

Molecular Recognition of Redox-Switchable Bis-Crown Moieties Assembled on a Dicobalt Complex

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A new dinuclear complex of cobalt(III) having double bis-crown moieties (**1**) was synthesized in a one-pot multistep reaction between the dinucleating ligand (H_2L^1), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and 4'-aminomethylbenzo-15-crown 5-ether under aerobic conditions. The complex was characterized by UV–vis, IR, NMR, and CSI-mass spectroscopies, and the axial coordination of the 4'-aminomethylbenzo-15-crown 5-ether on both cobalt centers was confirmed. The bis-crown moieties of **1** acted as a potassium ion binding site with a large association constant (K) of $1.97 \times 10^5 \text{ M}^{-1}$ (1:1) caused by the preorganized bis-crown structure. Solvent extraction of K^+ (potassium picrate) with **1** was investigated by UV–vis and NMR, and the extracted K^+ was quantified by an atomic absorption/flame emission spectrophotometer. The cyclic voltammogram of **1** showed irreversible redox waves at -0.57 V and $+0.16 \text{ V}$ versus Ag/AgCl in DMF, which are ascribed to the $\text{Co}(\text{III})$ and $\text{Co}(\text{II})$ redox couple. The large peak separation ($\Delta 0.73 \text{ V}$) of this redox couple indicates the association and dissociation of the axial amine on the cobalt centers. The irreversible reduction peak of **1** at -0.57 V was shifted in the positive direction by 80 mV in the presence of the potassium ion, showing the complexation of **1** with the potassium ion. The reversible formation and decomposition of the double bis-crown moieties in **1** caused by the electrical stimulus were also investigated by thin-layer UV–vis spectroelectrochemistry. The switching of the double bis-crown structure of **1** was established over four trials with response to electrical energy.

Introduction

Crown ether has a storied history in supramolecular chemistry and plays a broad and prominent role in host–guest chemistry and molecular recognition.^{1,2} During the development of this field, significant advances have been established to construct a switching system, in which the structure and function of the molecules were controlled by external stimuli such as light, electrical, and chemical energy.³ Pioneering work by Shinkai et al. of the molecular switch based on the crown ether emerged in the 1980s. Photoresponsive⁴ and

redox-switched⁵ crown ethers have been synthesized, and smart switching systems were reported. On the basis of these studies, a variety of crown-based molecular switches has been reported.⁶

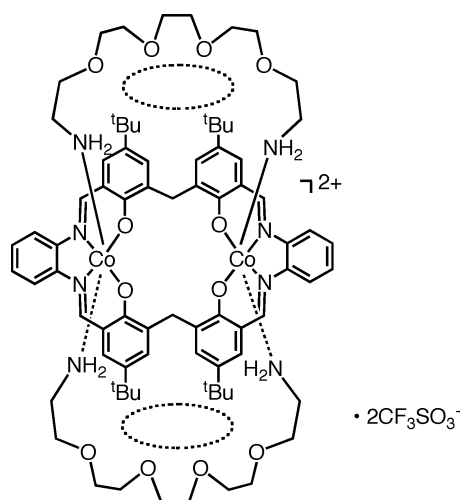
Recently, significant interest has focused on coordination chemistry for the buildup of a supramolecular material utilizing metal coordination.^{7–10} Metal coordination is a powerful and useful tool for the construction of the supramo-

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- (1) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.
- (2) Bradshaw, J. S.; Izatt, R. M.; Bordunov, A. V.; Zhu, C. Y.; Hathaway, J. K. *Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 1, pp 35–95.
- (3) (a) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001. (b) *Molecular Devices and Machines*; Balzani, V.; Venturi, M.; Credi, A., Eds.; Wiley-VCH: Weinheim, Germany, 2003.
- (4) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111–115.

