

# Photoinduced Phase Transition of the Coordinationally Unsaturated $d^9$ Metal Centers of Bis(*N,N*-diethylethylenediamine)copper(II) Perchlorate within the Thermal Hysteresis of the Spin-Exchange Interaction

Panče Naumov,<sup>\*,[a,b,c]</sup> Kenji Sakurai,<sup>[d]</sup> Toru Asaka,<sup>[e]</sup> Alexei A. Belik,<sup>[a]</sup> Shin-ichi Adachi,<sup>[c,f]</sup> Junichi Takahashi,<sup>[c,f]</sup> and Shin-ya Koshihara<sup>[c,f,g]</sup>

**Keywords:** Photoinduced phase transitions / Jahn–Teller effect / Photodiffraction / Photochromism / Thermochromism

Diffraction evidence is presented that the structure of one-dimensional arrays of strained, coordinationally unsaturated  $d^9$  pseudo-Jahn–Teller centers of bis(*N,N*-diethylethylenediamine)copper(II) perchlorate is affected by excitation of the

LMCT bands within the hysteresis region of a low-temperature ferromagnetic-to-antiferromagnetic phase transition. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Novel materials with physical properties that can be efficiently controlled by light is one of the main goals of modern materials science.<sup>[1]</sup> Particularly interesting are the solid-to-solid phase transitions which can be induced by light, termed photoinduced phase transitions.

In some cases, such as the photoinduced metal–insulator phase transitions of organic one-dimensional molecular complexes,<sup>[2–4]</sup> the solid-state cooperativity enables very high efficiencies (more than one hundred molecules can be converted per absorbed photon through a domino-like mechanism), as well as ultra-fast photoresponses (pico-second scale). These two exotic properties are very prospective as a basis for the design of ultrafast devices that operate in the photon mode. Therefore, in addition to their importance for understanding fundamental solid-state phenomena, photoinduced phase transitions are very important for future applications in ultrafast photoelectronics. However, the number of known compounds undergoing photoinduced phase transitions is limited. The most studied are a group of iron complexes capable of light-induced spin-

crossover<sup>[5,6]</sup> and organic molecular complexes similar to tetrathiafulvalene-chloranil which undergo light-induced intermolecular charge transfer followed by metal-to-insulator transition.<sup>[2–4]</sup> In this paper we report on a new strategy to build systems capable of photoinduced phase transition.

Nonlinear molecules with a partially filled set of degenerate orbitals are inherently Jahn–Teller (JT) unstable,<sup>[7]</sup> an effect which is considered to underpin important phenomena such as high-temperature superconductivity<sup>[8]</sup> and colossal magnetoresistance.<sup>[9]</sup> In this study, a pseudo-JT crystal composed of  $d_{z^2}$  arrays of coordinationally unsaturated copper(II) ions was utilized as a potentially light-susceptible medium for which significant structural perturbations are expected upon excitation.

As a coordinationally unsaturated unit, the *trans*-square-planar bis(*N,N*-diethylethylenediamine)copper(II) cation in its perchlorate salt,  $[\text{Cu}(\text{dieta})_2](\text{ClO}_4)_2$ , was selected (Figure 1A).<sup>[10]</sup> The bulky *gem*-dialkylamine ligands play multiple structural roles: first, they determine the square-planar geometry by shielding the apical metal valences from the approach of the anions beyond nonbonded distances; second, they effectively space out the metal ions, preventing dimerization; and third, they provide sufficient flexibility for distortions of the primary coordination sphere. The resulting instability can be compensated by pressure<sup>[11]</sup> or by heating above 317.6 K,<sup>[12]</sup> where the internal strain overweighs the energy gain from the electronic state ordering and the respective lattice distortions, resulting in spontaneous transition of the triclinic lattice ( $P\bar{1}$ , A) to a monoclinic one ( $I2$ , B) with doubled volume and tetrahedral distortion of the square-planar ligand plane (Figure 1).<sup>[13]</sup> Cooling of the crystal from ambient temperature results in a gradual change of the red color to orange, due to continuous change of the ligand field strength of the metal.<sup>[12]</sup>

[a] ICYS, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan  
Fax: +81-29-860-4706

E-mail: naumov.pance@nims.go.jp

[b] Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Arhimedova 5, P. O. B. 162, 1000 Skopje, Macedonia

[c] Exploratory Research for Advanced Technology (ERATO), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

