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Thermal Expansion Matching via Framework Flexibility in Zinc Dicyanometallates

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Framework materials that incorporate highly underconstrained structural linkages include a number of important systems whose mechanical properties differ fundamentally from those of "traditional" crystalline materials. In the family of "MIL"-type frameworks, for example, hinging of polycarboxylate linkages allows a massive "breathing" response to guest sorption, with volume differences in excess of 270% between filled and empty forms.[1] Likewise, highly flexible dicyanoargentate linkages permit thermal expansion behavior in $Ag_3[Co(CN)_6]$ that is an order of magnitude greater than that in "normal" materials (dubbed "colossal"), coupled to an equally strong negative thermal expansion (NTE) effect in a perpendicular direction.[2] In both cases—and as appears to be increasingly general across, e.g., large families of metal−organic frameworks,[3] transition metal cyanides,[4] and zeolitic imidazolate frameworks[5]—structural underconstraint leads to mechanical behavior that is dictated not by the strength of individual covalent or ionic interactions but by the much weaker forces associated with bond-bending or torsional vibrational modes.[6] This fundamental shift in energy scale means that weak supramolecular interactions and second-order strain effects can actually determine *bulk* mechanical properties in these systems.

Here we show that framework flexibility can be used to engineer materials whose thermal expansivities actually vary to accommodate those of adhered phases, such as substrates, sorbates, or cocrystallized species. We reason that even weak interfacial strains are able to modify the mechanical behavior of sufficiently flexible framework systems. Our results illustrate the inherent ability of flexible materials to "match" the thermal expansivity of adhered phases that suggests a general methodology of eliminating thermal strain in multicomponent assemblies.

Our approach is to study two isostructural zinc dicyanometallates, namely $Zn[Au(CN)_2]_2$ [**1**] and $Zn[Ag(CN)_2]_2 \cdot x AgCN$ ($x \sim 0.58$) [**2**], that crystallize without (**1**) and with (**2**) the inclusion of a secondary crystalline phase. Comparison of their thermal expansivities then allows us to assess the way in which framework flexibility accommodates (or otherwise) the mismatch between host and adhered phases.

The structure of **1** has been reported previously[7,8] and consists of tetrahedral Zn centers connected by nearly linear $[NC{-}Au{-}CN]^-$ units to form a 6-fold interpenetrated β-quartz network structure in which the Zn atoms occupy Si sites and Au atoms occupy O sites (Figure 1a). As in β-quartz, the structure has hexagonal symmetry and is intrinsically chiral, belonging to either one of the enatiomorphic groups $P6_222$ or $P6_422$.[7] Synthetic substitution of $K[Ag(CN)_2]$ for $K[Au(CN)_2]$ yields the isostructural host phase **2**,[8] in which the interpenetrating β-quartz nets are themselves interpenetrated by disordered one-dimensional chains of AgCN, the periodicity of which is incommensurate with respect to the host lattice (see Figure 1b). Evidence for the inclusion of these AgCN chains comes from the presence[9] of both uniform rods of electron density within the 1-D channels along **c** (electron density ca. 1.3 e^- Å^{-3}; cf. average 1.13 e^- Å^{-3} for AgCN)[10] and 2-D planes of diffuse X-ray scattering perpendicular to **c*** (Figure 1c) with the expected periodicity (5.2(1) Å; cf. 5.28 Å for AgCN).[10] The lack of Au^+ aqueous chemistry and the lability of the $[Ag(CN)_2]^-$ ion precluded the preparation of direct $\mathbf{1} \cdot x$AuCN or guest-free **2** analogues. However, we note that in general one expects isostructural dicyanoargentate and dicyanoaurate frameworks to exhibit very similar thermal expansivities.[11]

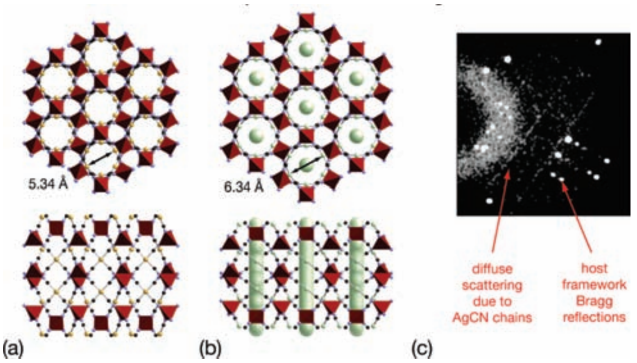

Figure 1. Representations of the crystal structures of **1** (a) and **2** (b) down [001] (top) and [110] (bottom); Zn atoms shown as tetrahedra, Ag/Au, C and N as spheres, and incommensurate 1-D AgCN chains in **2** as green rods. (c) Single crystal X-ray diffraction image showing the presence of planes of diffuse scattering associated with the AgCN inclusion in **2**.

