

MS35-P3 Elucidating the mechanism responsible for anisotropic thermal expansion in a Metal-Organic Framework

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Anomalous thermal expansion of a three-dimensional metal-organic framework (compound **1**) is examined by means of theoretical calculations. The methanol solvate ($[\text{Zn}(\text{L})(\text{OH})] \cdot n\text{CH}_3\text{OH}$, **1**_{MeOH}, **L** = 4,4'-bis(2-methylimidazol-1-ylmethyl)-1,1'-biphenyl) was obtained following the procedure developed by Grobler *et al.* and subsequently desolvated in a single-crystal to single-crystal transformation to yield the apohost form, **1**_{apo}.^[1] Variable temperature single crystal X-ray diffraction (SCD) analysis on the same crystal of **1**_{apo} under static vacuum revealed colossal positive thermal expansion along the *c* axis ($\alpha_c = 123 \times 10^{-6} \text{ K}^{-1}$) and biaxial negative thermal expansion along the *a* and *b* axes ($\alpha = -21 \times 10^{-6} \text{ K}^{-1}$). Inspection of the 100, 190, 280 and 370 K SCD structures pointed towards a concerted change in the labile coordination sphere of the zinc centre so as to elongate the coordination spiral in the *c* direction (Zn-O(H)-Zn angles enlarge), while the largely unaltered ligands (Zn...**L**...Zn distance constant) are pulled closer together in the *ab* plane.

In this study Molecular Dynamics simulations in the NPT ensemble successfully reproduce the observed trend in unit cell parameters of **1**_{apo}. Computed internal coordinates involving zinc are, however, generally underestimated owing to shortcomings of the DREIDING force field. A mechanistic model that reproduces the convergent expansion of the material's coordination spiral is developed and evaluated at the DFT level of theory. The linear increase in energy calculated for the extension of a model consisting of six zinc centres and truncated ligands compares favourably to results obtained from a periodic DFT evaluation of the SCD structures.

[1] I. Grobler, V.J. Smith, P.M. Bhatt, S.A. Herbert, L.J. Barbour *J. Am. Chem. Soc.* (2013), 135, 6411.

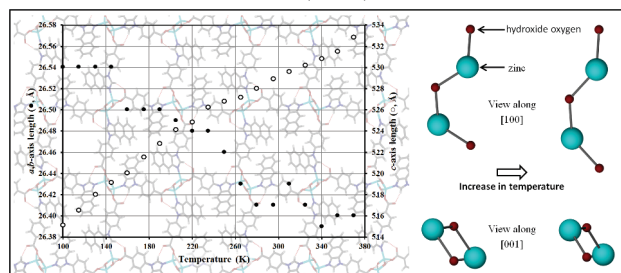


Figure 1. Left: Graph of unit cell lengths determined by variable temperature SCD on the same crystal of **1**_{apo} under static vacuum.^[1] Right: schematic representation of the convergent expansion mechanism of the coordination spiral of **1** showing elongation in the *c* direction and contraction in the *ab* plane.

Keywords: Thermal Expansion, DFT

MS36. Molecular crystals offering new insight into intermolecular interactions

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MS36-P1 Solvent-free and solution based synthesis of *o*-hydroxy imines with non-planar molecular geometry

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Solvent-free methods of synthesis (neat, liquid-, seeding-, ion-assisted grinding) have been recognised as faster, environmentally more friendly and economically more acceptable ways to prepare new but also already known compounds.[1] *o*-Hydroxy Schiff bases are well known organic compounds that can possess photo- and/or thermochromic properties in the solid state due to possibility of keto-enol tautomeric change *via* intramolecular O...N hydrogen bond.[2] They can be easily obtained by condensation of aldehydes (or ketones) and primary amines[3] and thereafter used as ligands in coordination chemistry of transition metals.[4] For the reason of their ability to reversibly change their colour upon changing external conditions their structure-property correlation has been extensively studied. For almost 30 years it was thought that Schiff bases with non-planar molecular geometry cannot show thermochromism[2] so much work was done in the past 20 years to find ones that do.[5] Herein, we report solvent-free and solution based syntheses of *o*-hydroxy Schiff bases with non-planar geometry obtained from salicylaldehyde and its derivatives and α -aminodiphenylmethane. The successfulness of method used was studied by means of PXRD, DSC and TG thermal analysis and NMR. Their thermochromic properties were checked by repeated exposure to temperature change from room to liquid-nitrogen temperature. The supramolecular impact on the keto-enol tautomerism (Figure 1) was studied using SCXRD.

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