DOI: 10.1002/ange.200803925

Metal–Organic Frameworks

Negative Thermal Expansion in the Metal–Organic Framework Material Cu_3(1,3,5-benzenetricarboxylate)$_2$**

*Yue Wu, Atsushi Kobayashi, Gregory J. Halder, Vanessa K. Peterson, Karena W. Chapman, Nina Lock, Peter D. Southon, and Cameron J. Kepert**

In recent years the phenomenon of negative thermal expansion (NTE; that is, contraction upon warming) over a broad temperature range has been detected in a select group of materials[1] and attributed to mechanisms that include electronic and magnetic transitions[2] and transverse atomic and molecular vibrations.[1,3–8] Among the vibrational systems, materials that have received particular attention include AM_2O_8, AM_2O_7, $A_2M_3O_{12}$, and a number of zeolites,[3] which contain M−O−M′ bridges that undergo transverse vibration to cause contraction of the M–M′ distance, and a diverse family of metal cyanides,[4–8] which contain M−C≡N−M′ bridges that show an analogous effect but with increased vibrational flexibility. The presence of a highly flexible diatomic linker in the cyanide phases leads to pronounced thermal expansion behavior, examples of which include the largest isotropic[4] and anisotropic[5] NTE reported to date. A common NTE mechanism proposed for both the oxide and cyanide systems is the coupling of these transverse vibrations into concerted low-energy lattice modes that involve the rotation and/or translation of undistorted metal-coordination polyhedra, known as rigid unit modes (RUMs).[9] With thermal population, these modes counteract the higher-energy longitudinal modes that cause bond-length expansion, thereby leading to bulk NTE behavior.

Recently, NTE has also been proposed in a series of isoreticular metal–organic framework (IRMOF) materials following the detected thermal contraction of gas-sorbed samples of IRMOF-1.[10] Theoretical simulations[11] of these materials have suggested an NTE mechanism closely analogous to that of the metal cyanide phases,[6,7] involving the transverse vibration of linear organic linkers. Following a more general investigation of such materials, herein we present the NTE properties of [Cu_3(btc)$_2$] (btc = 1,3,5-benzenetricarboxylate), a metal–organic framework that consists of dicopper tetracarboxylate "paddlewheels" and aromatic ring motifs.[12] Through crystallographic characterization we elucidate a structural mechanism that involves two unique components: transverse vibration of planar, rather than linear, linkers, and local molecular vibrations within the framework.

The highly symmetric structure of [Cu_3(btc)$_2$] can be conveniently considered as consisting of octahedral supramolecular cages that link through their vertices to form a three-dimensional cubic framework (Figure 1 inset). As the material readily binds atmospheric water and gases at the coordinatively unsaturated Cu sites,[13] samples for powder and single-crystal X-ray diffraction measurement were sealed under vacuum in glass capillaries following their thorough

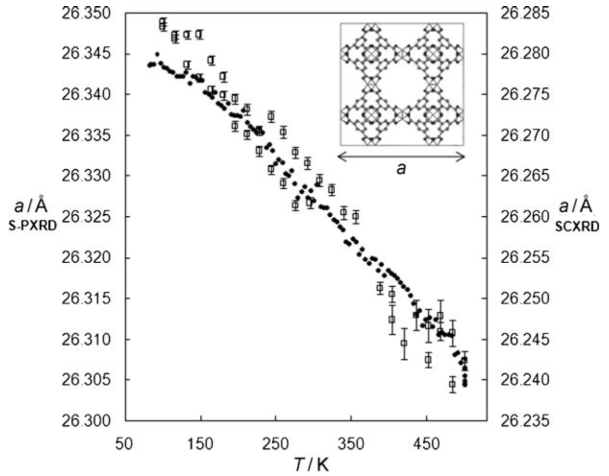

Figure 1. Temperature-dependent variation in the lattice parameter of [Cu_3(btc)$_2$] by PXRD (filled circles) and SC-XRD (open squares). Error bars show one estimated standard deviation (esd). A representation of the unit cell of [Cu_3(btc)$_2$] is depicted in the inset.

