synthesize that particular MOF. However, fundamental research and understanding of cation exchange in MOFs is an open field. Here, we study cation exchange in MOF-5, a simple MOF system which can be illustrative in general principles of MOF behavior. Co exchange into Zn-MOF-5 is found to be zeroth order with respect to the Co cluster concentration.

Introduction

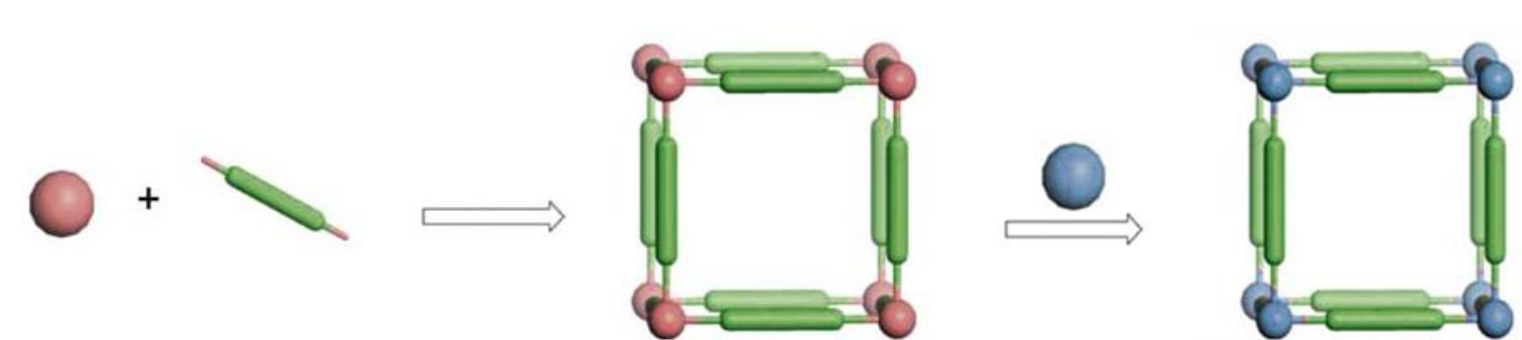


Figure 1: General MOF formation scheme and scheme for cation exchange. Adapted from figure by Huxford et al, 2010.¹

