J|A|C|S
COMMUNICATIONS

Valence Tautomeric Transitions with Thermal Hysteresis around Room Temperature and Photoinduced Effects Observed in a Cobalt−Tetraoxolene Complex

Jun Tao,[†,‡] Hiroyuki Maruyama,[†] and Osamu Sato*[,†]

Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, 816-8580 Fukuoka, Japan, and Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

Received November 2, 2005; E-mail: sato@cm.kyushu-u.ac.jp

The design of molecular materials whose physical properties can be controlled by external parameters, such as temperature, light, and electric field, has been attracting much attention because of their potential applications as molecular electronic devices.[1] Molecules that exhibit labile electronic properties, usually incorporating changes in magnetism, are characteristic of spin-crossover, valence tautomeric, and mixed-valence complexes.[2−4] It is well-known that certain spin-crossover transitions occur in association with thermal hysteresis effects that are due to structural phase changes in the lattice, or with intramolecular structural changes that are cooperative with effective intermolecular interactions.[5] On the basis of these same principles, valence tautomeric transitions should show hysteresis effects when any intermolecular cooperative effects that occur are sufficiently strong. However, it is unusual to observe any significant hysteresis effects in valence tautomeric compounds. It has been reported that several compounds do exhibit hysteresis, but that the width is generally small and the transition is not abrupt.[6] Hence, the presence of bistability is not distinct. Pierpont et al. have also reported a large hysteresis (230 K) in $[\mathrm{Co^{III}(DBCat)(DBSQ)(py_2O)}]$ (where DBCat, DBSQ = catecholato and semiquinonato forms of 3,5-di-*tert*-butyl-*o*-benzoquinone, respectively, and $\mathrm{py_2O}$ = 2,2′-bis(pyridine) ether).[7a] However, the same author described in a review article that repeated traces show a gradual breakdown in the hysteresis.[7b] Hence, it is still a great challenge to achieve valence tautomeric transitions with large hysteresis. Indeed, it has been mentioned in a recent article by Hendrickson and Pierpont that the future direction in this field is the preparation of valence tautomeric compounds with hysteresis arising from intermolecular interactions and with photoswitching effects.[3e] Here, we report a new valence tautomeric complex that exhibits distinct hysteresis and photoinduced valence tautomerism at low temperature. An important characteristic of the material is that the hysteresis is observed at around room temperature, not at low temperature.

The title complex $[\mathrm{(CoTPA)_2(DHBQ)](PF_6)_3}$ ($\mathbf{1}\cdot\mathrm{(PF_6)_3}$, TPA = tris(2-pyridylmethyl)amine, DHBQ = deprotonated 2,5-dihydroxy-1,4-benzoquinone) was prepared as long, dark red parallel-piped crystals by the one-electron chemical oxidation of $[\mathrm{(CoTPA)_2(DHBQ)](PF_6)_2}$ ($\mathbf{2}\cdot\mathrm{(PF_6)_2}$) with $\mathrm{AgNO_3}$ in acetone/water solution. To elucidate its structural details, a fully oxidized product, $[\mathrm{(CoTPA)_2(DHBQ)](PF_6)_4(acetone)_2}$ ($\mathbf{3}\cdot\mathrm{(PF_6)_4(acetone)_2}$), was also synthesized. The detailed synthetic methods are described in the Supporting Information.

Crystal analysis of the three complexes was successfully performed at 173 K.[8] The metal-to-ligand bond length shows that the oxidation and spin states of compounds $\mathbf{1}^{3+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{4+}$ can be expressed as $\mathrm{Co^{III-LS}-DHBQ^{3-}-Co^{III-LS}}$, $\mathrm{Co^{II-HS}-DHBQ^{2-}-Co^{II-HS}}$, and $\mathrm{Co^{III-LS}-DHBQ^{2-}-Co^{III-LS}}$, respectively. That is, the average Co−N distance in $\mathbf{1}^{3+}$ is 1.920 Å, which is almost the same as that in $\mathbf{3}^{4+}$ (1.921 Å). The ligand-to-metal distances are consistent with those for the $\mathrm{Co^{III-LS}-N}$ structure.[3a] The average Co−N distance in $\mathbf{2}^{2+}$ is rather long (2.131 Å), which is consistent with the general $\mathrm{Co^{II-HS}-N}$ distance.[6a] Furthermore, the Co−O distances of $\mathbf{1}^{3+}$ (1.879 and 1.885 Å) are close to those of $\mathbf{3}^{4+}$ (1.889 and 1.925 Å) and much shorter than those of $\mathbf{2}^{2+}$ (2.006 and 2.172 Å). These values are also in agreement with the Co−O distances of $\mathrm{Co^{III-LS}}$ in $\mathbf{1}^{3+}$ and $\mathbf{3}^{4+}$ and of $\mathrm{Co^{II-HS}}$ in $\mathbf{2}^{2+}$, respectively.[9] Note that the longer ligand-to-metal bond length in $\mathbf{2}^{2+}$ can be explained by the fact that two electrons occupy the e_g orbital with antibonding character, which weakens the chemical bond and hence results in a longer bond length than those of $\mathbf{1}^{3+}$ and $\mathbf{3}^{4+}$.