[d] X-ray Physics Group, MEL, National Institute for Materials Science,

1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

[e] HVEMS, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

[f] High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

[g] Department of Materials Science, Tokyo Institute of Technology, 1-12-1 O-okayama, Meguro, Tokyo 152-8551, Japan

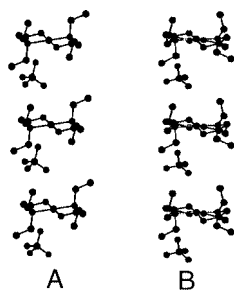


Figure 1. Structure of one-dimensional cationic chains in the low-temperature ordered (A) and high-temperature disordered (B) phases of  $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$  from single-crystal diffraction data.

The magnetic susceptibility (see Experimental Section) of  $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$  single crystals cycled thermally in the dark below the phase transition  $\text{A} \leftrightarrow \text{B}$  (2–300 K) exhibits reproducible anomalies at low temperature (Figure 2A). On cooling ( $\downarrow$ ) from ambient temperature, a single-step transition occurs at 48 K ( $T_{\downarrow}$ ), with onset at 60 K. During subsequent heating ( $\uparrow$ ) from 2 K to 300 K, the susceptibility is recovered in two steps between 25 and 57 K: at 30 ( $T_{\uparrow,1}$ ) and 52 K ( $T_{\uparrow,2}$ ). The hysteresis is reproducible by repeated thermal cycling with the magnetic field vector oriented perpendicular to each of the three crystal faces. The modified Curie–Weiss model<sup>[14]</sup> reveals a change of the weak-exchange interaction at  $T_{\downarrow}$  from the high-temperature ferromagnetic regime I, phase A [80–290 K,  $\Theta = 2.6(3)$  K,  $\mu_{\text{eff}}$ ,  $g = 1.743(3)$ ,  $2.0126$ ,  $\chi_0 = -3.36(3) \cdot 10^{-4} \text{ cm}^3/\text{Cu-mol}$ ], to a low-temperature antiferromagnetic regime II, phase C [2–28 K,  $\Theta = -0.467(15)$  K,  $\mu_{\text{eff}}$ ,  $g = 1.916(2)$ ,  $2.2124$ ,  $\chi_0 = -1.0(4) \cdot 10^{-5} \text{ cm}^3/\text{Cu-mol}$ ], with hysteresis in the range 25–55 K. The two steps at  $T_{\uparrow,1}$  and  $T_{\uparrow,2}$  resolved on heating reveal that the one-step transition at  $T_{\downarrow}$  on cooling from region I to region II involves two simultaneous processes. From the two steps on heating, the one at  $T_{\uparrow,1}$  probably corresponds to switching of the exchange interaction of the antiferromagnetic phase C in region II to an intermediate phase in region III, which, by structural change of the lattice at  $T_{\uparrow,2}$ , is transformed back to the lattice A in region I.

From the combination of internal strain and the weak electronic coupling along the one-dimensional cationic chains, it is expected that local perturbations of this structure in the region of bistability are feasible and that they might influence the long-range structural order. In order to test this hypothesis, the effect of photoexcitation was examined with a specially designed system for temperature-controlled powder photodiffraction at laboratory scale (Figure 3).<sup>[15]</sup> Upon 365 nm flash-excitation of the ligand-to-metal-charge-transfer bands of  $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$  (200–400 nm), the strong reflections shift  $0.04^\circ$  on average, with various trends of change in the intensity and a remarkable change in color from bright orange to violet. The long time needed for data collection relative to the time of irradiation assured that the respective cell shrinkage was not due to heating effects but to the creation of a long-lived photoinduced ground state. From the peak shift, the overall effect of the excitation on the lattice is analogous to the cooling

