Preparation and Valence Tautomeric Behavior of a Cobalt–Dioxolene Complex with a New TTF-functionalized Phenanthroline Ligand

Shinji Kanegawa, Soonchul Kang, and Osamu Sato*

Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580

(Received February 15, 2013; CL-130118; E-mail: sato@cm.kyushu-u.ac.jp)

In this study, a new tetrathiafulvalene-functionalized phenanthroline ligand (TTF-phen) and a mononuclear cobalt(II) complex with a redox active 3,6-di-*tert*-butylsemiquinonato (3,6-dtsq) ligand was synthesized. Magnetic measurements and IR spectroscopy suggested that the Co complex [Co(3,6-dtsq)₂(TTF-phen)] exhibited thermally induced valence tautomerism in the temperature range 130–400 K. This complex is the first example of a valence tautomeric complex with a TTF-functionalized ligand.

The development of multifunctional materials, in which more than two properties interact in a compound is one of the most attractive research fields in molecular-based materials.¹ Some hybrid molecular systems constructed with magnetic and conducting molecules, have been reported to exhibit interesting multifunctional behavior such as the coexistence of ferromagnetism and metallic conductivity,1a and field-induced superconducting transitions.^{1b} However, the control of the electrical properties in hybrid materials by external stimuli is still challenging. Spin-crossover (SCO) complexes are among the most widely evaluated magnetic molecules with switching properties,2 and some SCO-based hybrid materials with conductive moieties have been reported.³ In these materials, the coupling of a spin transition and electric conductivity is understood to be mainly due to a chemical pressure effect in the crystal lattice following a structural change caused by SCO. On the other hand, valence tautomeric complexes are another class of magnetic molecules that exhibit thermal and photoinduced switching properties.4-7 A large number of examples of mononuclear, dinuclear,⁶ and polynuclear⁷ cobalt complexes that exhibit valence tautomerism have been synthesized, and their magnetic and photomagnetic properties have been reported. Typical mononuclear cobalt valence tautomeric complexes exhibit electron transfer between the metal center and a redox-active dioxolene ligand, a process expressed as $[Co^{II-HS}(dtsq)_2(L)] \rightleftharpoons [Co^{III-LS}(dtcat)(dtsq)(L)]$ (L is a bidentate N-donor ligand: 2,2'-bipyridine, 1,10-phenanthroline, or N,N,N',N'-tetramethylethylenediamine; dtsq and dtcat are 3,5or 3,6-di-tert-butylsemiquinonato and di-tert-butylcatecholato, respectively; HS: high spin, LS: low spin). Note that not only the spin state but also the valence state of the central Co ion changes between 2+ and 3+ in this thermal and/or photoirradiationinduced process. Because there is such a large dynamic change in the electronic state, we believe that valence tautomeric complexes are a more suitable class of molecules than SCO complexes for developing multifunctional materials. In order to achieve interaction between the conducting π electrons and paramagnetic d electrons in hybrid molecular systems, a large number of metal complexes based on tetrathiafulvalene (TTF) derivatives have been synthesized.8 When TTF and the



Scheme 1. Synthesis of the TTF-functionalized ligand (TTFphen) and its mononuclear cobalt complex [Co(3,6-dtsq)₂(TTFphen)].

coordination moiety are connected though a conjugated π system, they exhibit a through-bond interaction. In fact, a through-bond electronic interaction has been reported as an intramolecular charge transfer that is induced by the metal ion in acetylenic-, ethylenic-, and imine-conjugated TTF- π -pyridine-type molecules.^{9,10} Although an example of SCO complexes with TTF functional ligands has been reported by Oshio and coworkers,¹¹ to the best of our knowledge, there has been no report on the observation of valence tautomerism in complexes with π -conjugated TTF ligands. In this paper, we report the synthesis and crystal structure of a new imine-conjugated TTF ligand and the magnetic properties of a cobalt complex.

The synthesis of TTF-phen was performed, as shown in Scheme 1, via an aza-Wittig reaction between formyltetrathiafulvalene and iminophosphorane (PPh3-phen). PPh3-phen was prepared from 5-amino-1,10-phenanthroline and an excess amount of dibromotriphenylphosphorane, (PPh3Br2) according to a modified literature procedure.^{10a} All compounds were readily purified by precipitation or recrystallization and have been fully characterized. The cobalt complex was first obtained as a deep blue-black powder via the reaction of TTF-phen, dicobalt octacarbonyl, and 3,6-di-tert-butyl-o-quinone (3,6-dtbq) in methylcyclohexane. The powder was purified by recrystallization from AcOEt/heptane, and the cobalt complex was obtained as fiber-like microcrystals. Unfortunately, the obtained crystals of the complex were too small for crystal structure analysis. The air-dried crystals were checked by thermogravimetry (TG) and elemental analysis. The results of TG (Figure S-1)¹² and elemental analysis allowed us to safely conclude the formation of the pure cobalt mononuclear complex [Co(3,6-dtsq)₂(TTF-phen)] without any solvent molecules in the crystalline lattice. The synthetic details are presented in the Supporting Information.¹²

