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Redox-Switchable Molecular Containers Consisting of Dicobalt Complexes

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Doubly bridged dicobalt complexes with bidentate diamine ligands were synthesized and characterized by X-ray diffraction studies. Reversible formation and decomposition of the doubly bridged structure utilizing the redox couple between Co(II) and Co(III) were investigated by cyclic voltammetry and UV–vis.

Molecuar switches are the attractive components of molecular electronic devices capable of inducing chemical and physical changes in response to external stimuli such as electrical current, light, and heat.[1−3] In this study, switching systems were established by using the structural change of dicobalt complexes. Cobalt complexes prefer a six-coordinated structure at the Co(III) state, while the Co(II) species prefer a four-coordinated structure.[4] A reversible redox change of dicobalt complexes between Co(III) and Co(II) provides a stable molecular switching system. We constructed a switching system using this strategy as a molecular container containing a crown ether moiety (Figure 1).

Doubly bridged dicobalt(III,III) complexes were prepared by one-pot synthesis as shown in Scheme 1. To a solution of dinucleating ligand **L1**[5,6] (0.01 mmol) in 2 mL of chloroform was dropwise added $Co(OAc)_2{\cdot}4H_2O$ (0.036 mmol) in 2 mL of methanol under air at room temperature.

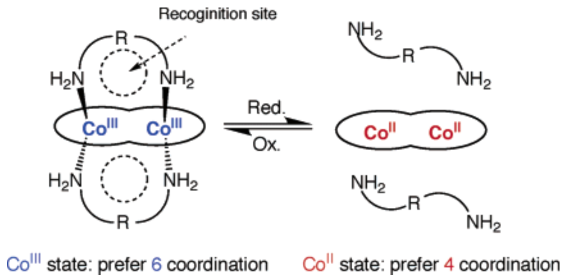
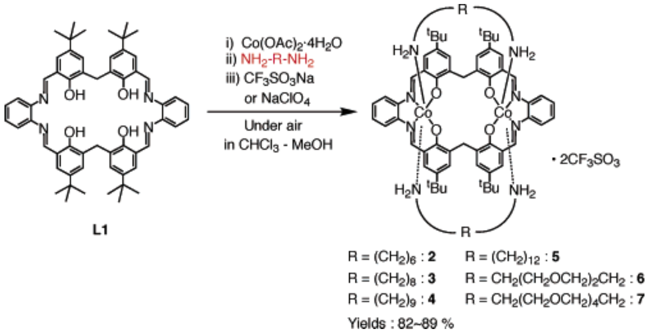


Figure 1. Strategy for redox-switchable molecular containers.

Scheme 1. Synthesis of Doubly Bridged Dicobalt Complexes (**2**−**6**)



After stirring for 30 min, diamine (0.027 mmol) and a methanol solution of CF_3SO_3Na or $NaClO_4$ (0.11 mmol) were added to it, and then the solution was further stirred overnight. The gradually precipitated reddish-brown solids were collected by filtration, washed with a small amount of methanol and water, and then dried under vacuum.

The precipitates were characterized by UV−vis, NMR, IR, and electrospray ionization (ESI) mass (time-of-flight) spectroscopy (MS). In the proton NMR analyses, all of the complexes (**2**−**6**) showed sharp proton NMR peaks in the diamagnetic region, which indicates that the complexes are diamagnetic cobalt(III) of the low-spin d_6 state. The proton NMR spectrum showed a symmetrical pattern, and amino protons coordinating to cobalt centers appeared at 3.0−3.4

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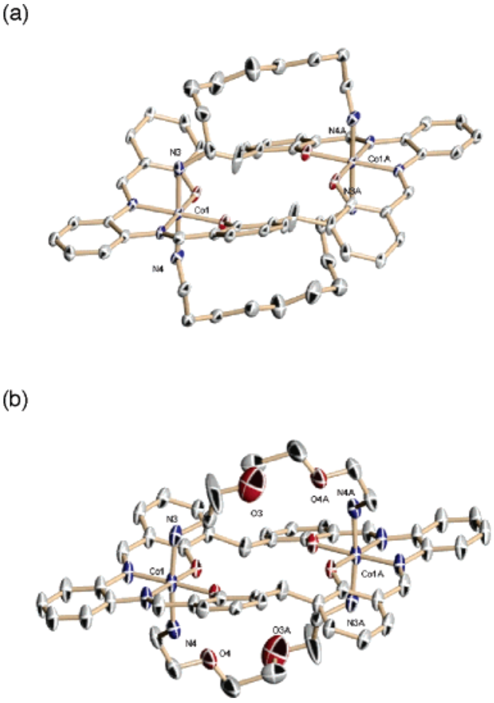

Figure 2. ORTEP drawing of (a) **4** and (b) **6** with thermal ellipsoids at 50% probability. Hydrogen atoms, *tert*-butyl groups, and CF_3SO_3 and ClO_4 anions are omitted for clarity.