Additionally, by considering charge balance, it was deduced that the DHBQ ligand in $\mathbf{1}^{3+}$ should be conjugated $\mathrm{DHBQ^{3-}}$ radical, not $\mathrm{DHBQ^{2-}}$. By contrast, the DHBQ ligand in $\mathbf{2}^{2+}$ and $\mathbf{3}^{4+}$ should be the diamagnetic $\mathrm{DHBQ^{2-}}$. The presence of $\mathrm{DHBQ^{3-}}$ moieties in $\mathbf{1}^{3+}$ can be confirmed by the ESR signal, the C−O distances, and the IR spectra. The ESR spectra measured at 295 K showed only one strong signal at $g = 2.00$ (Supporting Information). The C−O distances in $\mathbf{1}^{3+}$ are 1.324 and 1.326 Å, which lie between the values for coordinated benzosemiquinone (1.29 Å) and catecholate (1.35 Å) ligands.[9] Furthermore, when measured at room temperature, the IR spectrum of $\mathbf{1}\cdot\mathrm{(PF_6)_3}$ (Supporting Information) shows a weak peak around 1530 $\mathrm{cm^{-1}}$, but appears as very strong bands in the spectra of $\mathbf{2}\cdot\mathrm{(PF_6)_2}$ and $\mathbf{3}\cdot\mathrm{(PF_6)_4(acetone)_2}$ and can be assigned to a typical $\mathrm{DHBQ^{2-}}$ band.[10] These results suggest that $\mathbf{1}^{3+}$ contains $\mathrm{DHBQ^{3-}}$ moieties.

The $\chi_M T$ value (where χ_M is the molar magnetic susceptibility and T is temperature) of $\mathbf{2}\cdot\mathrm{(PF_6)_2}$ at 300 K was 4.81 $\mathrm{cm^3\ mol^{-1}\ K}$, which is consistent with the $\mathrm{Co^{II-HS}-DHBQ^{2-}-Co^{II-HS}}$ structure. The structure of compound $\mathbf{3}\cdot\mathrm{(PF_6)_4}$ with $\mathrm{Co^{III-LS}-DHBQ^{2-}-Co^{III-LS}}$ was diamagnetic. Furthermore, it was found that $\mathbf{1}\cdot\mathrm{(PF_6)_3}$ does exhibit thermally induced interconversion between $\mathrm{Co^{III-LS}-DHBQ^{3-}-Co^{III-LS}}$ and $\mathrm{Co^{III-LS}-DHBQ^{2-}-Co^{II-HS}}$. The temperature dependence of $\chi_M T$ for $\mathbf{1}\cdot\mathrm{(PF_6)_3}$ is shown in Figure 1. At 5 K, the $\chi_M T$ value is 0.33 $\mathrm{cm^3\ K\ mol^{-1}}$ (Supporting Information), which is consistent with the $S = 1/2$ of $\mathrm{Co^{III-LS}-DHBQ^{3-}-Co^{III-LS}}$ state. On warming, an abrupt variation in $\chi_M T$ was observed around $T_{1/2}\uparrow = 310$ K, reaching 1.26 $\mathrm{cm^3\ K\ mol^{-1}}$ at 330 K and 1.84 $\mathrm{cm^3\ K\ mol^{-1}}$ at 400 K, where $T_{1/2}\uparrow$ is defined as the transition temperature in the warming mode. Conversely, when the temperature decreased, the $\chi_M T$ value decreased sharply at $T_{1/2}\downarrow = 297$ K and recovered to the original value at around 250 K, where $T_{1/2}\downarrow$ is defined as the transition temperature in the cooling mode. The width of the thermal hysteresis loop was 13 K. It is important to note that this thermal hysteresis loop was reproducible.

A space group determination at 393 K on the same single crystal showed the same symmetry as that at 173 K, indicating that there

---

[†] Kyushu University.
[‡] Xiamen University.