An ORTEP view of the TTF-phen ligand with atomic numbering is shown in Figure S-2.^{12,13} TTF-phen is crystallized

in the monoclinic space group $P2_1/c$. The C13–N3 bond length (1.28 Å) is consistent with a C=N double bond and indicates that the TTF and phenanthroline moieties are bridged by an imine. In addition, the small dihedral angle between the TTF and phenanthroline planes (36°) suggests that π -electron interactions can be expected between the TTF and phenanthroline groups.

The absorption spectrum for the TTF-phen ligand in CHCl₃ had an absorption band in the region below 650 nm (Figure S-3).¹² This absorption band ($\lambda_{max} = 494 \text{ nm}$) in the visible light region corresponds to intramolecular charge transfer (ICT) from the TTF to phenanthroline. The observation of the ICT band suggests that an efficient electronic communication exists between the TTF and phen moieties via the imine linkage. It has been reported that the red shift of the ICT band was induced by the formation of metal complexes in a TTF-iminepy system.¹⁰ This is because the interaction between metal and ligand changes the energy level of the pyridine moiety. In the absorption spectra of the cobalt complex [Co(3,6-dtsq)₂(TTFphen)] in CHCl₃, the absorption maximum shifted to a lower energy region (+29 nm). This indicates electronic interaction between the cobalt ion and TTF-phen ligand. In addition, in both the solution and solid state, a broad absorption band was observed in the 650-1200 nm, range that corresponds to the charge transfer between cobalt and its ligands and is the characteristic of cobalt valence tautomeric systems.

The temperature dependence of the $\chi_{mol}T$ product of [Co(3,6-dtsq)₂(TTF-phen)] is shown in Figure 1. At room temperature, $\chi_{mol}T$ is equal to $1.57 \,\mathrm{cm}^3 \,\mathrm{K} \,\mathrm{mol}^{-1}$, the value gradually decreases until 130 K, and it becomes constant below that temperature on cooling. The nearly constant value of $\chi_{mol}T$ $(0.42-0.49 \text{ cm}^3 \text{ K mol}^{-1})$ at temperatures below 130 K is consistent with the expected value for the [Co^{III-LS}(3,6-dtcat)(3,6dtsq)(TTF-phen)] species ($\chi_{mol}T = 0.4 \text{ cm}^3 \text{ K mol}^{-1}$). On warming, the $\chi_{mol}T$ value gradually increased and reached 2.04 cm³ K mol⁻¹ at 400 K. This value was less than the expected value for the pure [Co^{II-HS}(3,6-dtsq)₂(TTF-phen)] state ($\chi_{mol}T =$ 2.6 cm³ K mol⁻¹) and indicated that the electron transfer from 3,6-dtsq to cobalt was incomplete. The molar fractions of the [Co^{II-HS}(3,6-dtsq)₂(TTF-phen)] state was estimated to be ca. 75% at 400 K (Figure S-4).¹² It is important to note that the thermal dependence of $\chi_{mol}T$ was reproducible through warming-cooling cycles from 10 to 400 K.

In order to elucidate the electronic state of [Co(3,6dtsq)₂(TTF-phen)], its IR spectrum was measured at different temperatures (Figure 2). The spectral region from 1700 to 1000 cm⁻¹ contains strong bands associated with the C-O stretching modes that are sensitive to the electronic state of dioxolene ligand moieties.⁴ The IR spectrum at 80 K shows an absorption peak at approximately $1270 \,\mathrm{cm}^{-1}$, which is a characteristic of the C-O stretching vibrations for dtcat. On warming, the peak significantly decreased up to 293 K, although it was still observed at 400 K. Furthermore, the intensity of the peak at around 1440 cm⁻¹, which is attributed to the C-O stretching vibrations of 3,6-dtsq, increased upon warming. This result is consistent with the fact that the 3,6-dtcat ligand in the complex at low temperature [Co^{III-LS}(3,6-dtcat)(3,6-dtsq)(TTFphen)] is oxidized to 3,6-dtsq because of thermally induced valence tautomerism and that the electron transfer was not completed even at 400 K.