---

[*] Y. Wu, Dr. A. Kobayashi, Dr. G. J. Halder, Dr. V. K. Peterson, N. Lock, Dr. P. D. Southon, Prof. C. J. Kepert
School of Chemistry, The University of Sydney
Sydney NSW 2006 (Australia)
Fax: (+61) 2-9351-3329
E-mail: c.kepert@chem.usyd.edu.au
Homepage: http://www.chem.usyd.edu.au/about/staff_kepert.html

Dr. A. Kobayashi
Division of Chemistry, Hokkaido University (Japan)

Dr. G. J. Halder
Materials Science Division, Argonne National Laboratory (USA)

Dr. V. K. Peterson
Bragg Institute
Australian Nuclear Science & Technology Organisation

Dr. K. W. Chapman
X-ray Science Division, Argonne National Laboratory (USA)

N. Lock
Department of Chemistry, University of Aarhus (Denmark)

[**] This work was supported by an Australian Research Council Discovery Project Grant (C.J.K.) and the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. Work done at Argonne National Laboratory and use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We thank Nadia Leyarovska for beamline support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803925.

desolvation under dynamic vacuum at 180°C. To determine the temperature dependence of the lattice parameter, synchrotron-based powder X-ray diffraction (PXRD) patterns were recorded over the temperature range 80–500 K. Lattice parameters obtained from Le Bail fits to the diffraction data demonstrated that the cubic lattice undergoes pronounced, near-linear NTE with an average coefficient of thermal expansion $\alpha = \mathrm{d}l/l\,\mathrm{d}T = -4.1(1)\times10^{-6}\,\mathrm{K}^{-1}$ over this range (l = length; Figure 1). No phase transitions were evident.

To elucidate the structural mechanism of NTE, single-crystal X-ray diffraction (SC-XRD) structural determinations were carried out over the temperature range 100–500 K in 16 K steps. The thermal expansion behavior derived from these data is in close agreement with that documented using PXRD (Figure 1). A small degree of thermal damage was evidenced following heating above 400 K (see the Supporting Information). Systematic structural refinements yielded temperature-dependent changes in both the crystallographic geometries and atomic displacement parameters, associated with the thermal excitation of framework vibrations.

In considering the temperature-dependent atomic positions of $[\mathrm{Cu_3(btc)_2}]$, we note firstly that the framework has inherent structural distortion, whereby the ideal perpendicular arrangement of the paddlewheel and planar benzoic carboxylate cannot both be maintained within the framework's $\mathrm{Pt_3O_4}$-net topology; in its ideal geometry this net consists of distorted square units (with angles 70.5 and 109.5°) and regular planar triangular units.[14] This results in a structure in which the triangular btc linkers lie slightly out of the plane of the copper atoms to form undulating hexagonal sheets. With increasing temperature there is a slight flattening of these sheets, with the deviation of the btc units from the Cu planes decreasing from 0.448 Å at 100 K, to 0.441 Å at 356 K. Concomitant with this flattening is an apparent contraction of the btc unit, with each of its crystallographic bond distances decreasing with increasing temperature (Figure 2b). That the btc sheets contract despite their adoption of a more planar geometry indicates that the NTE behavior is due to a dynamic rather than static deformation, with the decrease in btc bond lengths resulting from libration (that is, dynamic tilting) of these linkers. Two types of btc mode may be differentiated: translation perpendicular to the plane (Figure 3a) and tilting about axes within the plane (Figure 3b), each of which potentially contributes to the NTE behavior. Investigations of the atomic displacement parameters (ADPs) for the btc units (Figure 2a) and, more pertinently, their rate of change with temperature ($\mathrm{d}U/\mathrm{d}T$; Figure 2c),[7,15] indicate that the largest and most rapid thermal excitation of the btc atoms occurs out-of-plane, thus confirming the importance of their transverse motion to the NTE behavior.