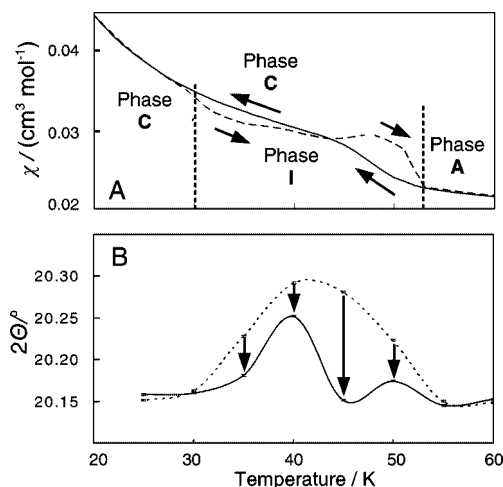


Figure 2. (A) Magnetic susceptibility recorded with the magnetic field vector  $\perp \{100\}$  face of a  $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$  crystal cycled at low temperature (solid line: cooling, dashed line: heating). (B) Thermal profile of the position of the  $(1\bar{1}0)$  reflection before (dotted line) and after (solid line) 1 s excitation with polychromatic UV light ( $\lambda_{\text{max}} = 365 \text{ nm}$ ). The sample was annealed by heating to 300 K between each two temperatures. The abscissa is the same for both plots.

of the crystal. The temperature dependence of the photoinduced structural change, monitored by the position of the  $(1\bar{1}0)$  reflection (Figure 3 and Figure 2B) showed that the photoexcitation strongly affects the lattice on cooling within the hysteresis region III, where phase C and the intermediate phase exist on cooling and heating, respectively. From the magnitude of the shift, it is concluded that the largest structural change occurs at 45 K, right after the transition of A to C has been completed (Figure 2B). This is an indication that the excitation induces transition from the low-temperature phase C, obtained in situ from cooled A, to the intermediate phase I between C and A, close to the transition point. Excitation below 30 K is less effective and results in qualitatively different structural changes, which was confirmed by comparison of the difference patterns in the  $2\theta$  region  $5\text{--}60^\circ$ . The photoinduced phase persists at 50 K, but it decays by thermal annealing at 300 K or by irradiation with visible light. Therefore, the diffraction experiments are conclusive that within and around the bistable region III, the photoexcitation significantly affects the crystal and electronic structure, particularly of the coupled cationic centers. Detailed structural studies are now underway.

In conclusion, the electronically coupled planar pseudo-JT cations in the one-dimensional cationic chains of  $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$  are subject to internal strain, balanced by a relatively strong, but moderately flexible ligand field. The lattice can withstand such strain only between 60 and 318 K; it can be collapsed by applying external pressure, or by altering the internal pressure by heating/cooling out of this temperature range. Above 318 K, the strain is released by tetrahedral distortion of the valence orbital orientation, enhanced ring puckering, disorder of the side ligand chains, and positional and rotational disorder of the counteranion.

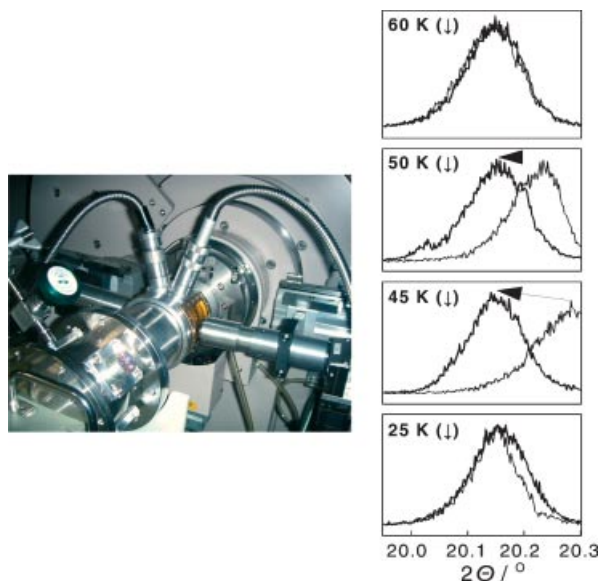


Figure 3. Left: Laboratory-built, low-temperature cryostat for powder X-ray photodiffraction. The double optical input on the top is connected to the UV output through a system of replaceable UV-transparent optics. The X-ray beam diffracts and is detected in horizontal  $\theta - 2\theta$  geometry. Right: Temperature profile of the (110) reflection before (thin line) and after (thick line) flash excitation of cooled  $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$  powder. The ordinate represents intensity in arbitrary units. The sample was flash-excited at  $\lambda_{\text{max}} = 365$  nm, through biconvex fused-silica lenses and quartz windows, with polychromatic output from a high-pressure Hg lamp (SP-7, Ushio) and annealed at 300 K between the consecutive flashes.