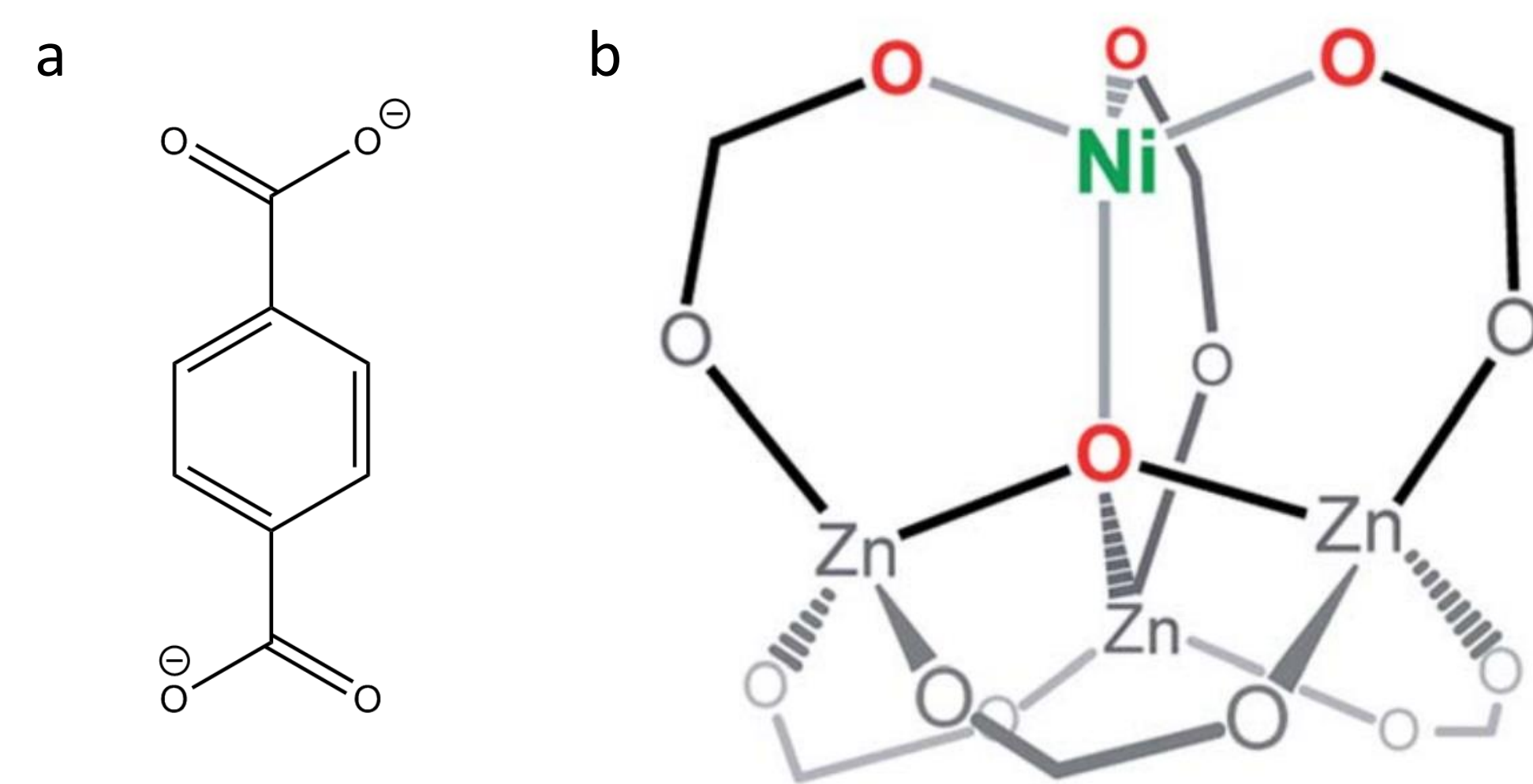


Figure 2: MOF-5 is a particular type of MOF with terephthalic acid organic linkers (a) and various metal clusters. Typically, MOF-5 is synthesized with ZnO metal clusters. In (b), one of these Zn atoms has been replaced by a Ni atom through cation exchange.²