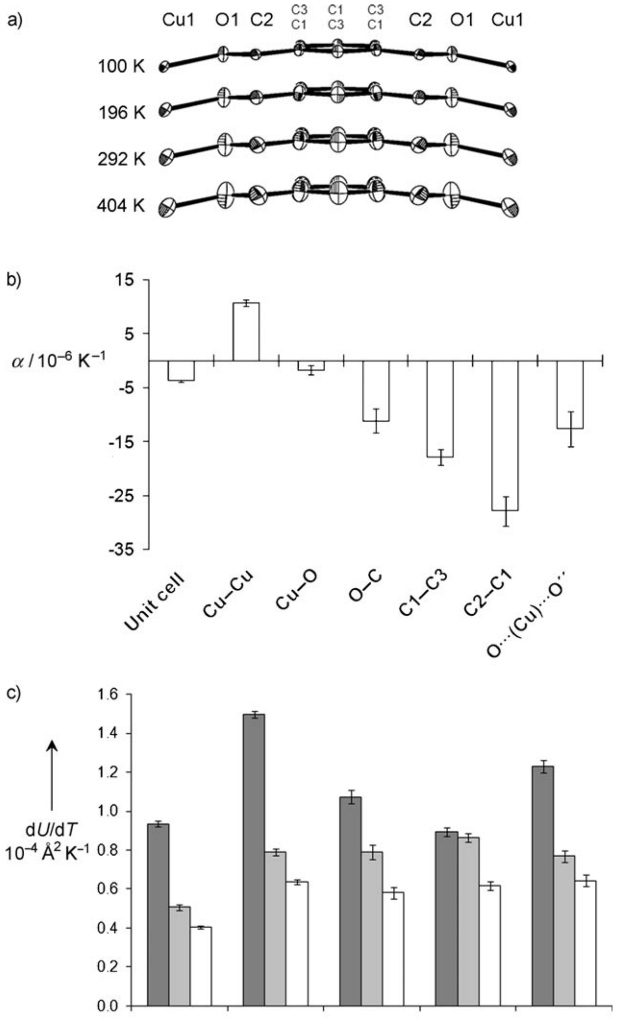

Figure 2. Temperature-dependent structural data derived from SC-XRD structural refinements. a) Anisotropic displacement parameters, represented by thermal ellipsoids set at 50% probability, for a fragment of the $[\mathrm{Cu_3(btc)_2}]$ structure in the temperature range 100–404 K. Hydrogen atoms are omitted for clarity. b) Rate of change of interatomic distances and the unit cell parameter in the temperature range 100–356 K; O···(Cu)···O″ is the distance between *trans* oxygen atoms across the paddlewheel. Error bars shown to 1 esd. c) Rates of change of anisotropic displacement parameters (ADPs) with temperature. Rates are given for the three ADP axes; the major, intermediate, and minor axes are shown in dark gray, light gray, and white, respectively. No cross-over of these axes occurred over the recorded temperature range. Error bars to 1 esd.

A more extensive investigation of the temperature-dependent ADPs indicates that the greatest rate of thermal displacement occurs for the carboxylate oxygen atom perpendicular to the btc plane. This increase is approximately 70% more rapid than that for the neighboring carboxylate carbon atom, C2. These ADPs extrapolate to similarly low values at low temperature, indicating that the carboxylate displacement is dynamic rather than static (see the Supporting Information). These observations suggest that a large component of the carboxylate motion is associated with rotation rather than just translation of this unit, as evidenced by a rapid apparent contraction of the intra-carboxylate O–O′ distance ($\alpha = -60.7(4)\times10^{-6}\,\mathrm{K}^{-1}$; compare Figure 2b). Such a rotation seems likely to be coupled at low energy to the other three paddlewheel carboxylate units, giving a concerted distortion of the $\mathrm{Cu_2O_8}$ square prism that involves rotation of the square $\mathrm{CuO_4}$ planes in opposite directions (that is, towards a square antiprism; Figure 3c). Across the paddlewheel, there is an associated contraction of the O···(Cu)···O″ distance (the

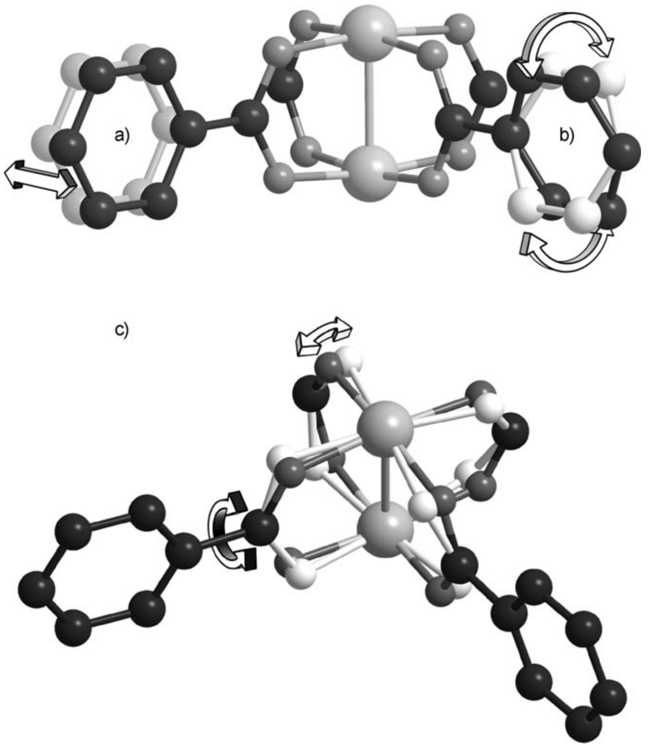

Figure 3. Vibrational motions proposed to be responsible for NTE in $[Cu_3(btc)_2]$: a) Translation of the aromatic ring; b) libration of the aromatic ring; c) local twisting vibrations of the paddlewheel unit. C black, O dark gray, Cu light gray; distortions shown in white. Hydrogen atoms are omitted for clarity.