- (5) Minami, T.; Shinkai, S.; Manabe, O. *Tetrahedron Lett.* **1982**, *23*, 5167–5170.
- (6) (a) Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133–137. (b) Takeshita, M.; Irie, M. *J. Org. Chem.* **1998**, *63*, 6643–6649. (c) Horie, M.; Suzuki, Y.; Osakada, K. *J. Am. Chem. Soc.* **2004**, *126*, 3684–3865. (d) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433–444. (e) Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845–1849.
- (7) Chen, C.-T. *Comprehensive Supramolecular Chemistry*; Suslick, K. S., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 5, pp 91–140.
- (8) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.
- (9) Constable, E. C. *Coord. Chem. Rev.* **2008**, *252*, 842–855.
- (10) Suh, M. P.; Cheon, Y. E.; Lee, E. Y. *Coord. Chem. Rev.* **2008**, *252*, 1007–1026.

Chart 1



lecular assembly because of its high stability and geometrical variation. These properties are dependent on the redox state of the metal center, which was changed in response to an electrochemical stimulus. Therefore, structural changes within the metal complexes in response to the electrochemical conversion of the redox state have been the subject of a number of investigations focused on constructing a molecular switch.^{11,12} The electrochemical conversions of Cu(II) to Cu(I)¹³ and Fe(III) to Fe(II)¹⁴ resulting in a geometrical change in the complex were applied for molecular redox switches. In the case of cobalt, the cobalt complex prefers a six-coordinated structure at the Co(III) state, while the Co(II) species prefers a four-coordinated structure.¹⁵ A reversible redox change in the cobalt complex between Co(III) and Co(II) also provides a stable molecular switching system.

Previously, we reported a redox-switchable molecular container consisting of a dicobalt complex having bidentate diamine ligands, as shown in Chart 1.¹⁶ Doubly bridged diamine ligands were expected to work as a pseudocrown ether. As an expansion of this study, we introduced bis-crown moieties at the axial sites of the dicobalt complex. In this report, we described the synthesis of a new dicobalt complex having double bis-crown moieties, in which the bis-crown moiety should work as an alkali metal receptor. The new crown-assembled approach to molecular recognition combined with electrochemical conversion of the molecular structure, as shown in Figure 1, was reported.

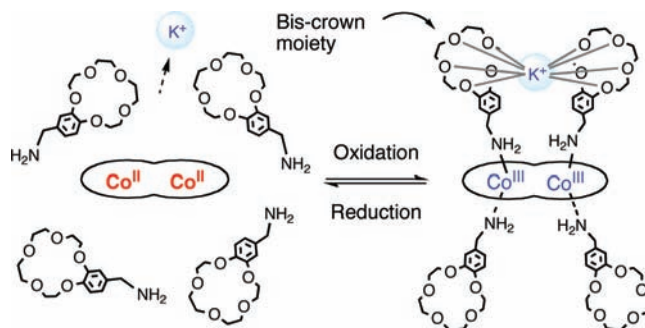


Figure 1. Strategy for redox-switchable bis-crown moieties.

Experimental Section

Chemicals. All solvents and chemicals used in the syntheses were of reagent grade and were used without further purification. For the electrochemical studies, *N,N*-dimethylformamide (DMF) was stirred for one day in the presence of barium oxide under a nitrogen atmosphere and distilled under reduced pressure. The distillation was performed with the exclusion of light, and purified DMF was stored in a refrigerator under nitrogen in the presence of activated molecular sieves (4A). Tetra-*n*-butyl ammonium perchlorate (*n*-Bu₄NClO₄) was purchased from Nakalai Chemicals (special grade) and dried at room temperature under a vacuum before use. 4'-Aminomethylbenzo-15-crown 5-ether was synthesized by a reported method.¹⁷ The dinucleating Schiff-base ligand H₂L¹ and corresponding Co(II)Co(II) complex **3** (See Chart 2) were synthesized by a previously reported method.¹⁸ Potassium picrate was prepared in ethanol by neutralizing picric acid with potassium hydroxide.¹⁹

