

## Observation of Symmetry Lowering and Electron Localization in the Doublet-States of a Spin-Frustrated Equilateral Triangular Lattice: $\text{Cu}_3(\text{O}_2\text{C}_{16}\text{H}_{23})_6 \cdot 1.2\text{C}_6\text{H}_{12}$

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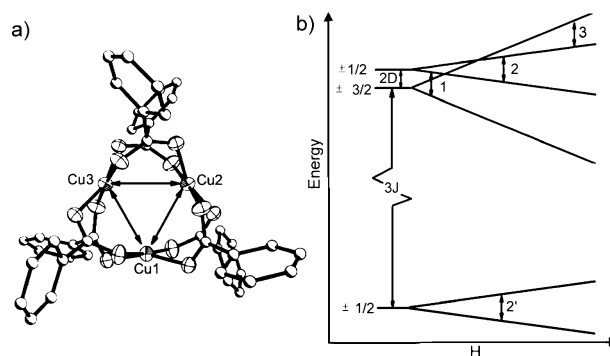
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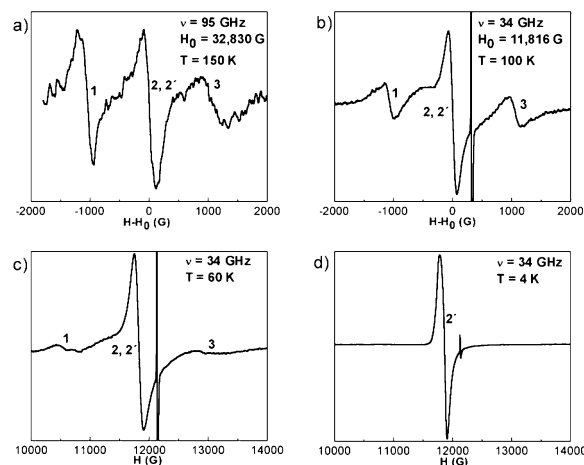
We here report that  $\text{Cu}_3(\text{O}_2\text{C}_{16}\text{H}_{23})_6 \cdot 1.2\text{C}_6\text{H}_{12}$ , synthesized recently,<sup>1</sup> appears to be a versatile model system for investigating the phenomenon of intramolecular magnetic exchange and spin-frustration in a lattice containing three unpaired electrons. It contains a  $\text{Cu}_3^{6+}$  core in which three  $\text{Cu}^{2+}$  ( $3d^9$ ) ions are bridged together in an equilateral-triangular geometry with rigorous three-fold symmetry<sup>1</sup> (Figure 1), thus constituting the simplest case of a spin-frustrated lattice. This study was undertaken because studies of magnetic exchange in simple polynuclear paramagnetic clusters are a topic of current focus in magnetochemistry.<sup>2</sup> A particularly important issue is to find well-characterized compounds for which one could obtain precise information on both the ground state and the excited states of a strongly coupled paramagnetic system. For example, in the single molecule magnets<sup>3</sup> such as  $\text{Mn}_{12}$ -acetate<sup>4</sup> and  $\text{Fe}_8\text{Br}_8$ ,<sup>5</sup> which have received extensive attention recently,<sup>6</sup> the magnetic properties seem to indicate the involvement of excited spin multiplets, in addition to the  $S = 10$  ground state, but the complexity due to the large number of possible energy levels has made it difficult to confirm their involvement.<sup>7</sup> Iron-sulfur clusters have also been studied,<sup>8</sup> but they are more complex than the tricopper type triangle. In fact, to our knowledge, there has been no report of a detailed characterization of the (three) spin multiplets of even a three-electron spin system.

On general grounds, a simple system would involve a  $\text{Cu}_3^{6+}$  core. The three unpaired electrons on this core interact magnetically via superexchange involving  $\text{Cu}^{2+}-\text{O}-\text{Cu}^{2+}$  pathways. The core could exist in either a spin-frustrated ( $S_{\text{total}} = 1/2$ , doubly degenerate) state or in a  $S_{\text{total}} = 3/2$ , quartet state, separated by an energy of  $3J$ , where  $J$  is the spin-exchange constant in the Hamiltonian  $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_1 \cdot S_3)$ , see Figure 1b.