Below 60 K, switching of the exchange interaction in virgin single crystals occurs from a ferromagnetic to an antiferromagnetic regime, with hysteresis between 25 and 55 K. In the region of low-temperature bistability, the phase transition can also be induced from the excited state by partial charge transfer, which results in overall shrinkage of the lattice. The possibility of employing the interplay between the JT instability and the ligand field strain, determined by a moderate flexibility of the primary coordination sphere, for triggering structural transitions by light, pressure, and temperature, paves the way to switching devices capable of multi-stimulus control.

## Experimental Section

Magnetic susceptibilities,  $\chi = M/H$ , were measured with a SQUID magnetometer (Quantum Design, MPMS) between 2 and 300 K in an applied field of 10 kOe [ $1 \text{ Oe} = (10^3/4\pi) \text{ A m}^{-1}$ ]. The temperature steps were 1 K between 2 and 100 K, and 5 K between 105 and 300 K. The heating/cooling rate was  $10 \text{ K} \cdot \text{min}^{-1}$  between the steps.

- [1] a) O. Sato, *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, 5, 203–223; b) P. Gülich, Y. Garcia, T. Woike, *Coord. Chem. Rev.* **2001**, 219–221, 839–879.
- [2] E. Collet, M.-H. Lemée-Cailleau, M. Buron-Le Cointe, H. Cailleau, M. Wulff, T. Luty, S. Koshihara, M. Meyer, L. Toupet, P. Rabiller, S. Techert, *Science* **2003**, 300, 612–615.
- [3] L. Guérin, E. Collet, M.-H. Lemée-Cailleau, M. Buron-Le Cointe, H. Cailleau, A. Plech, M. Wulff, S. Koshihara, T. Luty, *Chem. Phys.* **2004**, 299, 163–170.
- [4] M. Chollet, L. Guérin, N. Uchida, S. Fukaya, H. Shimoda, T. Ishikawa, K. Matsuda, T. Hasegawa, A. Ota, H. Yamochi, G. Saito, R. Tazaki, S. Adachi, S. Koshihara, *Science* **2005**, 307, 86–89.
- [5] V. Legrand, C. Carbonera, S. Pillet, M. Souhassou, J. F. Létard, P. Guionneau, C. Lecomte, *J. Phys.: Conf. Ser.* **2005**, 21, 73–80.
- [6] J.-F. Létard, J. Sanchez Costa, S. Marcen, C. Carbonera, C. Desplanches, A. Kobayashi, N. Daro, P. Guionneau, J.-P. Ader, *J. Phys.: Conf. Ser.* **2005**, 21, 23–29.
- [7] L. R. Falvello, *J. Chem. Soc., Dalton Trans.* **1997**, 4463–4476.
- [8] D. V. Fil, O. I. Tokar, A. L. Shelankov, W. Weber, *Phys. Rev. B* **1992**, 45, 5633–5640.
- [9] S. Jin, T. H. Tiesel, M. McCormack, R. A. Fastnacht, R. Ramesh, L. H. Chen, *Science* **1994**, 264, 413–415.
- [10] T. Yokoyama, K. Takahashi, O. Sato, *Phys. Rev. B* **2003**, 67, 172104–172108.
- [11] J. R. Ferraro, L. J. Basile, L. R. Garcia-Iniguez, P. Paoletti, L. Fabrizzi, *Inorg. Chem.* **1976**, 15, 2342–2345.
- [12] A. Nishimori, M. Sorai, E. A. Schmitt, D. A. Hendrickson, *J. Coord. Chem.* **1996**, 37, 327–340.
- [13] I. Grenthe, P. Paoletti, M. Sandström, S. Glikberg, *Inorg. Chem.* **1979**, 18, 2687–2692.
- [14] The modified Curie–Weiss law of the form  $\chi(T) = \chi_0 + (\mu_{\text{eff}}^2 N_A / 3k_B(T - \theta))^{-1}$  was used, where  $\chi_0$  is the temperature-independent term,  $\mu_{\text{eff}}$  is the effective magnetic moment,  $N_A$  is Avogadro's number,  $k_B$  is Boltzmann's constant,  $\theta$  is the Weiss constant, and  $g$  is the  $g$ -value. Heating/cooling rate:  $10 \text{ K} \cdot \text{min}^{-1}$ .
- [15] There is one previous report on the formation of a light-induced “metastable state” in this compound: K. Takahashi, R. Nakajima, Z. Gu, H. Yoshiki, A. Fujishima, O. Sato, *Chem. Commun.* **2002**, 1578–1579.

Received: November 28, 2005

Published Online: February 21, 2006