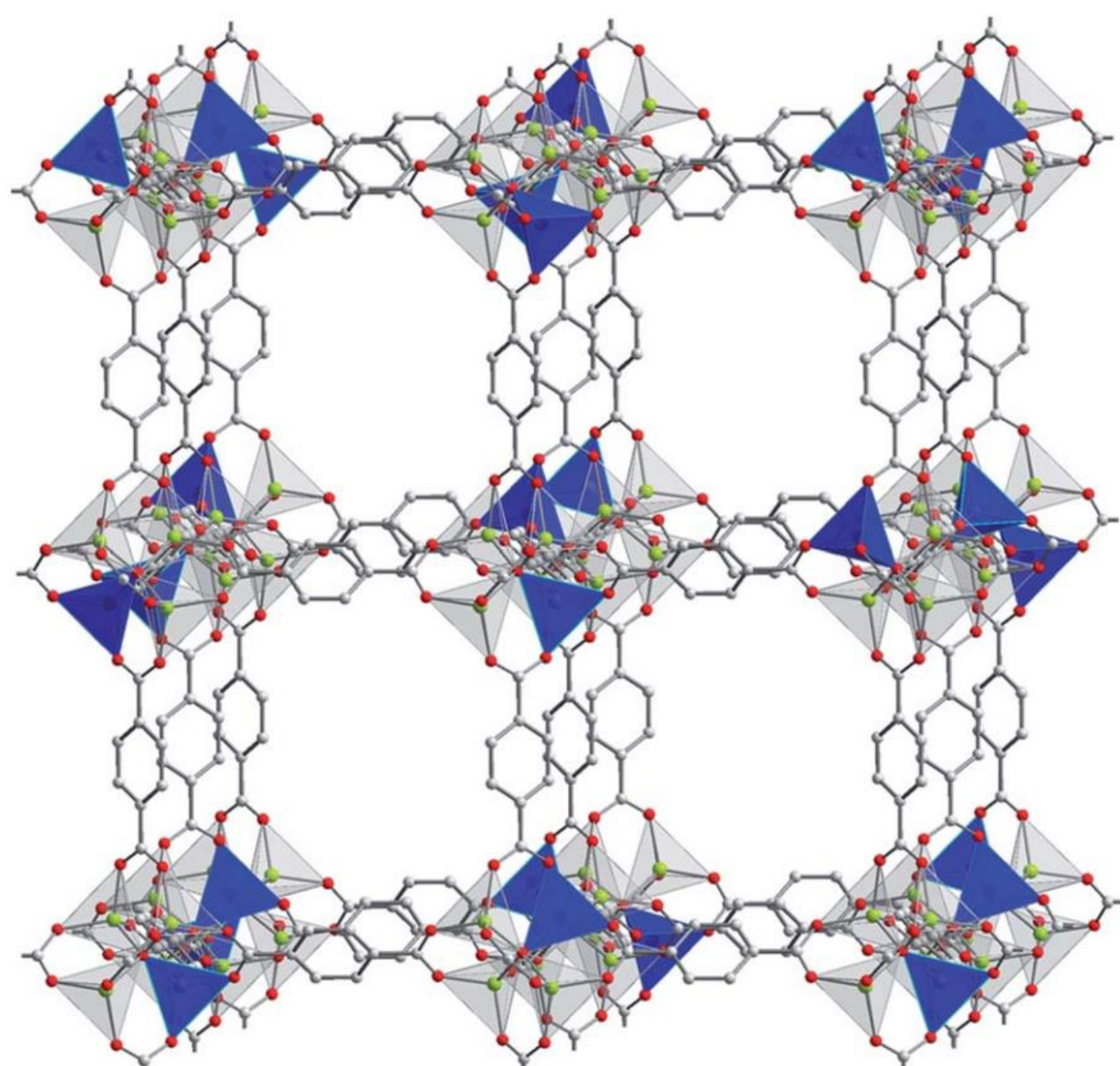


Figure 3: MOF-5 has been found to undergo cation exchange of up to 25% with various metals. Up to one Zn per cluster can be exchanged. In this figure, one atom per cluster is highlighted blue to indicate exchange has occurred.^{2,4}

Synthesis

MOF-5 was synthesized in high yield by combining $Zn(NO_3)_2 \cdot 6H_2O$ with terephthalic acid in a DMF/ H_2O (49:1) solution and heating at $100^\circ C$ for 8h. It was then washed with DMF 3x once daily, then DCM 3x once daily. Finally, MOF-5 was activated by heating crystals under vacuum for 12 h (4 mtorr, $200^\circ C$). This desolvated the pores, allowing cation exchange to occur. Successful synthesis was verified via PXRD. This procedure and PXRD match previously published procedures and values.²

