

# A solid-state phase transition at 41 K involving the cooperative ordering of a fluxional pseudo-Jahn–Teller Cu<sup>II</sup> system

Michael A. Leech,<sup>\*a</sup> Nayan K. Solanki,<sup>b</sup> Malcolm A. Halcrow,<sup>c</sup> Judith A. K. Howard<sup>a</sup> and Slimane Dahaoui<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE.  
E-mail: m.a.leech@dur.ac.uk

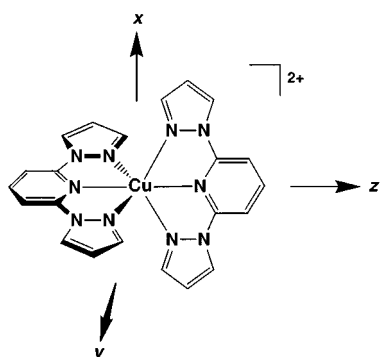
<sup>b</sup> Department of Chemistry, University of Cambridge, Cambridge, UK CB2 1EW

<sup>c</sup> School of Chemistry, University of Leeds, Leeds, UK LS2 9IT

Received (in Cambridge, UK) 24th August 1999, Accepted 7th October 1999

The complex [Cu{2,6-di(pyrazol-1-yl)pyridine}<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> undergoes a solid-state phase transition at 41 K, involving the cooperative ordering of its planar dynamic pseudo-Jahn–Teller system; this unique phase transition is characterised by single-crystal X-ray diffraction techniques, employing an open-flow helium cryostat.

The structural and electronic consequences of the Jahn–Teller effect in transition metal chemistry continue to be well studied.<sup>1</sup> For Cu<sup>II</sup> complexes of meridional tris-N-donor ligands, the Jahn–Teller distortion takes the form of an elongated axis, which in the solid state is often dynamically disordered in the molecular *xy* plane (Scheme 1).<sup>2–4</sup>



Scheme 1 Molecular axes of [CuL<sub>2</sub>]<sup>2+</sup>.

We have recently described one compound that undergoes this behaviour, namely [CuL<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> [L = 2,6-di(pyrazol-1-yl)pyridine], whose powder EPR spectrum at room temperature exhibits the ‘inverse’  $g_{\perp} > g_{\parallel} > g_e$  pattern typical of a planar dynamic { $d_{x^2-y^2}$ }<sup>1</sup> Jahn–Teller system.<sup>4</sup> At lower temperatures, this spectrum becomes rhombic as the Jahn–Teller fluxionality is frozen out and the static  $g_{\parallel} > g_{\perp} > g_e$  spectrum is reached only below 20 K.<sup>4,5</sup> In order to quantify the solid state fluxionality in [CuL<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>6</sup> we have undertaken a variable temperature X-ray diffraction study of this compound. We describe herein that it undergoes a unique<sup>1</sup> reversible phase transition at 41 K, involving a complex ordering of the Jahn–Teller axis of elongation in the molecular *xy* plane.

The structure was determined both above (1: 50 K) and below (2: 31 K) the phase transition. The structure at 50 K reveals one [CuL<sub>2</sub>]<sup>2+</sup> and two [BF<sub>4</sub>]<sup>−</sup> ions in the asymmetric unit (Fig. 1). One [BF<sub>4</sub>]<sup>−</sup> ion is disordered over two positions [0.69(3) and 0.31(3) occupied] equivalent to a rotation of approximately 23° about one B–F bond vector. The Cu coordination is distorted slightly from octahedral geometry owing to the conformational requirements of the tridentate ligands. The bond distances within the Cu coordination sphere (Table 1), show short bonds along the molecular *z*-axis, long bonds along the molecular *x*-axis and intermediate length bonds along the molecular *y*-axis. This range reflects the disorder of the Jahn–Teller axis of elongation about the molecular *x*- and *y*-vectors, with the longer

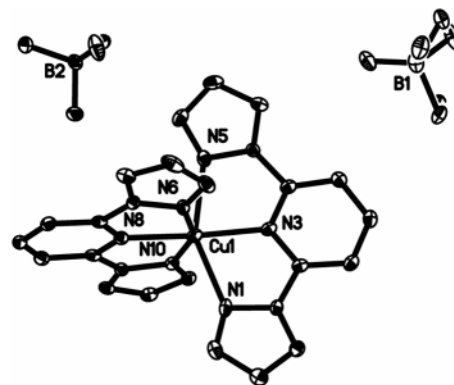


Fig. 1 Crystallographic asymmetric unit at 50 K.

Table 1 Cu–N distances (Å) at 50 and 31 K

	50 K	Cu–N distance (Å)		
		31 K A	B	C
Cu–N6 ( <i>y</i> -axis)	2.1080(17)	2.058(2)	2.261(2)	2.056(2)
Cu–N10 ( <i>y</i> -axis)	2.1210(17)	2.076(2)	2.286(2)	2.077(2)
Cu–N5 ( <i>x</i> -axis)	2.2259(18)	2.282(2)	2.072(2)	2.266(2)
Cu–N1 ( <i>x</i> -axis)	2.2527(18)	2.290(2)	2.088(2)	2.306(2)
Cu–N3 ( <i>z</i> -axis)	2.0175(15)	2.028(2)	1.963(2)	2.026(2)
Cu–N8 ( <i>z</i> -axis)	1.9763(14)	1.967(2)	2.037(2)	1.958(2)

Cu–N bonds along the molecular *x*-axis indicating a larger statistical population in this direction.

