Solid-state isolation of reactive complexes in a metal-organic framework matrix

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While small molecule activation processes underpin transformations in catalysis, gathering structural information about the reactive metal-based species responsible can be challenging. Such species are often coordinatively unsaturated or possess labile ligands; they are therefore highly reactive and transient. Building on research trapping reactive species within the cavities of supramolecular assemblies or frameworks,[1] we have been using metal-organic frameworks (MOFs) to "matrix isolate" and structurally characterise catalytically important metal-based species.[2, 3] The building block synthetic approach of MOFs using chemically mutable links, coupled with long range order (crystallinity), and excellent chemical and thermal stability,[4] allows them to be used to stabilise and characterise reactive species.

To garner these insights we use a bespoke, flexible Mn-based MOF, [Mn_3L_2L'] (**MnMOF-1**, where L = bis-(4-carboxyphenyl-3,5-dimethylpyrazolyl)methane) with a site poised for allowing single crystal-to-single crystal (SCSC) post-synthetic metalation.[2, 3] This contribution will expand these ideas and examine ligand exchange chemistry occurring at trigonal planar Cu(I) sites chemically isolated in the MOF.[5] Insights into catalysis obtained by structurally characterising the initial catalysts and by targeting sequential “snapshots” of the catalytically active structure by single crystal X-ray crystallography will be reported.

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