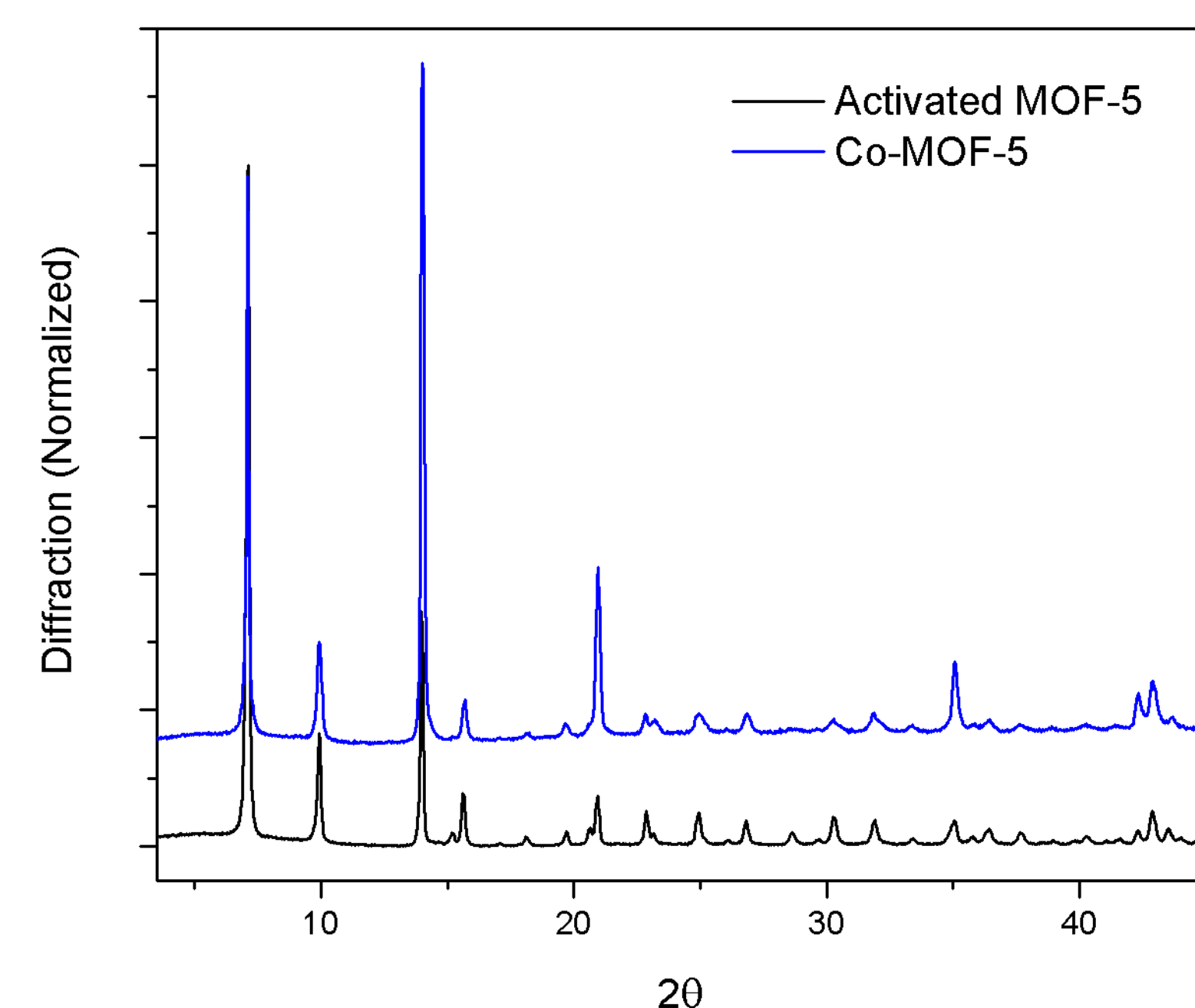


Figure 4: PXRD of activated MOF-5 and of MOF-5 after soaking in a $Co(NO_3)_2 \cdot 6H_2O$ solution and undergoing cation exchange. This reveals that the two are isostructural and thus confirms the basic premise of cation exchange - facilitating creation of a certain MOF morphology with a metal which cannot normally be used.

Cation Exchange

Cation exchange was studied by soaking activated MOF-5 in a $Co(NO_3)_2 \cdot 6H_2O$ solution in DMF. The concentration of Co in solution was 100:1 Co:Zn cluster. This was chosen such that any effects on rate would be minimal with expected levels of cation exchange of up to 25%. Even at a full exchange of 25%, Co concentration in solution would drop by just 1%. Soaks were stopped at various time points, filtered and washed, then ICP-AES was employed to test the Zn/Co ratio. Analysis of the results revealed a zeroth order dependence on the Co cluster concentration.