On cooling, the crystal undergoes a sharp, reversible phase transition at 41 K accompanied by a tripling of the crystallographic *b* axis. The transition was followed successfully using a CCD diffractometer, by taking a series *hk0* zone images intermediate to cooling the crystal in −1 K steps. Two such images are shown in Fig. 2, taken at 42 and 40 K. The additional

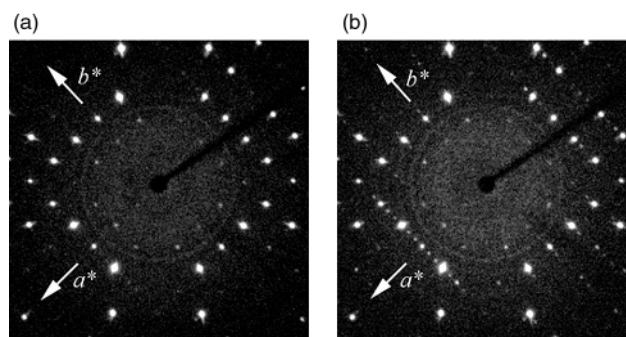


Fig. 2 *hk0* zone images with the two reciprocal-lattice axes labelled: (a) above the phase change at 42 K and (b) below the phase change at 40 K. The additional reflections in the 40 K image correspond to the tripling of crystallographic *b* axis.

reflections in the 40 K image correspond to the tripling of  $b$  axis.

The structure at 31 K reveals three  $[\text{CuL}_2]^{2+}$  and six  $[\text{BF}_4]^-$  ions in the asymmetric unit (Fig. 3). The Jahn–Teller elongated axis, which is disordered in the molecular  $xy$  plane above 41 K, is now ordered. The elongated axis of two of the three independent cations (**A** and **C**) are aligned along the molecular  $x$ -axis, while in the third cation (**B**), it is aligned along the molecular  $y$ -axis; see Cu–N distances in Table 1. It is interesting to note that the mean Cu–N distances for all three molecules correspond closely to those found in the disordered 50 K structure. This indicates that the population distribution of the elongated axis along the  $x$  and  $y$  vectors is similar, both above, and below the phase change. Furthermore, the  $[\text{BF}_4]^-$  ion, which is disordered above 41 K, is now ordered into three non-equivalent sites, two in one orientation and the third in another. Again, this corresponds to the populations of the two orientations in the disordered structure (0.69:0.31). Thus, the ordering of the Jahn–Teller elongated axis in the cation and of the  $[\text{BF}_4]^-$  ion are intimately linked, suggesting cooperative van der Waals interactions between the two moieties. Cooperative ordering of the Jahn–Teller elongated axis has been seen previously in Tutton salts<sup>7</sup> and copper methoxyacetate.<sup>8</sup> However, these

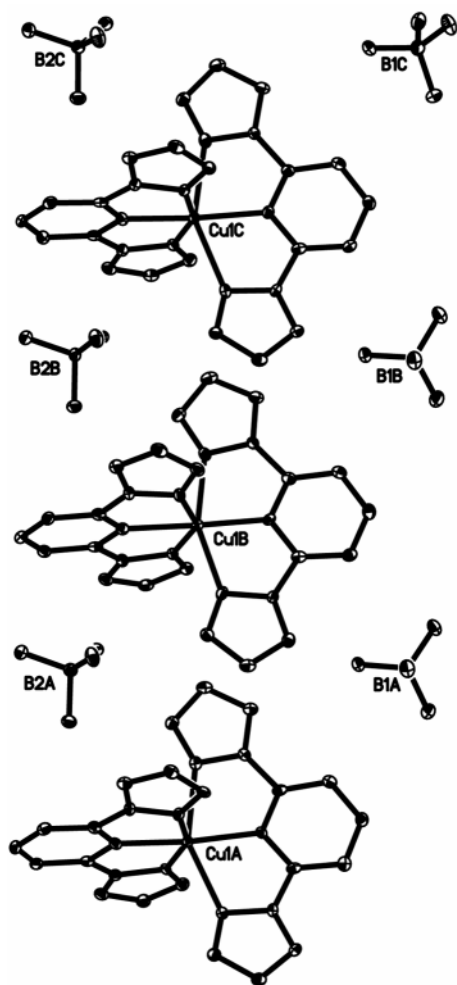


Fig. 3 Crystallographic asymmetric unit at 31 K.

materials possess H-bonded networks, which may act as the mechanism for mediating the cooperative interactions.

