Thermal and Photo-Responsibility of Axial Semi-Coordination Bonds in a Copper(II) Complex

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The thermal and photo-responsibility of the axial semi-coordination Cu–O bonds in $[Cu(en)_2](ClO_4)_2$ (**1**) (en = ethylenediamine) have been investigated. We discovered a new photoresponsive behavior that was attributed to photo-induced ClO_4^- cleavage accompanied by compression of the Cu–O bonds using the structural degree of freedom of the semi-coordination bonds.

Photoresponsive metal complexes have attracted much attention in recent years because of their potential applications to memory devices.[1] Light-induced spin crossover of iron(II) complexes[2] and ligand racemization of cobalt(III) complexes[3] are well-known examples in the solid states. One of the prevailing approaches for discovering such complexes is examining the photo-responsibility of the complexes, which exhibit thermally-induced changes of the electronic states or structures. Therefore, the complexes described by bistable potentials may be candidates for new kinds of photoresponsive ones. Copper(II) complexes exhibit flexible coordination geometries by the Jahn–Teller effect.[4,5] The tetragonal distortion is formulated by the second-order Jahn–Teller theorem (1) and described by bistable Mexican-hat potentials,

$$E(0) = \langle 0|H_q|0\rangle q + 1/2[\langle 0|H_q|0\rangle - 2\Sigma(\langle 0|H_q|0\rangle^2/\Delta E_{0n})]q^2, \quad (1)$$

where q denotes the distortion coordinates and the q^2 term provides a second-order or a pseudo Jahn–Teller contribution for stabilizing the systems by a tetragonal distortion coupled with a splitting of degenerated orbitals in D_{4h} symmetry.[6,7] Accordingly, it is known that the axial semi-coordination Cu–O bonds are considerably long for *trans*-$[CuN_4(O_2)]$ complexes having en ligands. Here, we consider the thermal and photo-responsibility of **1**, and present new kind of photo-induced behavior related to the structural degree of freedom of the semi-coordination bonds.

The temperature dependence of the crystal structures of **1** has been investigated at 297, 274, and 120 K (Fig. 1). The overall structures were essentially identical to the previous results,[8] even at low temperature. Centrosymmetric complex **1** in D_{4h} symmetry affords a tetragonally distorted *trans*-$[CuN_4(O_2)]$ environment dominated by the Jahn–Teller effect, and one of the two en ligands is in the λ-conformation and the other is in the δ-conformation. Upon cooling to 120 K, the volume of the cell decreased in 2.26% without a phase transition. The dynamic Jahn–Teller effect emerged remarkably as compression of the axial Cu–O bonds: 2.583(1), 2.576(1), 2.554(2) Å, that is $T = R_S/R_L$ 0.780, 0.785, and 0.791, respectively. A tetragonal distortion (T) is defined by the ratio of the in-plane Cu–N (R_S) bond distances to the axial Cu–O (R_L) ones, and small T values suggest a large distortion and unstabilization of the $3d_{z^2}$ level. A slight structural change was also observed in the N–Cu–N–C torsion angles. On the other hand, little difference in IR spectra (400–4000 cm^{-1}, 7–300 K) elucidated that a tetrahedral distortion of the $[CuN_4(O_2)]$ chromophores was not caused by the puckering of en ligands.[9] Therefore, structural degree of freedom is mainly attributed to the semi-coordination Cu–O bonds.

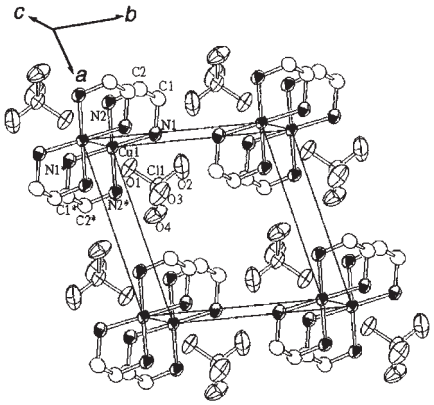

Fig. 1. Crystal structure of **1** omitted hydrogen atoms for clarity. Selected geometric parameters (Å, °) at 297, 274, and 120 K: Cu(1)···O(1) = 2.583(1), 2.576(1), 2.554(2), Cu(1)–N(1) = 2.019(2), 2.024(2), 2.026(4), Cu(1)–N(2) = 2.013(2), 2.019(2), 2.013(4), N(1)–C(1) = 1.474(3), 1.481(3), 1.474(6), N(2)–C(2) = 1.477(2), 1.484(2), 1.496(5), C(1)–C(2) = 1.506(4), 1.514(3), 1.509(7). N(1)–Cu(1)–N(2) = 84.52(7), 84.57(7), 84.5(1), N(1)–Cu(1)–N(2*) = 95.48(7), 95.43(7), 95.5(1). N(1)–Cu(1)–N(2)–C(2) = −16.6(1), −17.4(1), −18.5(2), N(2)–Cu(1)–N(1)–C(1) = −12.3(1), −11.9(1), −10.6(2), N(1)–C(1)–C(2)–N(2) = −53.1(2), −53.6(1), −53.5(4). The atoms with * are expanded by symmetry operation $(-x, -y, -z-2)$.