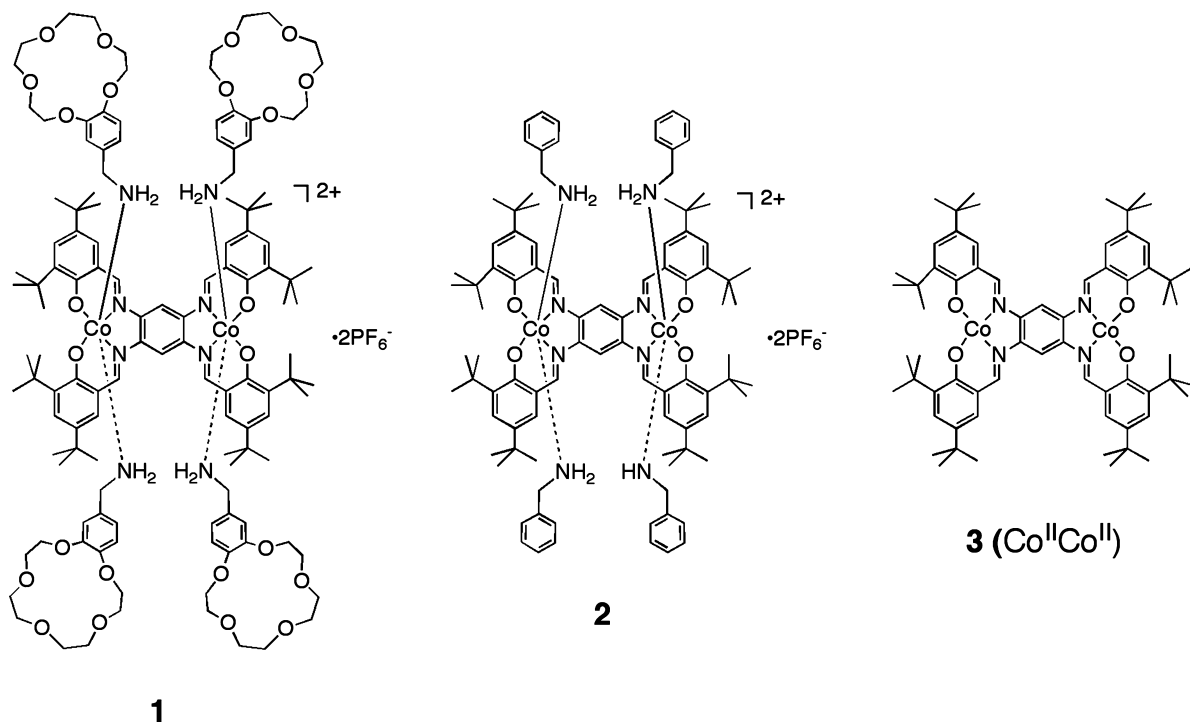
Instrumentation. The ¹H, ¹³C, and 2-D correlation spectroscopy NMR spectra were recorded using a Bruker Avance 500 spectrometer installed at the Center of Advanced Instrumental Analysis at Kyushu University, and the chemical shifts (in parts per million) were referenced relative to the residual protic solvent peak. The UV-vis absorption spectra were measured using a Hitachi U-3300 spectrophotometer. The IR spectra were recorded with a JASCO FT-IR 460 plus KH spectrophotometer using KBr discs. The matrix-assisted laser desorption/ionization-time-of-flight mass spectra were obtained using a Bruker autoflex II with dithranol as the matrix. Cryospray ionization (CSI) mass spectra were obtained using a Bruker micrOTOF in acetonitrile at -40 °C. The potassium ion analysis was carried out with a Shimadzu AA-6700 atomic absorption/flame emission spectrophotometer.

The cyclic voltammograms (CV) were obtained using a BAS CV 50 W electrochemical analyzer. A three-electrode cell equipped with a 3.0-mm-diameter glassy carbon rod and 1.6-mm-diameter platinum wire as the working and counter electrodes, respectively, was used. A Ag/AgCl (3.0 M NaCl) electrode served as the reference. Nonaqueous DMF solutions containing **1** (5.0 × 10⁻⁴ M) and *n*-Bu₄NClO₄ (1.0 × 10⁻¹ M) were deaerated prior to each measurement, and the inside of the cell was maintained under a nitrogen atmosphere throughout each measurement. All measurements were carried out at 25 °C. The *E*_{1/2} value of the ferrocene/