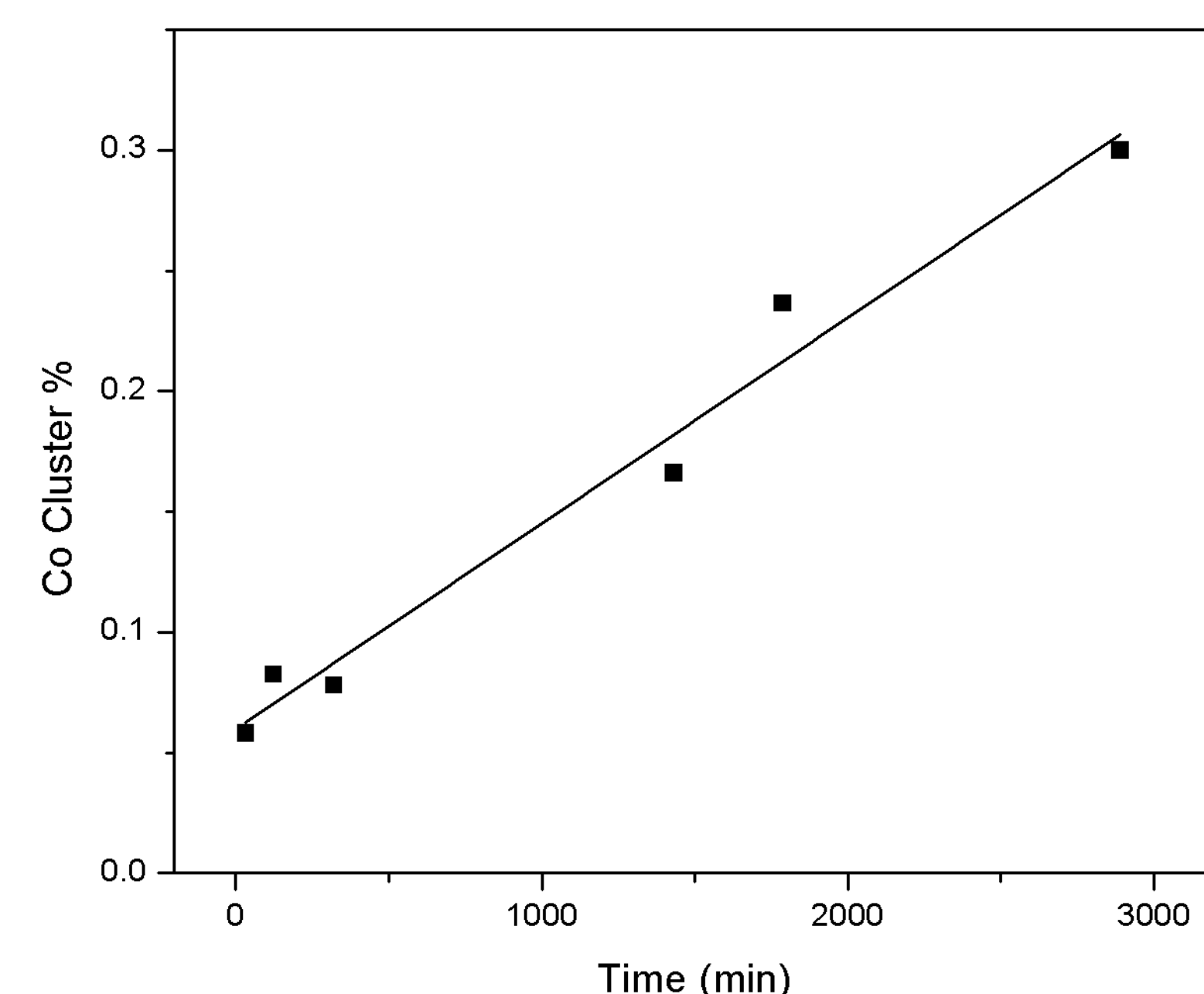


Figure 5: Co cluster concentration is plotted versus soak time, along with the line of best fit, revealing approximately zeroth order kinetics.