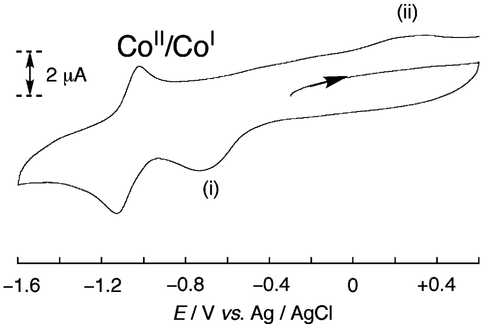

Figure 3. Cyclic voltammogram of **7** (1.0×10^{-3} M) in DMF containing 1.0×10^{-1} M n-Bu_4NClO_4 at room temperature; sweep rate = 100 mV s^{-1}.

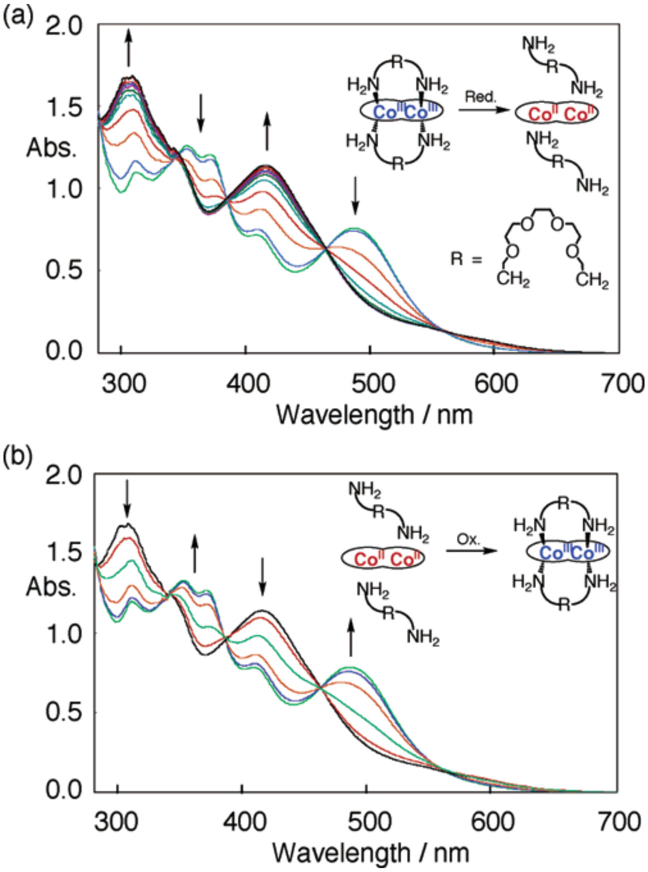

Figure 4. Electronic spectra observed during electrolysis of a DMF solution containing **7** (1.0×10^{-3} M) and n-Bu_4NClO_4 (1.0×10^{-1} M): (a) at −0.90 V vs Ag/AgCl; (b) at +0.50 V vs Ag/AgCl.

ppm with 8H integration numbers ascribed to two molecules of diamines. ESI-MS analysis also supported the doubly bridged structure. ESI-MS showed intense peaks ascribed to $[Co_2\mathbf{L1}(diamine)_2](CF_3SO_3)^+$ or $[Co_2\mathbf{L1}(diamine)_2]^{2+}$. These data suggested the existence of a doubly bridged structure.[7] Fortunately, the complexes **4** and **6** afford crystals suitable for X-ray analysis, and their molecular structures are shown in Figure 2.[8] As expected, the dinucleating ligand **L1** holds two cobalt ions at each N2−O2 coordinating site and two diamine molecules were intramolecularly coordinated at each cobalt ion and occupy the four axial positions of the distorted octahedral complex. The Co···Co intramolecular nonbonded distance for **4** and **6** is 7.53 and 7.44 Å, respectively. It is noteworthy that each salicylaldiminato residue is bent to a symmetric umbrella but away from each other to reduce the steric strain of the two octahedral coordination centers.

The redox behavior of the complex was investigated by cyclic voltammetry. The cyclic voltammogram of **7** in the potential range between 0.60 and −1.60 V vs Ag/AgCl in a dimethylformamide (DMF) solution is shown in Figure 3. A scan in the positive direction at −0.30 V vs Ag/AgCl reveals no oxidative wave, while a scan in the negative direction reveals a first reduction wave at −0.80 V vs Ag/AgCl, which is due to process i.

$$[Co^{III}Co^{III}\mathbf{L1}(diamine)_2] \rightarrow [Co^{II}Co^{II}\mathbf{L1}] + 2(diamine) \quad \text{(i)}$$