distance between *trans* oxygen atoms, Figure 2(b)), consistent with both this vibration and the rotation of the paddlewheel through btc translation and libration. Also of note is the elongation of the Cu–Cu vector (the only close interaction for which expansion is observed crystallographically; Figure 2b), which we attribute to thermal population of an anharmonic Cu–Cu stretching mode at low energy; this mode may further contribute to the thermal contraction of the paddlewheel within its plane. These are expected to be the lowest energy paddlewheel deformation modes, with distortion of the square-planar connectivity known to occur only at much higher energies.[16] Paddlewheel modes that are decoupled from btc libration and involve only the rotation or stretching of the carboxylate unit are expected to be essentially "local" in nature, as there is little communication of carboxylate orientation through the btc linker.

Whereas no obvious mechanism is apparent for the paddlewheel modes to be coupled throughout the structure, the same is clearly not true for the transverse btc modes, which involve a net translation rather than rotation of the carboxylate units and, therefore, a rotation or translation of the paddlewheels. Analysis of the Cu ADPs (Figure 2b) corresponding to the latter motion indicates a relatively rapid thermal excitation in the plane of the paddlewheel units that corresponds to a concerted tilting of the octahedral cages reminiscent of that seen in perovskites.[17] Notably, both the rotation and translation of the paddlewheels serve locally to decrease the distortion of two btc linkers at the expense of increased distortion of the neighboring two units (see the Supporting Information for a full description). A broad spectrum of low energy RUMs that maintain the square-planar geometry of the paddlewheel are therefore envisaged for this system, each with varying degrees of btc translation and libration. Notably, the triangular connectivity adopted appears to lead to a degree of geometric frustration in which btc libration must necessarily be involved to some extent in all such concerted modes. The existence of such distortions at low energy is consistent with the recent report of very high lattice compressibility for this material.[18]

The overall impression of NTE we obtain can be uniquely described in terms of both concerted lattice modes and local vibrations. In comparing this system with other NTE materials, we note firstly that the multiple transverse vibrational modes of the btc linker render this system loosely analogous to the metal cyanide[7] and IRMOF series,[11] in which the presence of multiply hinged linkers allows independent rotation and translation of neighboring mono/polynuclear metal centers at low energy. Such a feature gives these systems fundamentally more flexibility than oxide-based materials, in which the single-atom M–O–M′ bridge constrains the relative motion of neighboring MO_x polyhedra.[9] An important point that distinguishes $[Cu_3(btc)_2]$ from all other NTE systems is the presence of triangular rather than linear framework linkages, prompting us to propose a "trampoline" rather than "skipping rope" analogy for transverse modes in this system. Whereas the detected concerted transverse vibrations are at least loosely analogous to other NTE systems, the presence of local vibrational modes within a polynuclear metal complex represents a fundamentally new mechanism for NTE. Notably, such local modes appear not to have been considered in the analysis of lattice dynamical simulations of the IRMOF series.[11] Such a mechanism suggests a novel future approach for the generation of anomalous expansion materials in which "predesigned" components are incorporated into framework lattices to direct specific expansion properties.

To conclude, through analysis of the changes in atomic positions and rates of change of vibrational amplitudes we have derived a novel vibrational mechanism for NTE of the metal–organic framework $[Cu_3(btc)_2]$. This mechanism is considerably more complex than that seen in other NTE framework systems and, uniquely, involves local molecular vibrations within a polynuclear metal center and concerted transverse vibrations of two-dimensional rather than one-dimensional linkers.

Experimental Section

Phase-pure crystalline $[Cu_3(btc)_2]$ samples were grown hydrothermally from mixtures of $Cu(NO_3)_2$ solution (3.37 g in 12 mL H_2O) and H_3btc suspension (1.47 g in 12 mL ethanol) held at 95 °C for 15 h in teflon-lined bombs and cooled immediately to room temperature, then repeatedly washed with methanol at 50 °C and decanted, until pure octahedral crystals were obtained. PXRD data were collected at the Advanced Photon Source (APS) on beam line 12BM ($\lambda = 0.61992$ Å). SC-XRD data were collected on a Bruker-Nonius FR591 Kappa APEX II equipped with Oxford Cryosystems nitrogen cryostreams and graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a rotating anode.