Figure 1. $\chi_{mol}T$ vs. *T* plots for [Co(3,6-dtsq)₂(TTF-phen)]. Measurements were conducted from 5 to 400 K in the temperature sweep mode with a 2 K min⁻¹ rate.



Figure 2. IR spectra of $[Co(3,6-dtsq)_2(TTF-phen)]$ at 80 (blue), 293 (black), and 400 K (red). The spectra were measured upon warming from 80 to 400 K.

In this paper, we reported the detailed synthesis and structure of a new imine-conjugated TTF-functionalized ligand, TTF-phen, and the first Co complex $[Co(3,6-dtsq)_2(TTF-phen)]$ with this ligand. Although it was not possible to obtain single crystals of this complex, elemental analysis, absorption spectra, magnetic measurements, and IR spectroscopy allowed us to characterize this material. The magnetic measurements revealed that the complex exhibits clear, thermally induced valence tautomerism in the temperature range 130-400 K ([Co^{III-LS}(3,6dtcat)(3,6-dtsq)(TTF-phen)] \rightleftharpoons [Co^{II-HS}(3,6-dtsq)₂(TTF-phen)]). Variable temperature IR spectroscopy showed the redox conversion of the 3,6-dtcat and 3,6-dtsq ligands, and these results agreed with the magnetic measurements. This complex is the first example of a valence tautomeric complex with a TTFfunctionalized ligand, and it is a potential multifunctional molecular material. In order to further study the intramolecular electronic state change due to the valence tautomerism effect on the conductivity, the preparation of a partially oxidized complex is under investigation.

This work was supported by a Grant-in-Aid for Young Scientists (B) (No. 23750164) from the Japan Society for the Promotion of Science (JSPS).

References and Notes

702

- a) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, V. Laukhin, *Nature* 2000, 408, 447. b) S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, H. Kobayashi, *Nature* 2001, 410, 908. c) O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* 1996, 272, 704. d) T. Liu, Y.-J. Zhang, S. Kanegawa, O. Sato, *J. Am. Chem. Soc.* 2010, 132, 8250. e) D.-P. Dong, T. Liu, S. Kanegawa, S. Kang, O. Sato, C. He, C.-Y. Duan, *Angew. Chem., Int. Ed.* 2012, 51, 5119.
- 2 For reviews on spin-crossover effect, see: a) Spin Crossover in Transition Metal Compounds I-III in Topics in Current Chemistry, ed. by P. Gütlich, H. A. Goodwin, Springer, Berlin/Heidelberg, 2004, Vol. 233 (doi:10.1007/b40394-9); Vol. 234 (doi:10.1007/b93641); Vol. 235 (doi:10.1007/ b96439). b) M. A. Halcrow, Chem. Soc. Rev. 2011, 40, 4119. c) M. Nihei, T. Shiga, Y. Maeda, H. Oshio, Coord. Chem. Rev. 2007, 251, 2606. d) P. Gütlich, P. J. van Koningsbruggen Koningsbruggen, F. Renz, Struct. Bonding 2004, 107, 27. e) P. Gütlich, Y. Garcia, H. A. Goodwin, Chem. Soc. Rev. 2000, 29, 419. f) P. Gütlich, A. Hauser, H. Spiering, Angew. Chem., Int. Ed. Engl. 1994, 33, 2024.
- 3 a) K. Takahashi, H.-B. Cui, Y. Okano, H. Kobayashi, H. Mori, H. Tajima, Y. Einaga, O. Sato, J. Am. Chem. Soc. 2008, 130, 6688. b) S. Dorbes, L. Valade, J. A. Real, C. Faulmann, Chem. Commun. 2005, 69. c) C. Faulmann, S. Dorbes, B. G. de Bonneval, G. Molnár, A. Bousseksou, C. J. Gomez-Garcia, E. Coronado, L. Valade, Eur. J. Inorg. Chem. 2005, 3261. d) C. Faulmann, K. Jacob, S. Dorbes, S. Lampert, I. Malfant, M.-L. Doublet, L. Valade, J. A. Real, Inorg. Chem. 2007, 46, 8548. e) L. C. J. Pereira, A. M. Gulamhussen, J. C. Dias, I. C. Santos, M. Almeida, Inorg. Chim. Acta 2007, 360, 3887.
- 4 a) D. N. Hendrickson, C. G. Pierpont, in Spin Crossover in Transition Metal Compounds II in Topics in Current Chemistry, Springer, Berlin/Heidelberg, 2004, Vol. 234, p. 63. doi:10.1007/b95413. b) R. M. Buchanan, C. G. Pierpont, J. Am. Chem. Soc. 1980, 102, 4951. c) D. M. Adams, D. N. Hendrickson, J. Am. Chem. Soc. 1996, 118, 11515. d) D. M. Adams, A. Dei, A. L. Rheingold, D. N. Hendrickson, Angew. Chem., Int. Ed. Engl. 1993, 32, 880. e) C. G. Pierpont, R. M. Buchanan, Coord. Chem. Rev. 1981, 38, 45. f) R. D. Schmidt, D. A. Shultz, J. D. Martin, Inorg. Chem. 2010, 49, 3162. g) R. D. Schmidt, D. A. Shultz, J. D. Martin, P. D. Boyle, J. Am. Chem. Soc. 2010, 132, 6261. h) T. T. Patricia, M. V. Sandra, L. Manuela, L. Andrea, F. Paolo, D. Andrea, R. Roberto, Phys. Chem. Chem. Phys. 2012, 14, 1038.
- 5 a) D. A. Shultz, in *Magnetism: Molecules to Materials II:* Models and Experiments, ed. by J. S. Miller, M. Drillon,

