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Comparing the dynamics of coordination polyhedra in a metal-cyanide framework

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The enormous amount of attention devoted to metal-organic framework materials over the past two decades has yielded substantial synthetic control over these materials, so that specific topologies can be explicitly engineered by carefully selecting metal and ligand “building blocks”. The dynamic behaviour of these materials, however, remains far less predictable: yet it is this behaviour that is the key to understanding the highly anomalous thermodynamic properties of many framework materials. When studying these compounds crystallographically it is important to acknowledge the limitations of Bragg scattering, which by revealing only a space- and time-averaged structure can give an incomplete or even actively misleading picture of the material’s dynamic behaviour. For this reason, complementary techniques, such as XAFS, that are sensitive to the local structure of materials are vitally important. We have studied the behaviour of a prototypical framework material exhibiting near-zero thermal expansion, tetramethylammonium copper(I) zinc(II) cyanide, by X-ray absorption spectroscopy at the Cu and Zn K edges in combination with total neutron and X-ray scattering, supported by reverse Monte Carlo and density-functional theory calculations, thus simultaneously modelling the long-range and local structure of this material. Our results resolve for the first time the individual flexibility of the copper and zinc coordination tetrahedra, suggesting substantially higher flexibility of both types of polyhedra than was previously thought. These results shed new light on the atomic origins of this material’s flexibility, and explain the mobility of guest molecules through the framework structure. More generally, this methodology points the way to being able to choose framework components for their dynamic properties, and hence to the rational synthesis of flexible framework materials with targeted thermodynamic properties.

[1] *AE Phillips, GJ Halder, KW Chapman, et al, J Am Chem Soc 132, 10-11 (2010)*

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