Received: August 8, 2008

Keywords: coordination frameworks · materials science · metal–organic frameworks · microporous materials · thermal expansion

---

[1] A. W. Sleight, *Annu. Rev. Mater. Sci.* **1998**, *28*, 29; J. S. O. Evans, *J. Chem. Soc. Dalton Trans.* **1999**, 3317; C. J. Kepert, *Chem. Commun.* **2006**, 695.

[2] Y. M. Hao, Y. Gao, B. W. Wang, J. P. Qu, Y. X. Li, J. F. Hu, J. C. Deng, *Appl. Phys. Lett.* **2001**, *78*, 3277; J. R. Salvador, F. Gu, T. Hogan, M. G. Kanatzidis, *Nature* **2003**, *425*, 702; J. Arvanitidis, K. Papagelis, S. Margadonna, K. Prassides, A. N. Fitch, *Nature* **2003**, *425*, 599; K. Takenaka, H. Takagi, *Appl. Phys. Lett.* **2005**, *87*, 261902.

[3] V. Korthuis, N. Khosrovani, A. W. Sleight, N. Roberts, R. Dupree, W. W. Warren, *Chem. Mater.* **1995**, *7*, 412; T. A. Mary, J. S. O. Evans, T. Vogt, A. W. Sleight, *Science* **1996**, *272*, 90; J. S. O. Evans, Z. Hu, J. D. Jorgensen, D. N. Argyriou, S. Short, A. W. Sleight, *Science* **1997**, *275*, 61; C. Lind, A. P. Wilkinson, Z. B. Hu, S. Short, J. D. Jorgensen, *Chem. Mater.* **1998**, *10*, 2335; J. S. O. Evans, W. I. F. David, A. W. Sleight, *Acta Crystallogr. Sect. B* **1999**, *55*, 333; P. Lightfoot, D. A. Woodcock, M. J. Maple, L. A. Villaescusa, P. A. Wright, *J. Mater. Chem.* **2001**, *11*, 212.

[4] A. E. Phillips, A. L. Goodwin, G. J. Halder, P. D. Southon, C. J. Kepert, *Angew. Chem.* **2008**, *120*, 1418; *Angew. Chem. Int. Ed.* **2008**, *47*, 1396.

[5] A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters, M. G. Tucker, *Science* **2008**, *319*, 794.

[6] K. W. Chapman, P. J. Chupas, C. J. Kepert, *J. Am. Chem. Soc.* **2006**, *128*, 7009; A. L. Goodwin, K. W. Chapman, C. J. Kepert, *J. Am. Chem. Soc.* **2005**, *127*, 17980; K. W. Chapman, P. J. Chupas, C. J. Kepert, *J. Am. Chem. Soc.* **2005**, *127*, 11232; S. Margadonna, K. Prassides, A. N. Fitch, *J. Am. Chem. Soc.* **2004**, *126*, 15390.

[7] A. L. Goodwin, C. J. Kepert, *Phys. Rev. B* **2005**, *71*, 140301; A. L. Goodwin, *Phys. Rev. B* **2006**, *74*, 134302.

[8] T. Pretsch, K. W. Chapman, G. J. Halder, C. J. Kepert, *Chem. Commun.* **2006**, 1857; K. W. Chapman, P. J. Chupas, C. J. Kepert, *J. Am. Chem. Soc.* **2005**, *127*, 15630.

[9] A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, M. C. Warren, *J. Phys. Condens. Matter* **1996**, *8*, 10973.

[10] J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science* **2005**, *309*, 1350.

[11] D. Dubbeldam, K. S. Walton, D. E. Ellis, R. Q. Snurr, *Angew. Chem.* **2007**, *119*, 4580; *Angew. Chem. Int. Ed.* **2007**, *46*, 4496; S. S. Han, W. A. Goddard, *J. Phys. Chem. C* **2007**, *111*, 15185.

[12] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.

[13] V. K. Peterson, Y. Liu, C. M. Brown, C. J. Kepert, *J. Am. Chem. Soc.* **2006**, *128*, 15578; C. Prestipino, L. Regli, J. G. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P. L. Solari, K. O. Kongshaug, S. Bordiga, *Chem. Mater.* **2006**, *18*, 1337.

[14] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, **1984**.

[15] W. R. Busing, H. A. Levy, *Acta Crystallogr.* **1964**, *17*, 142.

[16] P. Drozdzewski, A. Brozyna, *Spectrochim. Acta Part A* **2005**, *62*, 703.

[17] A. M. Glazer, *Acta Crystallogr. Sect. B* **1972**, *28*, 3384.

[18] K. W. Chapman, G. J. Halder, P. J. Chupas, *J. Am. Chem. Soc.* **2008**, *130*, 10524.