- (11) Nishihara, H. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 407–428.
 (12) Nijhuis, C. A.; Ravoo, B. J.; Huskens, J.; Reinhoudt, D. N. *Coord. Chem. Rev.* **2007**, *251*, 1761–1780.
 (13) (a) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruña, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4422–4435. (b) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruña, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4436–4449. (c) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611–619. (d) Amendola, V.; Fabbri, L.; Pallavicini, P.; Sartirana, E.; Taglietti, A. *Inorg. Chem.* **2003**, *42*, 1632. (e) Korybut-Daszkiwicz, B.; Wieckowska, A.; Bilewicz, R.; Domagata, S.; Krzysztow, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 1668–1672. (f) Kume, S.; Murata, M.; Ozeki, T.; Nishihara, H. *J. Am. Chem. Soc.* **2005**, *127*, 490–491.
 (14) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, *374*, 790–792.
 (15) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, 1999.
 (16) Shimakoshi, H.; Takemoto, T.; Aritome, I.; Hisaeda, Y. *Inorg. Chem.* **2005**, *44*, 9134–9136.

- (17) Kryatova, O. P.; Kolchinski, A. G.; Rybak-Akimova, E. V. *Tetrahedron Lett.* **2003**, *59*, 231–239.
 (18) (a) Chichak, K.; Jacquemard, U.; Branda, N. R. *Eur. J. Inorg. Chem.* **2002**, 357–368. (b) Shimakoshi, H.; Hirose, S.; Ohba, M.; Shiga, T.; Okawa, H.; Hisaeda, Y. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1040–1046. (c) Kleiji, A. W.; Kuil, M.; Tooke, D. M.; Lutz, M.; Spek, A. L.; Reek, J. N. H. *Chem.—Eur. J.* **2005**, *11*, 4743–4750.
 (19) Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* **1975**, *97*, 3462–3467.

Chart 2



ferrocenium (Fc/Fc⁺) couple was +0.55 V versus Ag/AgCl with this setup. The thin-layer spectroelectrochemical measurements were carried out with a Hokuto Denko HA-501 potentiostat coupled with a galvanostat using a cell having an optical pathway of about 0.5 mm. The optical transparent thin-layer electrode was a platinum grid (200 mesh) placed in the optical pathway.

Synthesis of 1. To a solution of H₂L¹ (37.0 mg, 0.037 mmol) in 2 mL of chloroform was added dropwise Co(OAc)₂·4H₂O (32 mg, 0.13 mmol) in 2 mL of methanol under air at room temperature. After 30 min of stirring, a 2 mL chloroform solution of 4'-aminomethylbenzo-15-crown-5-ether (66 mg, 0.22 mmol) and a 2 mL methanol solution of *n*-Bu₄NPF₆ (50 mg, 0.13 mmol) were added to it, and then the solution was further stirred overnight. The solution was then concentrated using an evaporator; the precipitated reddish-brown solid was filtered and washed with a small amount of cooling methanol and then dried under a vacuum (see Chart 2). Yield: 80%. IR (KBr): $\nu(\text{C}=\text{N})$ 1593(m), $\nu(\text{PF}_6)$ 845(s), 558(m). ¹H NMR (CDCl₃; ppm): δ 1.36 (s, 36H, *t*-Bu), 1.72 (s, 36H, *t*-Bu), 2.49 (s, 8H, -NH₂), 3.08 (t, 8H, -CH₂-NH₂), 3.55–3.75 (m, 48H, -OCH₂CH₂O-), 3.91–3.95 (d, 16H, -OCH₂CH₂O-), 6.48 (d, 4H, Ph), 6.55–6.60 (m, 8H, Ph), 7.34 (s, 4H, Ph), 7.57 (s, 4H, Ph), 8.69 (s, 2H, Ph), 8.69 (s, 4H, N=CH). CSI MS: m/z [M - (PF₆)₂]²⁺, 1152.5749. UV-vis (in CHCl₃, nm), λ_{max} (ϵ) 270 (81800), 364 (41700), 383 (41100), 542 (49700). Anal. calcd for C₁₂₆H₁₇₈N₈Co₂F₁₂O₂₄P₂·4H₂O: C, 56.71; H, 7.03; N, 4.20. Found: C, 56.75; H, 6.78; N, 4.22.