10.1021/ja057488u CCC: $33.50

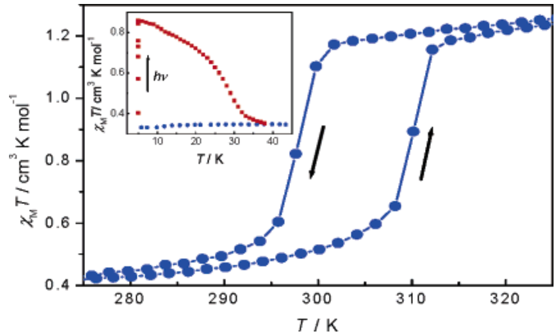

Figure 1. Temperature dependence of $\chi_M T-T$ plots of $\mathbf{1}\cdot(PF_6)_3$ and photoinduced changes after irradiation at 532 nm (inset).

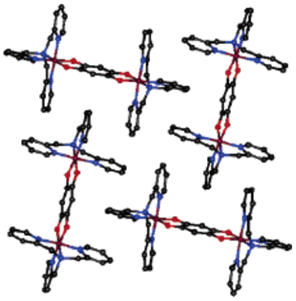

Figure 2. Two-dimensional cationic network showing the head-to-waist stacking mode.

is no crystallographic phase transition. Fairly abrupt transitions with thermal hysteresis of 13 K show the presence of a strong cooperative interaction. Indeed, careful investigation of the crystal structure shows that the cationic $\mathbf{1}^{3+}$ species are stacked in a head-to-waist mode (Figure 2) to form 2D layers that are separated by PF_6^- anions. Hence, it is thought that the presence of the hysteresis effect can be attributed to an off-set $\pi\cdots\pi$ interaction of the pyridine rings of the terminal TPAs and an edge-to-face interaction (tilted-T structure)[11] between the terminal TPA pyridine rings and the DHBQ benzene rings.

It should be noted that, prior to this work, valence tautomeric transitions had been reported in a dinuclear Co compound.[12] However, although its properties are indeed intriguing, its structure is uncertain and it shows no thermal hysteresis. It is believed that the introduction of the TPA ligand with pyridine rings enables the compounds to interact with each other through $\pi\cdots\pi$ interactions, allowing the observation of a significant hysteresis effect in the present compound.

Furthermore, we investigated the effect of light on $\mathbf{1}\cdot(PF_6)_3$. Absorption spectra of $\mathbf{1}\cdot(PF_6)_3$ measured at room temperature show two strong peaks at 492 and 536 nm. Because these bands are thought to be characteristic of charge transfer from $DHBQ^{3-}$ to Co^{III-LS},[12] photoeffects were investigated using 532 nm light. When $\mathbf{1}\cdot(PF_6)_3$ was irradiated at 5 K for 30 min, the magnetic moment increased abruptly and reached an almost saturation value of $\chi_M T = 0.85$ cm^3 K mol^{-1}. The relatively low efficiency of the photoinduced process is due to the strong opacity of the sample.[12] The photoprocess can be expressed as $Co^{III-LS}-DHBQ^{3-}-Co^{III-LS} \rightarrow Co^{III-LS}-DHBQ^{2-}-Co^{II-HS}$. IR spectra measured before and after irradiation support this idea. That is, the absorption peak at around 1530 cm^{-1}, which is characteristic of the $DHBQ^{2-}$ moiety, increased along with the strong 1550 cm^{-1} band, while the absorption peak at around 1210 cm^{-1}, which is characteristic of the $DHBQ^{3-}$ moiety, decreased. Moreover, the peaks at around 1250 and 1400 cm^{-1} that are associated with the C−O stretching mode evidently increased upon irradiation. This is consistent with the induction of light-induced valence tautomerism in $\mathbf{1}\cdot(PF_6)_3$. When the light was subsequently switched off and the sample was heated, the magnetic moment recovered to the initial value around 38 K. This means that the light-induced $Co^{III-LS}-DHBQ^{2-}-Co^{II-HS}$ moieties relaxed back to their original state, demonstrating that the photoreaction is reversible.

In conclusion, we have succeeded in synthesizing a dinuclear cobalt valence tautomeric complex that displays distinct hysteresis effect around room temperature. Furthermore, we have shown that the valence tautomerism can be induced by irradiation under low temperature.

Acknowledgment. This work was supported by the Japan Society for the Promotion of Science (JSPS) and by the National Natural Science Foundation of China (20301014).

Supporting Information Available: Synthetic details, X-ray data for $\mathbf{1}\cdot(PF_6)_3$, $\mathbf{2}\cdot(PF_6)_2$, and $\mathbf{3}\cdot(PF_6)_4(acetone)_2$ in CIF format, ORTEP drawings of asymmetric units of the three complexes, room temperature IR spectra of the three complexes, low temperature IR spectra before and after irradiation of $\mathbf{1}\cdot(PF_6)_3$, ESR spectra at room temperature and 77 K, absorption spectra of solid state $\mathbf{1}\cdot(PF_6)_3$ at room temperature, and magnetic properties of $\mathbf{1}\cdot(PF_6)_3$ and $\mathbf{2}\cdot(PF_6)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kahn, O.; Launay, J. P. *Chemtronics* **1988**, *3*, 140. (b) Kahn, O.; Kröber, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718. (c) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (d) Sato, O. *Acc. Chem. Res.* **2003**, *36*, 692.