Wiley-VCH, Weinheim, Germany, **2001**, p. 281. doi:10.1002/3527600590.ch8. b) K. D. Demadis, C. M. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655. c) P. Gütlich, H. A. Goodwin, in *Spin Crossover in Transition Metal Compounds I* in *Topics in Current Chemistry*, ed. by P. Gütlich, H. A. Goodwin, Springer, **2004**, Vol. 233, p. 1. doi:10.1007/b13527. d) O. Sato, A. Cui, R. Matsuda, J. Tao, S. Hayami, *Acc. Chem. Res.* **2007**, *40*, 361.

- a) C. Carbonera, A. Dei, J.-F. Létard, C. Sangregorio, L. Sorace, *Angew. Chem., Int. Ed.* 2004, 43, 3136. b) J. Tao, H. Maruyama, O. Sato, *J. Am. Chem. Soc.* 2006, *128*, 1790. c) K. G. Alley, G. Poneti, J. B. Aitken, R. K. Hocking, B. Moubaraki, K. S. Murray, B. F. Abrahams, H. H. Harris, L. Sorace, C. Boskovic, *Inorg. Chem.* 2012, *51*, 3944.
- 7 a) O.-S. Jung, C. G. Pierpont, J. Am. Chem. Soc. 1994, 116, 2229. b) I. Imaz, D. Maspoch, C. Rodríguez-Blanco, J. M. Pérez-Falcón, J. Campo, D. Ruiz-Molina, Angew. Chem., Int. Ed. 2008, 47, 1857. c) K. S. Murray, Eur. J. Inorg. Chem. 2008, 3101. d) B. Li, L.-Q. Chen, R.-J. Wei, J. Tao, R.-B. Huang, L.-S. Zheng, Z. Zheng, Inorg. Chem. 2011, 50, 424.
- 8 D. Lorcy, N. Bellec, M. Fourmigué, N. Avarvari, *Coord. Chem. Rev.* **2009**, *253*, 1398, and references therein.
- 9 a) Y.-P. Zhao, L.-Z. Wu, G. Si, Y. Liu, H. Xue, L.-P. Zhang, C.-H. Tung, J. Org. Chem. 2007, 72, 3632. b) M. Chahma, N. Hassan, A. Alberola, H. Stoeckli-Evans, M. Pilkington, Inorg. Chem. 2007, 46, 3807. c) N. Benbellat, Y. Le Gal, S. Golhen, A. Gouasmia, L. Ouahab, J.-M. Fabre, Eur. J. Org. Chem. 2006, 4237. d) H. Xue, X.-J. Tang, L.-Z. Wu, L.-P. Zhang, C.-H. Tung, J. Org. Chem. 2005, 70, 9727. e) X. Xiao, W. Xu, D. Zhang, H. Xu, H. Lu, D. Zhu, J. Mater. Chem. 2005, 15, 2557. f) A. Ota, L. Ouahab, S. Golhen, O. Cador, Y. Yoshida, G. Saito, New J. Chem. 2005, 29, 1135.
- 10 a) J.-Y. Balandier, A. Belyasmine, M. Sallé, *Eur. J. Org. Chem.* 2008, 269. b) J. Qin, C.-X. Qian, N. Zhou, R.-M. Zhu, Y.-Z. Li, J.-L. Zuo, X.-Z. You, *Eur. J. Inorg. Chem.* 2012, 234.
- 11 M. Nihei, N. Takahashi, H. Nishikawa, H. Oshio, *Dalton Trans.* 2011, 40, 2154.
- 12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/ index.html.
- 13 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-898555. Copies of the data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).