Co-MOF-5 Solvothermal Synthesis

An attempt to synthesize Co-substituted MOF-5 via a conventional solvothermal approach was performed which illustrates the usefulness of cation exchange. In addition to the standard reagents in the synthesis of Zn-MOF-5, a 5.5 equivalent excess of Co was added to the reaction mixture. Though synthesis of Ni-MOF-5 has been reported under similar conditions, crystalline Co-MOF-5 was unable to be synthesized on the first try. Though we expect that modifying conditions will allow synthesis of Co-MOF-5, it is far simpler to follow published procedures for Zn-MOF-5 synthesis then perform cation exchange than optimize conditions for solvothermal synthesis.

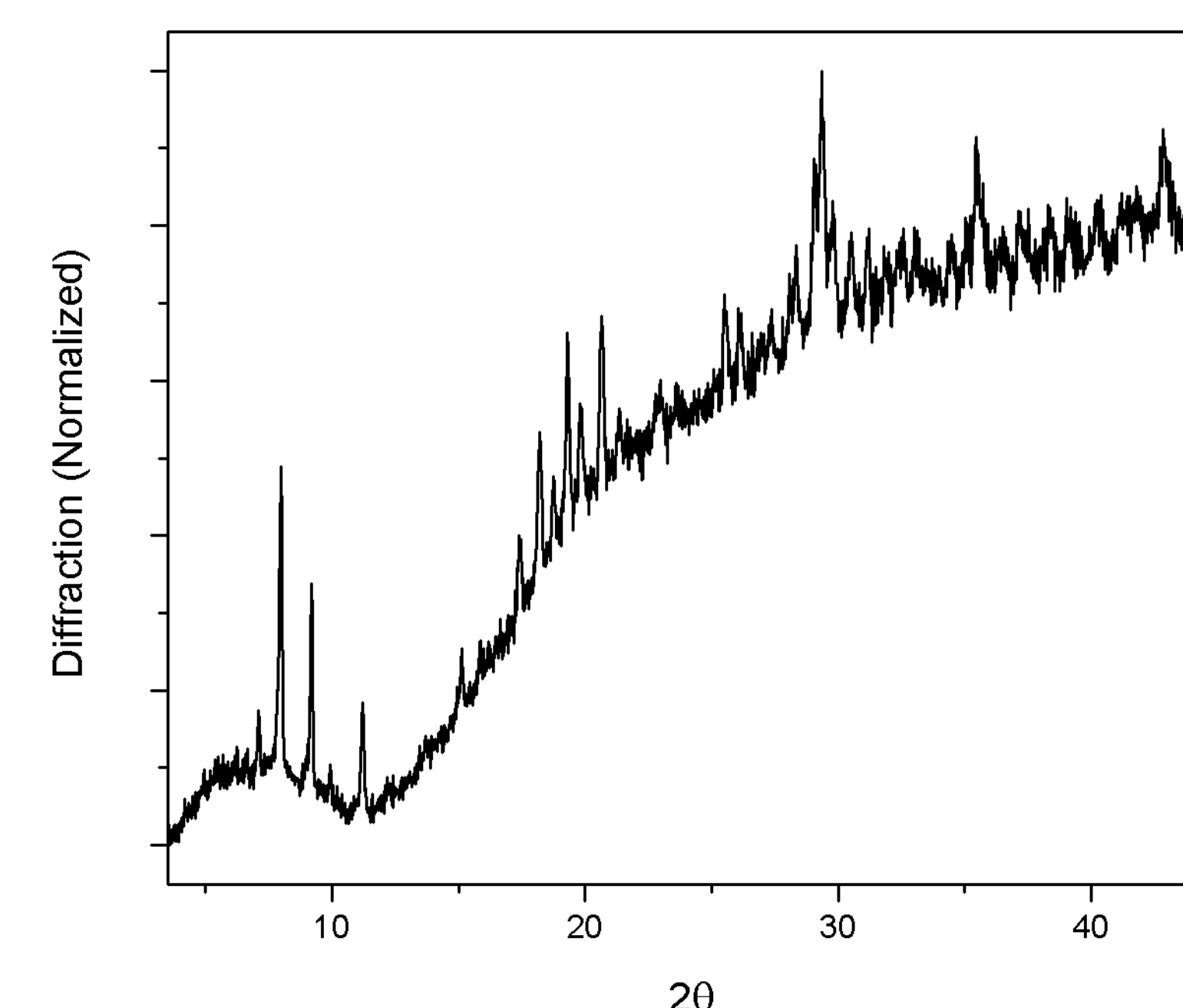


Figure 6: PXRD of unactivated "Co-MOF-5", revealing almost no crystallinity and with peaks that do not correspond to those of MOF-5 or Co-MOF-5 synthesized via cation exchange.

Discussion and Conclusions

Though current data is limited, it suggests zeroth order dependence on the Co cluster concentration. Previous studies have shown that Ni can exchange in up to one location per cluster, so the maximum Zn/Co ratio would be 1/3. This is hypothesized to be due to a rearrangement that must occur - tetrahedral Zn is preferentially substituted by octahedral Ni (where the additional two coordination points are solvent). Because of the strain this puts on the structure, only one atom per cluster can be exchanged. Due to this, we can ignore complicated kinetics involving multiple substitutions per cluster. This is one primary benefit of MOF-5.