Measurements of the temperature-dependent structures and unit cell parameters for **1** and **2** were performed using single crystal and synchrotron X-ray powder diffraction (see Figure 2 and Table 1, and Supporting Information for complete data). What is clear in both cases is that the frameworks expand on heating along the **a** and **b** crystal axes, while contracting along *c*. The most significant difference in behavior, however, is the magnitude of these effects: the coefficient $\alpha_a = (\partial \ln a/\partial T)_p$ is almost an order of magnitude smaller for **2** than for **1**; likewise there is a 3-fold difference between

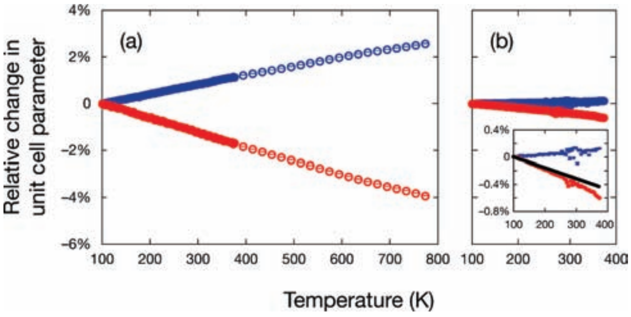

Figure 2. Anisotropic thermal expansion behavior for (a) **1** and (b) **2** as determined using single crystal (●) and powder (○) X-ray diffraction. Data are shown for the crystallographic *a* and *c* axes (blue and red symbols, respectively) and for the AgCN chain length in silver(I) cyanide (bold line in inset to panel (b)).[12]

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Table 1. Mean Coefficients of Thermal Expansion from X-Ray Single-Crystal and Powder Diffraction

	$\alpha_a{}^a$/MK^{-1}	$\alpha_c{}^a$/MK^{-1}	$\alpha_V{}^a$/MK^{-1}	$\alpha_{\mathrm{Zn...Zn}}{}^a$/MK^{-1}
1	+36.91(8)	−57.58(8)	+15.07(12)	−6.97(9)
2	+4.07(15)	−21.71(12)	−13.57(29)	−5.02(14)

[a] The errors in the values of α given are from the least-squares linear fits to the data over the temperature ranges 100−775 K (**1**) and 100−375 K (**2**).

the corresponding values of α_c. The overall behavior changes from positive to negative thermal expansion.

Because the Zn atoms occupy special positions within the unit cell,[7] it is possible to extract from the raw lattice parameter data a separate coefficient of thermal expansion $\alpha_{\mathrm{Zn...Zn}}$ that describes the relative thermal change in Zn...Zn separation across the covalent Zn−NC−Ag/Au−CN−Zn linkages (Table 1). These values are small, negative, and almost identical for **1** and **2**, which is consistent with a slight NTE effect associated with the transverse vibrational motion of the C and N atoms, as seen in many other cyanide materials.[4] Importantly, the equivalence in behavior between the two compounds indicates that there is no fundamental difference in the way the individual chemical components of the two frameworks respond to temperature. Instead the large discrepancy in lattice expansivities must arise from a different *geometric* response induced by inclusion of the AgCN chains in **2**.

Geometric flexing of the lattices takes place for both **1** and **2** as a function of temperature. For **1**, this effect is highly pronounced and appears to be driven principally by the elongation of aurophilic Au...Au contacts, which form 1-D chains within the *ab* plane; notably, the average Au...Au separation increases at a relative rate $\alpha_{\mathrm{Au...Au}} = +41$ MK^{-1} that correlates very well with the observed α_a of +36.91(8) MK^{-1} (see Supporting Information for description and analysis).[13] In response, the framework, constrained by its geometry and the moderate NTE across the $[\mathrm{Au(CN)_2}]^-$ linkages, is forced to contract even more strongly along **c**. This situation is closely analogous to the thermal expansion mechanism proposed for, e.g., $\mathrm{Ag_3[Co(CN)_6]}$.[2]

The mechanism for **2** appears to differ considerably in that the analogous Ag...Ag contacts expand much more rapidly with temperature (average $\alpha_{\mathrm{Ag...Ag}} = +23$ MK^{-1}) than the *ab* plane itself ($\alpha_a = +4$ MK^{-1}). We find instead that the value of α_c is remarkably similar to the coefficient of thermal expansion for AgCN chains in silver(I) cyanide itself ($\alpha_c = -15.9(27)$ MK^{-1}),[12] strongly suggesting that the contraction of **2** along **c** is essentially dictated by the intrinsic thermal expansion behavior of this included phase (the striking similarity in expansivity curves is shown in Figure 2b). To accommodate this NTE effect, the framework expands along **a**, but in this case at a much reduced rate to that seen for **1**. While the incommensurate guest inclusion in **2** precludes any crystallographic investigation of the microscopic host/guest interactions involved, the secondary phase certainly appears to control the thermal expansion behavior of the host framework to minimize the difference between the two expansivities.

This degree of control over host behavior can occur because the covalent linkages in **1** and **2** place only one constraint on the values of α_a and α_c: in this specific instance, one has $\alpha_{\mathrm{Zn...Zn}} = (27a^2\alpha_a + 4c^2\alpha_c)/(27a^2 + 4c^2)$. Hence while there are two degrees of freedom in the crystal dimensions, there is effectively only one constraint provided by the framework topology. The system is free to be influenced by much weaker interactions or forces, which we have shown here to include the strain associated with weakly interacting secondary phases.

We conclude by commenting that the thermal expansivities of underconstrained frameworks depend intimately on low energy distortions and interactions and, as such, are open to manipulation by lattice inclusion effects. More generally, given the high structural tolerance to strain effects, we expect that flexible phases similar to **1** or **2** might find application as “thermal buffers” in multicomponent assemblies, i.e., to prevent strain-induced microcracking caused by mismatch in thermal expansivities.

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Supporting Information Available: Synthesis; variable temperature crystallographic data and analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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