After UV light illumination at 298 K, reflectance spectra in the d–d region (Fig. 2) exhibited a low-wavenumber shift with an increase of the intensity from 19000 cm^{-1}, $\log F(R_d)$ 0.77, half width (Δ+, Δ−) 3400, 2800 cm^{-1} at 0 min to 18400 cm^{-1} $\log F(R_d)$ 0.94, half width 3300, 3100 cm^{-1} at 60 min. The irreversible spectral change saturated up to about 60 min, and vis light was inactive. On the other hand, no obvious differences were observed after UV light illumination in both IR spectra (ring C(en) 474 and Cu–N(en) 412 cm^{-1}) and in XRD (face and $2\theta/^\circ$ for five predominant peaks) (010) 11.54, (100) 11.74, $(1\bar{1}0)$ 18.30, $(11\bar{1})$ 18.22, and (111) 24.24. Thus, the crystal structures of **1** were maintained after UV light illumination.

We can propose two interpretions for the spectral shift: [1] A tetrahedral distortion of the $[CuN_4(O_2)]$ chromophores; the mechanism of d–d transition converted from vibronic coupling in D_{4h} to orbital symmetry in C_{2v}.[10–12] [2] A tetragonal distor-

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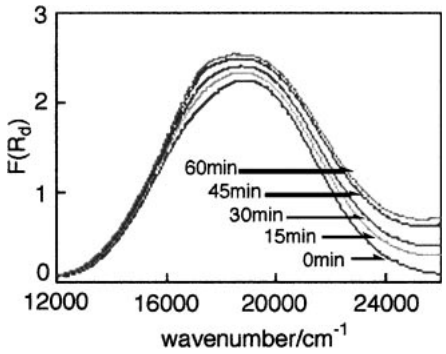

Fig. 2. Diffuse reflectance spectra of **1** after UV light illumination for 0, 15, 30, 45, and 60 min.

tion of the $[CuN_4(O_2)]$ chromophores; compressing the Cu–O bond and unstabilization of $3d_{z^2}(a_{1g})$ level resulted in decreasing of the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition energy.[13–15] Taking into account the experimental evidence mentioned above, we can accept interpretion [2]. Consequently, we discovered a new photoresponsive behavior that is attributed to a photo-induced ClO_4^- cleavage accompanied by compression of the Cu–O semi-coordination by the Jahn–Teller effect for the first time.

Experimental

Preparation. To a methanol solution (10 cm^3) of $Cu(ClO_4)_2$ (0.375 g, 1.01 mmol), en (0.122 g, 2.03 mmol) was added dropwise and kept standing at 25 °C. Blue prismatic crystals of **1** were obtained in a few days. Reddish violet prismatic single crystals were grown by slow evaporation of the chloroform–methanol (4:1 v/v) solution in hexane vapor at 5 °C overnight. Yield 19.1%. Found: C, 12.72; H, 4.39; N, 14.77%. Calcd for $C_4H_{16}Cl_2CuN_4O_8$: C, 12.56; H, 4.21; N, 14.64%. IR (Nujol mull) $\nu_{C=O}$(amide I) 1647 cm^{-1}.

Measurements. Diffuse reflectance electronic spectra were measured on a JASCO V-560 spectrophotometer equipped with an integrating sphere. IR spectra were recorded on a BIORAD FTS-60A and a JASCO FTIR 660plus spectrometer with KBr plates. XRD were recorded on a Rigaku RAD-C diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Light illumination experiments were performed with a Xe light source (400–700 nm, 1.0 mW/cm^2) by using optical filters (UV $\lambda = 200$–400 nm, $\lambda_{max} =$ 360 nm; vis $\lambda = 400$–700 nm; Sigma Koki Co. Ltd.).

X-ray Crystallography. Intensity data for the identical crystal of **1** (Triclinic, $P\bar{1}$, $C_4H_{16}Cl_2CuN_4O_8$, FW = 382.64, 0.40 × 0.30 × 0.20 mm) were collected at 297, 274, and 120 K on a Rigaku AFC-7R four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SIR92[16]) and expanded by Fourier techniques (DIRDIF94[17]). The structure was refined on F^2 anisotropically for non-hydrogen atoms by full-matrix least-squares methods (SHELXL97[18]) with a teXsan[19] program package. The data were corrected for Lorentz and polarization effects. Empirical absorption corrections based on ψ scans and decay corrections were applied for all of the data. All of the hydrogen atoms were located by geometrically calculated positions and all were fixed during refinement.