In this regard, we note that two other examples have recently been reported.<sup>9,10</sup> Padilla et al.<sup>9</sup> have investigated  $[\text{L}_3\text{Cu}_3(\text{Im})_3](\text{ClO}_4)_3$ ,  $\text{L} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane and  $\text{Im} = \text{imidizolate}$ , in which the  $\text{Cu}_3^{6+}$  core forms a quasi-equilateral triangle. López-Sandoval et al.<sup>10</sup> reported on  $[\text{Cu}_3(\text{cpse})_3(\text{H}_2\text{O})_3] \cdot 8.5\text{H}_2\text{O}$ , cpse = doubly deprotonated form of  $N$ -[2-hydroxyl-1( $S$ )-methyl-2( $S$ )-phenylethyl]- $N$ -methyl glycine, composing a truly equilateral  $\text{Cu}^{2+}$  triangle. These studies employed EPR spectroscopy, in addition to magnetization measurements, because EPR provides more precise data on the molecular orbital of the unpaired electron. However, neither study was able to resolve spin-spin splitting (fine structure) from the three electrons, or any electron-nuclear hyperfine structure from the Cu nuclei, possibly because of the use of low-frequency EPR in ref 9 or only powder samples in ref 10. To our knowledge, this is the first time that a lattice has been found that yielded such detailed information on the symmetry



**Figure 1.** (a) The molecular structure of  $\text{Cu}_3(\text{O}_2\text{C}_{16}\text{H}_{23})_6 \cdot 1.2\text{C}_6\text{H}_{12}$ . The arrows indicated the equilateral triangle formed by three  $\text{Cu}^{2+}$  ions separated by 3.131 Å and bridged by two carboxylate groups. (b) Energy level diagram and the expected EPR transitions.



**Figure 2.** (a,b) Measurement frequency/field dependence of the EPR spectrum. (b-d) Temperature dependence of the 34 GHz spectrum. The sharp line is DPPH ( $g = 2.0037$ ). The numbering corresponds to Figure 1b.

and bonding properties of a spin-frustrated triangular lattice. Single crystals of  $\text{Cu}_3(\text{O}_2\text{C}_{16}\text{H}_{23})_6 \cdot 1.2\text{C}_6\text{H}_{12}$ , prepared as in ref 1, were thick plates with well-developed faces, with the  $\text{Cu}_3$  triangle lying in the plane of the plates. Their authenticity was ascertained by X-ray diffraction and/or magnetic measurements. The EPR measurements were made with either a Bruker X/Q-band (9.5, 34.5 GHz) spectrometer or a locally developed W-band, 95 GHz system.<sup>11</sup>

Figure 2 shows some typical EPR spectra from single crystals, with the magnetic field aligned along the crystal's three-fold axis. A triplet begins to appear when the temperature reaches 60 K and becomes increasingly dominant, with the splitting being essentially

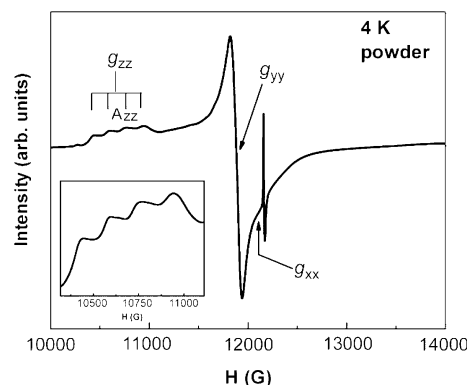
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independent of the magnetic fields employed (Figure 2a,b). The triplet decreases in intensity with a lowering of the temperature, becoming nonobservable below 30 K, showing that it originates from an excited state. Angular variation measurements in three mutually perpendicular crystal planes showed that the splitting followed a  $(3 \cos^2 \theta - 1)$  trend, where  $\theta = 0^\circ$  corresponds to the three-fold symmetry axis. The presence of the three transitions following this  $(3 \cos^2 \theta - 1)$  variation of their spacing enabled us to assign the triplet to the excited quartet ( $S = 3/2$ ) state with the parameters:  $D = -535$  G,  $E = 0$ ,  $g_{\parallel} = 2.209$ , and  $g_{\perp} = 2.057$ , confirming that the quartet state exhibits the full three-fold symmetry of the  $\text{Cu}_3^{6+}$  core. The negative sign on  $D$  was deduced from the observation that the lowest-field peak was always much stronger than that at the highest field.<sup>12</sup>