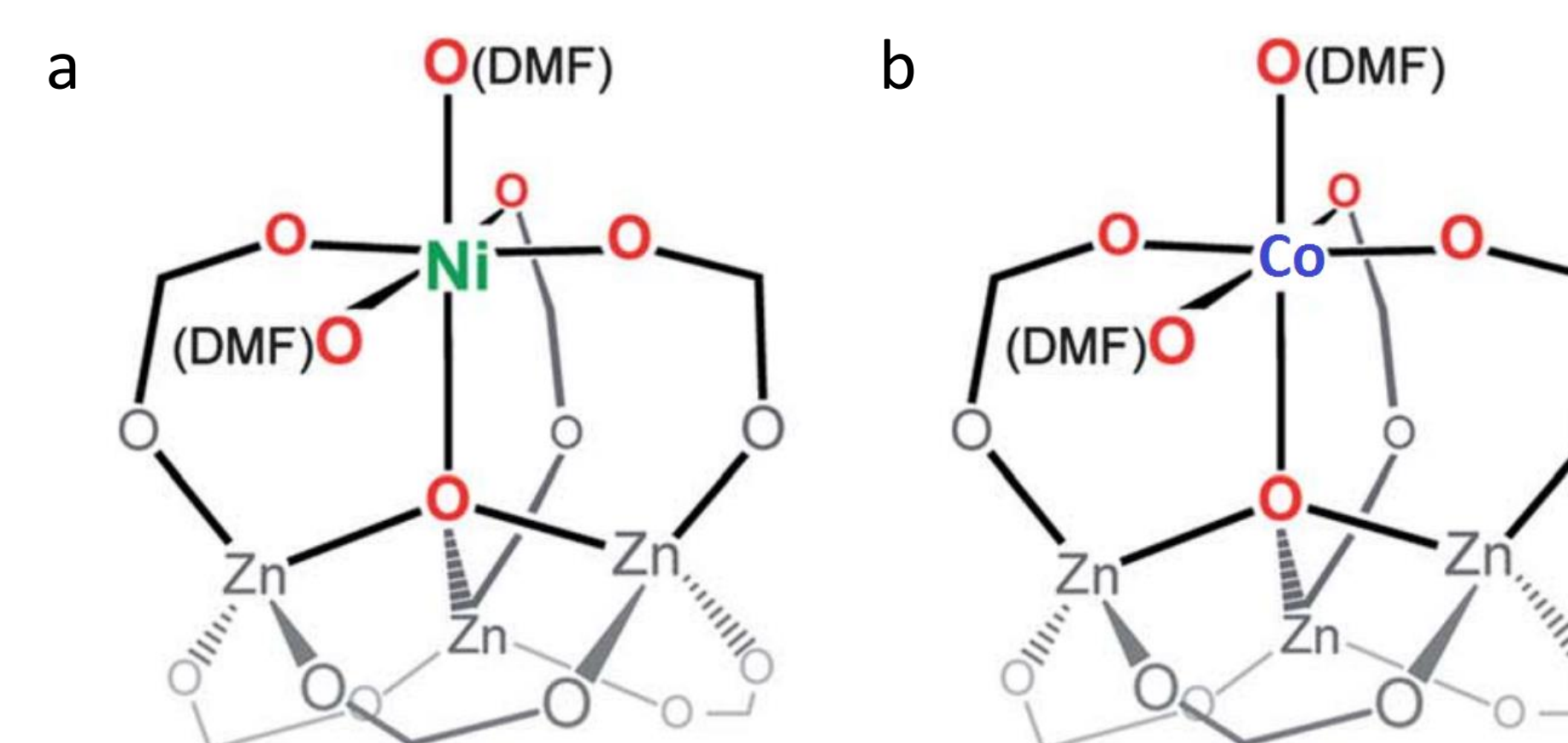


Figure 7: Solvation and octahedral arrangement of DMF around exchanged cation. This has been reported for Ni (a), and Co (b) is expected to follow the same substitution pattern. This could be confirmed via Single-crystal X-Ray Diffraction, as it was confirmed for Ni.²

Future Work

In order to develop a more complete theory of cation exchange in MOFs, the following areas remain promising research targets:

- Gather more data on Co exchange into Zn-MOF-5, in order to obtain a more accurate fit.
- Gather data on Co exchange into Zn-MOF-5 at different temperatures in order to calculate an activation energy for this exchange.
- Gather data on reverse exchange - after preparing Co-MOF-5, attempt to exchange another metal in, or exchange Zn back into Co-MOF-5.