Synthesis of [Co(III)₂L¹(benzylamine)₄](PF₆)₂ (2). To a solution of H₂L¹ (40.0 mg, 0.040 mmol) in 10 mL of chloroform was added dropwise Co(OAc)₂·4H₂O (22 mg, 0.088 mmol) in 2 mL of methanol under air at room temperature. After 2 h of stirring, a 2 mL chloroform solution of benzylamine (19 mg, 0.18 mmol) and a 2 mL methanol solution of *n*-Bu₄NPF₆ (50 mg, 0.13 mmol) were added to it, and then the solution was further stirred overnight. The solution was then concentrated using an evaporator; the precipitated reddish-brown solid was filtered and washed with a small amount of cooled methanol and then dried under a vacuum (see Chart 2). Yield: 89%. IR (KBr): $\nu(\text{C}=\text{N})$ 1592(m), $\nu(\text{PF}_6)$ 845(s), 558(m).

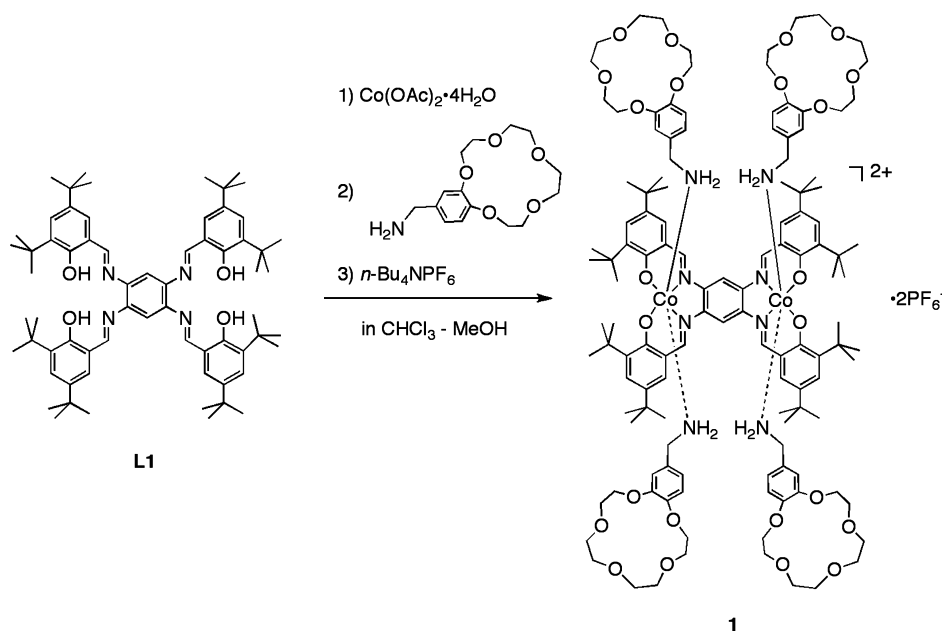
¹H NMR (CDCl₃; ppm): δ 1.34 (s, 36H, *t*-Bu), 1.74 (s, 36H, *t*-Bu), 2.75 (t, 8H, -NH₂), 3.22 (t, 8H, -CH₂-NH₂), 7.17 (s, 20H, Ph), 7.31 (s, 4H, Ph), 7.53 (s, 4H, Ph), 8.75 (s, 4H, N=CH), 8.78 (s, 2H, Ph). CSI MS: m/z [M - (PF₆)₂]²⁺, 772.6. UV-vis (in CHCl₃, nm), λ_{max} : 359, 378, 538. Anal. calcd for C₉₄H₁₂₂N₈Co₂F₁₂O₄P₂: C, 61.50; H, 6.70; N, 6.10. Found: C, 61.35; H, 6.80; N, 5.88.

Method of NMR Titration. To a 5.0 × 10⁻⁵ M solution of **1** in CD₃CN was added a stock solution of KPF₆ in CD₃CN at 25 °C, and the change in the chemical shift of the imino proton of **1** was monitored at 12 different potassium ion concentrations. The association constant (*K*) was calculated assuming a 1:1 complexation using a computer-assisted nonlinear curve fitting analysis. The KPF₆ concentration range was 1.52 × 10⁻⁵ M to 1.83 × 10⁻⁴ M.

