[MS27-P09] Comparing the dynamics of coordination polyhedra in a metal-cyanide framework

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It is increasingly apparent that the well-known structural diversity of oxides is shared by materials in which metal ions are linked by polyatomic units such as the cyanide or formate ions. Just as in the case of silicates, many different structural topologies are possible in these systems, meaning that they can be tailored for specific properties or applications. The framework material tetramethylammonium copper(I) zinc cyanide, $N(CH_3)_4[CuZn(CN)_4]$ is both an early example of a rationally designed structure [1] and a prototypical metal-organic framework. It consists of a network of Cu+ and Zn^{2+} ions, linked by cyanide ions, alternating to form an anionic framework analogous to cristobalite. The charge is balanced by tetramethylammonium ions encapsulated in the framework. This material and related metal-cyanide frameworks have attracted subsequent attention for their anomalous thermodynamic properties, including negative [2] and zero [3,4] thermal expansion and negative compressibility [5]. This behaviour relies on the dynamic flexibility of the individual metal coordination polyhedra, which enables the framework as a whole to distort with relatively low energetic penalty. These dynamic properties, however, remain far less understood than the geometric properties of the coordination tetrahedra. For instance, it is now possible deliberately to introduce, say, a d8 metal into a framework system with the goal of producing a square planar linkage. However, it is not generally possible to tune the flexibility of these sites in the same systematic way. The thermally accessible vibrational modes are linked not only to anomalous thermodynamic properties but also to other aspects of material behaviour, such as charge transfer transitions [4]; thus the ability to engineer this behaviour will be an important contribution to materials design. Materials, such as tetramethylammonium copper(I) zinc cyanide, which contain two different metal coordination polyhedra can yield important insight into the flexibility of these individual building blocks, since the behaviour of the polyhedra can be directly compared. However, when studying these materials crystallographically it is important to acknowledge the limitations of Bragg scattering, which by revealing only a spatial average structure can give an incomplete or even actively misleading picture of the material's dynamic behaviour. Previous studies of this material have relied on indirect evidence of local deviations from this average, including refined atomic displacement parameters and phase transitions [3]. Here I present a study of the same material via total neutron scattering. Modelling the Bragg and diffuse scattering together by reverse Monte Carlo simulation [6] gives for the first time a direct picture of the local fluctuations about the crystallographic average structure. The experimental models are corroborated by density-functional theory calculations. Our results suggest substantially higher flexibility of both the Cu(CN)4 and Zn(NC)4 polyhedra than was previously thought. These results shed new light on the atomic origins of this material's flexibility, and may explain the mobility of guest molecules through the framework structure.

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