$T = 297$ K: $a = 7.808(2)$, $b = 7.949(2)$, $c = 5.717(2)$ Å, $\alpha = 100.86(2)$, $\beta = 101.90(2)$, $\gamma = 75.35(2)°$, $V = 332.4(2)$ Å^3, $Z = 1$, $D_{calc} = 1.911$ g m^{-3}, $\mu = 2.084$ mm^{-1}, $F(000) = 195$, $2\theta_{max} = 55.0°$, measured 1769, independent 1537 reflections, $R_{int} = 0.021$, 89 parameters, $R1 = 0.024$, $R_w = 0.068$, $S = 1.10$.

$T = 274$ K: $a = 7.797(2)$, $b = 7.981(2)$, $c = 5.706(2)$ Å, $\alpha = 100.87(3)$, $\beta = 102.43(3)$, $\gamma = 75.18(2)°$, $V = 331.8(2)$ Å^3, $Z = 1$, $D_{calc} = 1.915$ g m^{-3}, $\mu = 2.088$ mm^{-1}, $F(000) = 195$, $2\theta_{max} = 55.0°$, measured 1764, independent 1532 reflections, $R_{int} = 0.029$, 89 parameters, $R1 = 0.029$, $R_w = 0.110$, $S = 1.06$.

$T = 120$ K: $a = 7.740(8)$, $b = 7.957(7)$, $c = 5.666(6)$ Å, $\alpha = 101.00(8)$, $\beta = 103.05(9)$, $\gamma = 74.88(7)°$, $V = 324.9(5)$ Å^3, $Z = 1$, $D_{calc} = 1.955$ g m^{-3}, $\mu = 2.132$ mm^{-1}, $F(000) = 195$, $2\theta_{max} = 44.9°$, measured 954, independent 849 reflections, $R_{int} = 0.010$, 89 parameters, $R1 = 0.038$, $R_w = 0.154$, $S = 1.55$.

Crystallographic data has been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained upon request, free of charge, by quoting the publication citation and the deposition numbers 225586–225588.

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References

1 O. Sato, S. Hayami, Y. Einaga, and Z.-Z. Gu, *Bull. Chem. Soc. Jpn.*, **76**, 443 (2003).

2 P. Gutlich, Y. Garcia, and T. Woike, *Coord. Chem. Rev.*, **219–221**, 839 (2001), and references therein.

3 Y. Ohashi, *Acc. Chem. Res.*, **21**, 268 (1988), and references therein.

4 B. J. Hathaway, *Struct. Bonding (Berlin)*, **57**, 55 (1987).

5 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

6 J. K. Burdett, *Inorg. Chem.*, **20**, 1959 (1981).

7 I. B. Bersuker, "Electronic Structure and Properties of Transition Metal Compounds," Wiley, New York (1996).

8 K. R. Maxcy and M. M. Turnbull, *Acta Crystallogr.*, **C55**, 1986 (1999).

9 A. B. P. Lever and E. Mantocani, *Inorg. Chem.*, **10**, 817 (1971).

10 T. Akitsu, S. Komorita, and Y. Kushi, *Inorg. Chim. Acta*, **315**, 18 (2001).

11 T. Akitsu, S. Komorita, and A. Urushiyama, *Bull. Chem. Soc. Jpn.*, **74**, 851 (2001).

12 T. Akitsu, S. Komorita, and H. Tamura, *Inorg. Chim. Acta*, **348**, 25 (2003).

13 T. Akitsu, S. Komorita, Y. Kushi, C. Li, N. Kanehisa, and Y. Kai, *Bull. Chem. Soc. Jpn.*, **70**, 821 (1997).

14 T. Akitsu, S. Komorita, and Y. Kushi, *Bull. Chem. Soc. Jpn.*, **72**, 447 (1999).

15 T. Akitsu and S. Komorita, *Bull. Chem. Soc. Jpn.*, **75**, 767 (2002).

16 A. Altomare, M. C. Burala, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, and G. Polidori, *J. Appl. Crystallogr.*, **27**, 435 (1994).

17 DIRDIF94; P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits (1994).

18 SHELXL97; G. M. Sheldrick, Program for the solution and the refinement of crystal structures, University of Göttingen, Germany (1997).

19 teXsan; Crystal Structure Analysis Package, Molecular Structure Corporation (1985&1992).