The central component of the triplet was always slightly asymmetric and more intense than the outer peaks due to the fact that the EPR transition from the doublet state occurs at the same field. This was confirmed by lowering the temperature, which resulted in increased intensity of the central component at the expense of the triplet based on the Boltzmann distribution. In fact, below 30 K, only the singlet can be observed, and it further grows in intensity down to the lowest temperature used, 4 K (Figure 2b–d). We analyzed the temperature dependence of the relative intensities of the signals from the quartet and the doublet transitions using the standard formula for the relative intensities of the signals from a ground-state doublet and an excited-state quartet located  $3J$  above:  $I_{3/2}(T)/I_{1/2}(T) = Ce^{3J/kT}/[1 + e^{3J/kT}]$ , where  $C$  is a constant of proportionality. The analysis yielded a value of  $3J = -321 \pm 6$  K, in good agreement with that ( $-324$  K) from the earlier magnetization data.<sup>1</sup> Also, for the  $H \parallel z$  orientation, as we lowered the temperature, the lowest-field component of the triplet became much stronger than that at the highest field. This observation clearly implies<sup>12</sup> that the sign of the  $D$  parameter is negative; that is, in the quartet state, the  $M_S = \pm 3/2$  states lie lower than the  $\pm 1/2$  states (Figure 1b).

Detailed angular variation measurements were carried out for the middle peak of the spectrum, which at 4 K was assignable solely to the ground state with  $S = 1/2$ . In general, as the orientation was changed from that for  $\theta = 0^\circ$ , the peak split broadly into four, as expected from the four chemically equivalent but magnetically distinct  $\text{Cu}^{2+}$  sites in the unit cell.<sup>1</sup> In particular, around  $\theta = 60^\circ$ , the lowest-field component exhibited a quartet hyperfine structure, characteristic of a single  $\text{Cu}^{2+}$  nucleus, with the nuclear spin  $I = 3/2$ . Note that from an equilateral triangle containing a spin on each vertex, we expected an equal probability for each vertex of the triangle to contain the single unpaired spin. If this were the case, the hyperfine component of the spectrum should be expected to consist of 10 peaks, considering three equivalent  $I = 3/2$  Cu nuclei. Instead, the spectrum reveals the presence of only four hyperfine lines, indicating that in its  $S = 1/2$  ground state, the unpaired spin density must be localized on a single Cu nucleus, in contrast to being spread with equal probability over the three Cu nuclei in the  $\text{Cu}_3$  core (as was found at  $T > 50$  K for the quartet state). To ensure that this splitting did not arise from site splitting in a possibly broken or misaligned crystal, we recorded spectra from a powder sample. The 4 K, 35 GHz powder spectrum (Figure 3) confirms the presence of only four hyperfine lines ( $A_{zz} = 157$  G) and the presence of the  $g_{xx}$  component of the  $g$ -tensor due to reduction of axial symmetry. Based on Figure 3, the ground state of this system is described by  $g_{xx} = 2.005$ ,  $g_{yy} = 2.050$ ,  $g_{zz} = 2.282$ ,  $A_{zz} = 157$  G, and  $\Delta H_{\text{pp}}$  peak-to-peak line width = 116 G.

