

High-pressure phase transitions in the Co(II) analogue of ZIF-8

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The adsorption properties and structural behaviour of zeolitic imidazolate frameworks (ZIFs) rely upon the interplay of their organic ligands, metal centres and the guest molecules contained within their framework.[1–5] ZIF-8 and its isostructural derivatives with SOD-type topologies, composed of a single metallic centre connected by bi-dentate imidazolate (Im) linkers, are well known to alter their guest-mediated uptake behaviour upon metal or functional group substitution.[2, 3, 6, 7] Replacement of the metal ion can be particularly interesting as it not only impacts the pressure at which SOD-type ZIFs may undergo a “gate-opening” phase transition, whereby the Im linker rotates to allow greater access to the central pore, but may also have implications for catalysis by supplying more active centres.[6, 7] One of the most studied of the SOD-type ZIFs is ZIF-67, a Co-based isostructural equivalent to ZIF-8(Zn).[8–12] However, despite a wide variety of studies utilising ZIF-67 as a catalyst or adsorbent,[10, 12] few studies have examined the structural response of ZIF-67 under applied pressure,[9] and none in a penetrating medium at high pressure.

This study is the first to use high-pressure single crystal X-ray crystallography to probe structural transitions in ZIF-67 during compression in hydrostatic media of a methanol/ethanol mixture, MeOH:EtOH (4:1), and liquid nitrogen (LN2), with the aim of examining the relative compressibility of ZIF-67 against ZIF-8. The results demonstrated that ZIF-67, similarly to ZIF-8(Zn), displayed the prototypical transition to the “gate-opened” high-pressure phase in both mediums, characterised by a change in the angle between the average 2-methylimidazolate (mIm) plane and the [100] plane (denoted θ). Similarly to ZIF-8,[1, 4] ZIF-67 begins with θ of 64.5 to 66.9° in the ambient structures. On conversion to the high-pressure (ZIF-67-HP) phase, the mIm linker is rotated to $\theta \approx 89^\circ$. In MeOH:EtOH, this occurs at 1.57 GPa and is followed by both a sharp decrease in the unit cell volume (-3.75%) and contraction of the cell axes (-1.01%). In LN2, the transition is noticeable at the lowest measured pressure (0.43 GPa) and is associated with an immediate expansion of the unit cell (+1.2%), followed by continuous contraction by as much as 10.5% by 3.49 GPa. LN2 adsorption was modelled in 6 adsorption sites that fill progressively as pressure increases. Maximum LN2 adsorption site occupancies corresponded to the first observation of a noticeable and fully reversible colour transition in a ZIF crystal on compression, which was not found to occur in alcohol. Despite the presence of a $\text{Co}^{2+} d^7$ metal centre, the change in colour could not be linked to any local change in metal or ligand conformation that would suggest spin-crossover but is instead related to super filling of the structure by the N₂. This work confirms and elucidates the nature of the guest-mediated gate-opening in both small alcohols and N₂ of ZIF-67 at high pressures.

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