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(7) The complex in which diamine was coordinated to the dimetal center was reported in the case of dizinc complexes: (a) Danks, I. P.; Lane, T. G.; Sutherland, I. O.; Yap, M. *Tetrahedron* **1992**, *48*, 7679. (b) Crossley, M. J.; Hambley, T. W.; Mackay, L. G.; Try, A. C.; Walton, R. *Chem. Commun*. **1995**, 1077. (c) Ema, T.; Misawa, S.; Nemugaki, S.; Sakai, T.; Utaka, M. *Chem. Lett*. **1997**, 487. (d) Hayashi, T.; Nonoguchi, M.; Aya, T.; Ogoshi, H. *Tetrahedron Lett*. **1997**, *38*, 1603. (e) Kubo, Y.; Ohno, T.; Yamanaka, J.; Tokita, S.; Iida, T.; Ishimaru, Y. *J. Am. Chem. Soc*. **2001**, *123*, 12700. (f) Crossley, M. J.; Thordarson, P. *Angew. Chem., Int. Ed*. **2002**, *41*, 1709. (g) Shinmori, H.; Ahn, T. K.; Cho, H. S.; Kim, D.; Yoshida, N.; Osuka, A. *Angew. Chem., Int. Ed*. **2003**, *42*, 2754. (h) Borovkov, V. V.; Fujii, I.; Muranaka, A.; Hembury, G. A.; Tanaka, T.; Ceulemans, A.; Kobayashi, N.; Inoue, Y. *Angew. Chem., Int. Ed*. **2004**, *43*, 5481.

(8) Diffraction data were collected on a Bruker SMART APEX CCD-based X-ray diffractometer operated at 100 K. The space groups ($P1$, triclinic for **4**; $P2(1)/n$, monoclinic for **6**) were determined based on systematic absences and intensity statistics. Cell dimensions for **4**: $a = 11.5150(13)$ Å, $b = 14.0098(16)$ Å, $c = 15.6716(18)$ Å with $\alpha = 65.817(2)°$, $\beta = 72.985(2)°$, $\gamma = 89.584(3)°$ and $V = 2186.9(4)$ Å^3, $Z = 1$. Cell dimensions for **6**: $a = 16.5413(12)$ Å, $b = 16.6742(13)$ Å, $c = 18.2228(13)$ Å with $\beta = 105.615(2)°$ and $V = 4840.6(6)$ Å^3, $Z = 2$. Full-matrix least-squares refinement based on F^2 converged to R1 [$I > 2\sigma(I)$] values of 0.0713 and 0.0678 and a wR2 values of 0.1895 and 0.1607; GOF = 1.051 and 1.037 for **4** and **6**, respectively.

The reduction of the Co(III) complex results in the loss of its axial ligands (diamine) in weakly coordinating solvents because the electron is added to the antibonding d_{z^2} orbital.[9] The second reduction potential due to Co(II)/Co(I) couples shows a reversible behavior at −1.10 V vs Ag/AgCl. Upon reversal of the scan direction, the thus-formed four-coordinate Co(II) complex is reoxidized to Co(III) at 0.30 V vs Ag/AgCl, which has much higher potentials because of the absence of a donating axial diamine at both cobalt centers (process ii).

$$[\mathrm{Co^{II}Co^{II}}\mathbf{L1}] \rightarrow [\mathrm{Co^{III}Co^{III}}\mathbf{L1}] \qquad \text{(ii)}$$

Then, in a rapid consecutive reaction (coordination of diamine), the six-coordinate complex with a doubly bridged structure will be reformed. In this way, the irreversible Co(III)/Co(II) redox couple is accompanied by the dissociation of the axial diamine.[10]

These structural changes were followed by UV−vis spectroscopy. The doubly bridged dicobalt complex **7** shows characteristic UV−vis spectrum at 351, 370, 408, and 485 nm in DMF. During the electrolysis at −0.90 V vs Ag/AgCl, the spectrum was changed to a new spectrum with four isosbestic points at 343, 384, 463, and 560 nm, as shown in Figure 4a. The final spectrum showed absorption maxima at 304, 347, and 415 nm, which were characteristic of those of the Co(II,II) complex in DMF. After electrolysis at −0.90 V vs Ag/AgCl, the potential was subsequently changed to 0.50 V vs Ag/AgCl. The spectrum was changed to the starting one with the same isosbestic points, as shown in Figure 4b.

The recovered species was characterized by ESI-MS analysis as an original doubly bridged complex. These reversible changes were repeated over five times without decomposition of the complex. The results presented above strongly suggested that the doubly bridged dicobalt complex should act as a redox-switchable molecular container.

In conclusion, doubly bridged dicobalt complexes having a molecular recognition moiety were readily synthesized in high yields. The coordinating diamines were reversibly bridged on the cobalt centers by the electrochemical method.

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Supporting Information Available: Crystallographic data in CIF format for **4** and **6**, synthesis and characterization for **2**−**6**, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Oxidation wave (process ii) appeared when the scan direction was reversed to the positive direction at −0.90 vs Ag/AgCl.