In conclusion, this is the first example of a structurally characterised phase transition, involving the low-temperature ordering of a dynamically disordered Jahn–Teller system. That the mechanism for co-operation between the molecules relies on weak van der Waals interactions alone makes this system unique. Additionally, the reversible phase transition is extremely sharp and shows no hysteresis effects, making this material highly suitable as a temperature standard in the sub-liquid nitrogen temperature range, which has recently become more accessible with the introduction of the open-flow helium cryostat.<sup>9</sup>

The authors would like to thank Dr J. E. Davies (Cambridge) for preliminary studies and the Royal Society (M. A. H.), EPSRC (M. A. L., N. K. S., S. D. and J. A. K. H., Senior Research Fellowship) and ICI R&T Division (N. K. S.) for financial support.

## Notes and references

† *Crystal data*: **1**,  $\text{C}_{22}\text{H}_{18}\text{CuN}_{10}\text{B}_2\text{F}_8$ ,  $M = 659.62$ , monoclinic, space group  $P2_1$ ,  $a = 8.414(1)$ ,  $b = 8.475(1)$ ,  $c = 18.683(2)$  Å,  $\beta = 97.371(2)^\circ$ ,  $V = 1321.2(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 0.918$  mm<sup>-1</sup> (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å),  $D_c = 1.658$  Mg m<sup>-3</sup>. Selected crystal mounted on nylon fibre using perfluoropolyether oil, cooled slowly to 50(2) K in chilled helium gas flow using Oxford Cryosystems HELIX.<sup>9</sup> 12227 reflections ( $2.20 < \theta < 28.01^\circ$ ) collected on a Bruker SMART-CCD diffractometer ( $\omega$ -scan,  $0.3^\circ/\text{frame}$ ) yielding 5261 unique data ( $R_{\text{int}} = 0.0158$ ). The structure was solved by direct methods and refined by full-matrix least squares based on  $F^2$  for all data using SHELXL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were placed geometrically at calculated positions and refined with a riding model. Final  $wR(F^2) = 0.0593$  and  $R(F) = 0.0232$  for all data (417 refined parameters), GOF = 1.047, residuals  $\Delta\rho_{\text{min,max}} = -0.37, 0.38$  e Å<sup>-3</sup>.

**2**,  $\text{C}_{22}\text{H}_{18}\text{CuN}_{10}\text{B}_2\text{F}_8$ ,  $M = 659.62$ , monoclinic, space group  $P2_1$ ,  $a = 8.4047(6)$ ,  $b = 25.389(2)$ ,  $c = 18.668(1)$  Å,  $\beta = 97.205(1)^\circ$ ,  $V = 3952.1(5)$  Å<sup>3</sup>,  $Z = 6$ ,  $\mu = 0.921$  mm<sup>-1</sup> (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å),  $D_c = 1.663$  Mg m<sup>-3</sup>,  $T = 31(2)$  K. Crystal mounting, cooling, data collection, structure solution and refinement methods as for **1**. 23287 reflections ( $2.39 < \theta < 27.57^\circ$ ) collected yielding 9396 unique data ( $R_{\text{int}} = 0.0265$ ) which were used in all calculations. Final  $wR(F^2) = 0.0738$  and  $R(F) = 0.0303$  for all data (1163 refined parameters), GOF = 1.046, residuals  $\Delta\rho_{\text{min,max}} = -0.44, 0.38$  e Å<sup>-3</sup>.

CCDC 182/1436. See <http://www.rsc.org/suppdata/cc/1999/2245/> for crystallographic files in .cif format.

- M. A. Hitchman, *Comments Inorg. Chem.*, 1994, **15**, 197; L. R. Falvello, *J. Chem. Soc., Dalton Trans.*, 1997, 4463.
- M. Duggan, B. J. Hathaway and J. Mullane, *J. Chem. Soc., Dalton Trans.*, 1980, 690.
- J.-V. Folgado, W. Henke, R. Allmann, H. Stratemeier, D. Beltrán-Porter, T. Rojo and D. Reinen, *Inorg. Chem.*, 1990, **29**, 2035.
- N. K. Solanki, E. J. L. McInnes, F. E. Mabbs, S. Radojevic, M. McPartlin, N. Feeder, J. E. Davies and M. A. Halcrow, *Angew. Chem., Int. Ed.*, 1998, **37**, 2221.
- N. K. Solanki, F. E. Mabbs and M. A. Halcrow, unpublished work.
- C. J. Simmons, *New J. Chem.*, 1993, **17**, 77.
- W. Rauw, H. Ashbahr, M. A. Hitchman, S. Lukin, D. Reinen, A. J. Schultz, C. J. Simmons and H. Stratemeier, *Inorg. Chem.*, 1996, **35**, 1902.
- K. Prout, A. Edwards, V. Mtetwa, J. Murray, J. F. Saunders and F. J. C. Rossotti, *Inorg. Chem.*, 1997, **36**, 2820.
- A. E. Goeta, L. K. Thompson, C. L. Sheppard, S. S. Tandon, C. W. Lehmann, J. Cosier, C. Webster and J. A. K. Howard, *Acta Crystallogr., Sect. C*, 1999, **55**, 1243.

Communication 9/06876G