- Gather data on more elements. Research is currently underway for Ni in addition to Co.
- Gather Single-crystal X-ray Diffraction data on Co-MOF-5 to check whether it displays the same octahedral distortion that has been reported for Ni-MOF-5.
- Expand cation exchange to more MOF systems to study how universal concepts displayed in MOF-5 are.
- Expand research to include ligand exchange as well. It has been shown previously that in addition to cation exchange, some MOFs can undergo ligand exchange as well.⁵

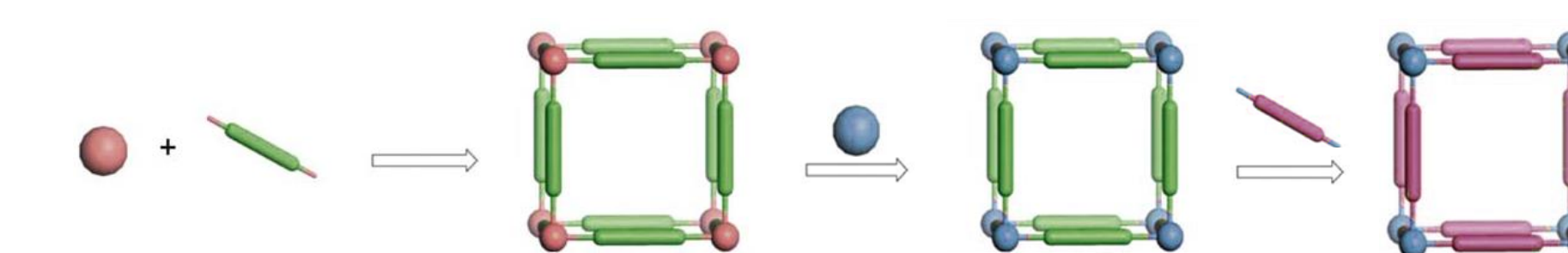


Figure 8: Modified MOF synthesis scheme, illustrating cation exchange and ligand exchange being used in conjunction to create an entirely new MOF which maintains only the morphology of the as-synthesized MOF.

References

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