Method of Solvent Extraction by UV-Vis, NMR, and IR Spectroscopies. Equal volumes of chloroform-*d* containing 1 × 10⁻³ M **1** and a deuterium aqueous solution containing 1.79 × 10⁻² M potassium picrate were agitated with a stirring bar for 5 min. The solution was equilibrated at 20 °C. The aliquot of the upper aqueous solution was withdrawn, and the UV-vis spectrum was recorded for a 50 times dilution in H₂O. The amount of picrate ions was determined by absorbance at 356 nm. The lower chloroform-*d* solution was directly analyzed by NMR. The signal ascribed to the extracted picrate ion was observed at 8.56 ppm. After the chloroform-*d* solution was concentrated, the IR spectrum of the residue was measured using KBr discs.

Method of Solvent Extraction by Potassium Ion Quantification. Equal volumes of chloroform containing 6.5 × 10⁻⁴ M **1** and an aqueous solution containing 4.0 × 10⁻³ M potassium picrate were agitated with a stirring bar for 5 min. The solution was equilibrated at 20 °C. The aliquot of the upper aqueous solution was withdrawn, and the potassium ion content was determined by an atomic absorption/flame emission spectrophotometer with dilution in 0.1 M aqueous HNO₃. When we used benzo-15-crown-5 as the extracting reagent, the concentration was adjusted to 2.6 × 10⁻³ M, four times greater than that of **1**, in order to make equal each concentration of the crown ether unit.

Scheme 1. Synthesis of Dicobalt Complex with Bis-Crown Moieties



Results and Discussion

Synthesis. The dicobalt complex having double bis-crown moieties, **1**, was prepared by a one-pot synthesis, as shown in Scheme 1. The tetradentate N_2O_2 Schiff-base unit in H_2L^1 and the amino group in 4'-aminomethylbenzo-15-crown 5-ether occupy equatorial and axial positions of both cobalt centers, respectively. It is noteworthy that the Schiff-base-based poly- N_2O_2 compartmental ligands are useful skeletons for the construction of a multimetallic complex, and a significant number of complexes have been designed and synthesized.^{20–25} The structure of the complex was identified by UV-vis, IR, NMR, and CSI-mass spectroscopies. The UV-vis spectrum showed a strong absorption band at 542

nm, which can be attributed to the metal–ligand charge transfer transition. In the IR spectrum, bands assignable to the C=N vibration of the coordinated azomethine group and the P–F vibration of the PF_6^- counteranion appeared at 1593 and 845 cm^{-1} , respectively. The $\nu(C=N)$ band is shifted to a lower energy by 17 cm^{-1} compared to that of H_2L^1 ($\nu(C=N)$, 1610 cm^{-1}), indicating that the ligand is coordinated to the cobalt ion through the nitrogen atoms of the azomethine group.