Summarizing,  $\text{Cu}_3(\text{O}_2\text{C}_{16}\text{H}_{23})_6 \cdot 1.2\text{C}_6\text{H}_{12}$  has been found to be unique among other triangular exchange systems because it has



**Figure 3.** The 34 GHz powder spectrum recorded at 4 K. Evidence for the reduction of three-fold symmetry at low temperatures is given by the presence of the  $g_{xx}$  component and only four hyperfine lines. The sharp line is from DPPH ( $g = 2.0037$ ).

enabled the measurements of the magnetic parameters of the ground as well as excited states of a spin frustrated system in an equilateral geometry. Surprisingly, in the spin-frustrated state, at very low temperature, the unpaired electron orbital is found to localize on only one of the three nuclei of the  $\text{Cu}_3$  trimer, with concomitant loss of the three-fold symmetry. It seems justified to hypothesize that a Jahn–Teller distortion (perhaps to an isosceles triangle) occurs. This point is not well understood at present and needs further theoretical investigations. Moreover, the  $\text{Cu}_3$  core ions can be extended to a larger polynuclear system, and it could also incorporate other paramagnetic ions. This molecule thus constitutes a good example of spin frustration, and the present study should motivate additional theoretical as well as experimental investigations.

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## References

- (1) Clérac, R.; Cotton, F. A.; Dunbar, K. R.; Hillard, E. A.; Petrukhina, M. A.; Smucker, B. W. *C. R. Acad. Sci. Paris, Chimie/Chemistry* **2001**, *4*, 315.
- (2) Kahn, O. *Chem. Phys. Rev.* **1997**, *265*, 165.
- (3) Aromí, G.; Aubin, S. M. J.; Bolcar, M. A.; Christou, G.; Eppley, H. J.; Foltling, K.; Hendrickson, D. N.; Huffman, J. C.; Squire, R. C.; Tsai, H.-L.; Wang, S.; Wemple, M. W. *Polyhedron* **1998**, *17*, 3005.
- (4) (a) Lis, T. *Acta Crystallogr.* **1980**, *B36*, 2042. (b) Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett.* **1996**, *76*, 3830. (c) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature (London)* **1996**, *383*, 145.
- (5) (a) Wieghart, K.; Pohl, K.; Jibril, H.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 77. (b) Sangregorio, C.; Ohm, T.; Paulsen, C.; Sessoli, R.; Gatteschi, D. *Phys. Rev. Lett.* **1997**, *78*, 4645.
- (6) For detailed references, see: Aubin, S. M. J.; Sun, Z.; Eppley, H. J.; Rumberger, E. M.; Guzei, E. A.; Foltling, K.; Gantzel, P. K.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **2001**, *40*, 2127.
- (7) (a) Hennion, M.; Pardi, L.; Mirebeau, E.; Suard, R.; Sessoli, R.; Gatteschi, D. *Phys. Rev. B* **1997**, *56*, 8819. (b) Gomes, A. M.; Novak, R.; Sessoli, R.; Caneschi, A.; Gatteschi, D. *Phys. Rev. B* **1998**, *57*, 5021. (c) Barbara, B.; Thomas, L.; Lionti, F.; Sulpice, A.; Caneschi, A. *J. Magn. Magn. Mater.* **1998**, *177*, 1324.
- (8) See, for example: (a) Duderstadt, R. E.; Staples, C. R.; Brereton, P. S.; Adams, M. W. W.; Johnson, M. K. *Biochemistry* **1999**, *38*, 10585. (b) Telser, J.; Huang, H.; Lee, H.-I.; Adams, M. W. W.; Hoffman, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 861. (c) Zhou, J.; Hu, Z.; Muenck, E.; Holm, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 1966.
- (9) Padilla, J.; Gatteschi, D.; Chaudhuri, P. *Inorg. Chim. Acta* **1997**, *260*, 217.
- (10) López-Sandoval, H.; Contreras, R.; Escuer, A.; Vicente, R.; Bernès, S.; Nöth, H.; Leigh, G. J.; Barba-Behrens, N. *J. Chem. Soc., Dalton Trans.* **2002**, 2648.
- (11) (a) Cage, B.; Geyer, W.; Abboud, K. A.; Dalal, N. S. *Chem. Mater.* **2001**, *13*, 871. (b) Cage, B.; Dalal, N. S. *Chem. Mater.* **2001**, *13*, 880.
- (12) (a) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Dover: New York, 1970. (b) Pilbrow, J. R. *Transition Ion Electron Paramagnetic Resonance*; Clarendon Press: Oxford, 1990. (c) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; John Wiley & Sons: New York, 1970.

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