Investigating the Structural Response of the CAU-64 Family of Compounds to Temperature and Humidity Through Combined Laboratory Single-Crystal and Powder Diffraction Studies

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The structures of many Metal-Organic Framework (MOF) compounds change in response to external stimuli, including pressure, temperature and adsorption/desorption of guest molecules.[1,2,3] The responsive nature of these compounds makes analysis of their structures fascinating but challenging. Moreover, these materials are often obtained only as very small crystals or microcrystalline powders. While powder X-ray diffraction (PXRD) and electron diffraction have proven capable of obtaining the structures of as-prepared MOFs, both techniques have their drawbacks. Recent advances in laboratory single crystal X-ray diffraction (SCXRD) enable structures to be determined from significantly smaller crystals, providing unparalleled insights into structural details, and thus the structural response mechanisms.

We report the structural analysis of the M-CAU-64 family of compounds ($[NaM(III)(H_2O)_2(C_2H_2O_3)_2]\cdot xH_2O$; M = Al, Fe, Ga; CAU – Christian-Albrechts-Universität). These mixed-metal MOFs are synthesised with glycolic acid as the linker and demonstrates a complex series of phase transitions in response to temperature and humidity. The framework compounds were discovered using high-throughput methods.[4] Structures were determined using the D8 VENTURE laboratory SCXRD, equipped with a DIAMOND II hybrid-diamond anode microfocus source combined with a PHOTON IV detector, enabling the study of minuscule crystals.

Water sorption studies of CAU-64 show a two-step absorption process. The structural origin of this behaviour was investigated through *in situ* PXRD variable temperature and humidity studies, which revealed a rich phase transition behaviour.

The use of multi-modal methods, reliant on high brilliance laboratory SCXRD instrumentation, to structurally characterise CAU-64 demonstrates the important contribution laboratory diffraction makes to the study of flexible framework materials.

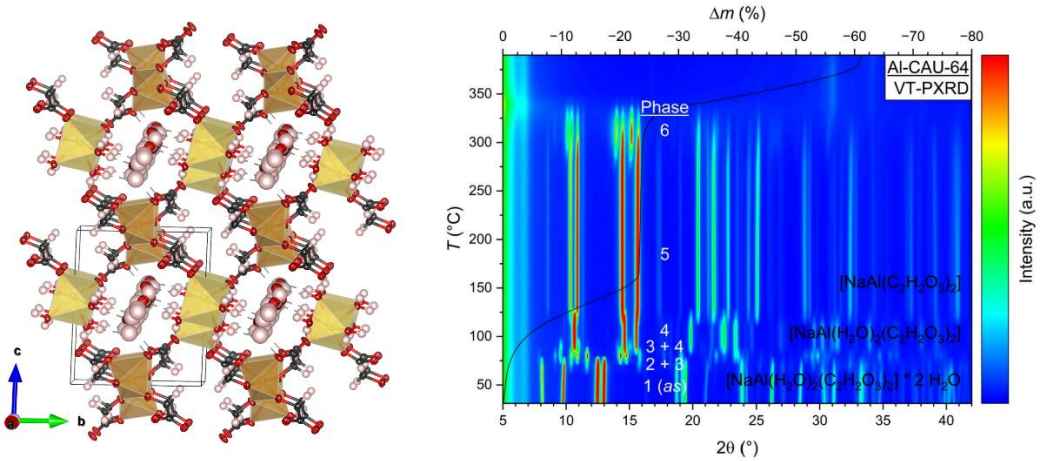


Figure 1. *Left: Structure of Fe-CAU-64 measured on a Bruker D8 VENTURE using Mo Kα radiation; Right: In Situ Variable Temperature PXRD study of Al-CAU-64 measured in a BTS-500 on a Bruker D6 PHASER showing the complex phase evolution of the compound, with thermogravimetric analysis curve overlayed for comparison.*

[1] A. Schneemann et al., Chem. Soc. Rev. (2014), 43, 6062-6096
[2] Pallach *et al.*, Nat. Commun., 12 (2021), 4097
[3] Li *et al.*, Acc. Chem. Res., 57 (2024), 2279-2292
[4] ChemRxiv. **2024**; doi:10.26434/chemrxiv-2024-cd3pj (pre-print)