(2) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed.* **1994**, *33*, 2024. (c) Sato, O. *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 203. (d) Real, J. A.; Gaspar, A. P.; Muñoz, M. C. *Dalton Trans.* **2005**, 2062.

(3) (a) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951. (b) Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515. (c) Shultz, D. A. In *Magnetism: Molecules to Materials II*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, Germany, 2001; p 281. (d) Sato, O.; Hayami, S.; Einaga, Y.; Gu, Z.-Z. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 443. (e) Hendrickson, D. N.; Pierpont, C. G. *Top. Curr. Chem.* **2004**, *234*, 63. (f) Ohtsu, H.; Tanaka, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 6301. (g) Dei, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L. *Acc. Chem. Res.* **2004**, *37*, 827. (h) Bin-Salamon, S.; Brewer S.; Franzen, S.; Feldheim, D. L.; Lappi, S.; Shultz, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 5328.

(4) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655.

(5) Gütlich, P.; Goodwin, H. A. *Top. Curr. Chem.* **2004**, *233*, 1.

(6) (a) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221. (b) Bodnar, S. H.; Caneschi, A.; Dei, A.; Shultz, D. A.; Sorace, L. *Chem. Commun.* **2001**, 2150. (c) Cador, O.; Dei, A.; Sangregorio, C. *Chem. Commun.* **2004**, 652.

(7) (a) Jung, O.-S.; Jo, D. H.; Lee, Y.-A.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1997**, *36*, 19. (b) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *216*, 99.

(8) Crystal data for $\mathbf{1}\cdot(PF_6)_3$: $C_{42}H_{38}Co_2F_{18}N_8O_4P_3$, $M = 1271.58$, orthorhombic, space group *Pccn* (No. 56), $T = 173(2)$ K, $a = 20.058(4)$, $b = 16.095(3)$, $c = 16.266(3)$ Å, $V = 5251.0(18)$ Å^3, $Z = 8$, $D_c = 1.608$ g/cm^3, $R_1 = 0.0696$, w$R_2 = 0.1965$. Crystal data for $\mathbf{2}\cdot(PF_6)_2$: $C_{42}H_{38}Co_2F_{12}N_8O_4P_2$, $M = 1126.60$, monoclinic, space group $P2_1/c$ (No. 14), $T = 173(2)$ K, $a = 11.478(2)$, $b = 16.101(3)$, $c = 11.446(2)$ Å, $\beta = 91.27(3)°$, $V = 2114.9(7)$ Å^3, $Z = 4$, $D_c = 1.769$ g/cm^3, $R_1 = 0.0567$, w$R_2 = 0.1276$. Crystal data for $\mathbf{3}\cdot(PF_6)_4(acetone)_2$: $C_{48}H_{50}Co_2F_{24}N_8O_6P_4$, $M = 1532.70$, orthorhombic, space group *Pbca* (No. 61), $T = 173(2)$ K, $a = 17.939(4)$, $b = 15.430(3)$, $c = 21.338(4)$ Å, $V = 5906(2)$ Å^3, $Z = 8$, $D_c = 1.724$ g/cm^3, $R_1 = 0.0417$, w$R_2 = 0.0812$.

(9) (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45. (b) Pierpont, C. G.; Larson, S. K.; Boone, S. R. *Pure Appl. Chem.* **1988**, *60*, 1331. (c) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *Angew. Chem., Int. Ed.* **1993**, *32*, 880. (d) Caneschi, A.; Dei, A.; Biani, F. F.; Gütlich, P.; Ksenofontov, V.; Levchenko, G.; Hoefer, A.; Renz, F. *Chem.—Eur. J.* **2001**, *7*, 3926. (e) Bencini, A.; Caneschi, A.; Carbonera, C.; Dei, A.; Gatteschi, D.; Righini, R.; Sangregorio, C.; Slageren, J. V. *J. Mol. Struct.* **2003**, *656*, 141.

(10) (a) Pierpont, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *17*, 2367. (b) Dei, A.; Gatteschi, D.; Pardi, L.; Russo, U. *Inorg. Chem.* **1991**, *30*, 2589.

(11) Jennings, W. B.; Farrell, B. M.; Malone, J. F. *Acc. Chem. Res.* **2001**, *34*, 885.

(12) (a) Carbonera, C.; Dei, A.; Létard, J.-F.; Sangregorio, C.; Sorace, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3136.

JA057488U