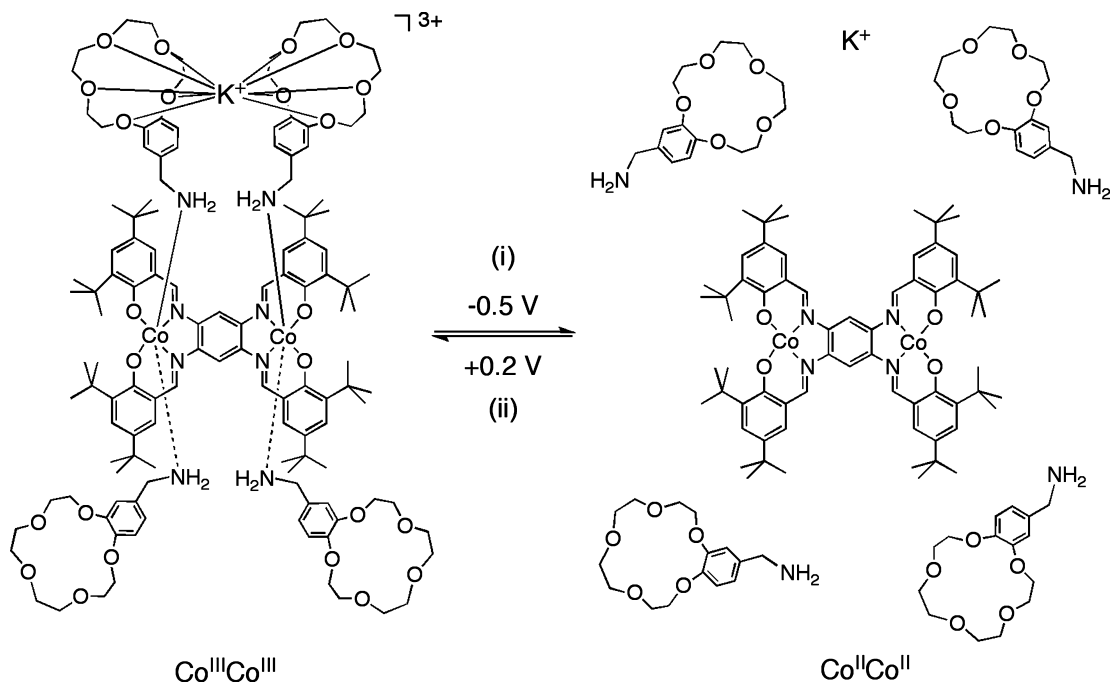
The diamagnetic Co(III) complex **1** shows a well-defined 1H NMR spectrum. A peak for the hydroxyl protons of H_2L^1 disappeared during the complexation with the cobalt ion, and the amino protons of the 4'-aminomethylbenzo-15-crown 5-ether coordinating to the cobalt centers appeared at 2.49 ppm with 8H integration numbers. The crown ether groups appeared at 3.55–3.95 ppm with the appropriate integration numbers. On the basis of these integration numbers, four equivalent moles of the 4'-aminomethylbenzo-15-crown 5-ether existed in **1**. Convincing evidence for the double bis-crown structure of **1** was provided by CSI-MS. The CSI-MS showed an intense peak at m/z 1152.57 ascribed to $[Co_2L^1(amine)_4]^{2+}$ that satisfied the isotope patterns, as shown in Figure S1 (Supporting Information). These spectral data strongly suggested the successful preparation of the desired dicobalt complex having double bis-crown moieties.

Redox Behavior. The redox behavior of **1** was investigated by CV. The CV of **1** in the potential range between +1.0 and –1.8 V versus Ag/AgCl in a DMF solution is

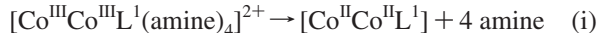
- (20) van Veggel, F. C. J. M.; Verboom, W.; Reinhoudt, D. N. *Chem. Rev.* **1994**, *94*, 279–299.
 (21) Borisova, N. E.; Reshetova, M. D.; Ustynyuk, Y. A. *Chem. Rev.* **2007**, *107*, 46–79.
 (22) Vigato, P. A.; Tamburini, S.; Bertolo, L. *Coord. Chem. Rev.* **2007**, *251*, 1311–1492.
 (23) Wezenberg, S. J.; Kleij, A. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 2354–2364.
 (24) (a) van Veggel, F. C. J. M.; Bos, M.; Harkema, S.; van de Bovenkamp, H.; Verboom, W.; Reedijk, J.; Reinhoudt, D. N. *J. Org. Chem.* **1991**, *56*, 225–235. (b) Choi, Y.-K.; Chjo, K.-H.; Park, S.-M. *J. Electroanal. Chem.* **1995**, *142*, 4107–4112. (c) Archer, R. D.; Chen, H. *Inorg. Chem.* **1998**, *37*, 2089–2095. (d) Li, Z.; Jablonski, C. *Inorg. Chem.* **2000**, *39*, 2456–2461. (e) Shimakoshi, H.; Goto, A.; Tachi, Y.; Naruta, Y.; Hisaeda, Y. *Tetrahedron Lett.* **2001**, *42*, 1949–1951. (f) Shimakoshi, H.; Ninomiya, W.; Hisaeda, Y. *Dalton Trans.* **2001**, 1971–1974. (g) Pike, J. D.; Rosa, D. T.; Coucouvanis, D. *Eur. J. Inorg. Chem.* **2001**, 761–777. (h) Shimakoshi, H.; Takemoto, H.; Aritome, I.; Hisaeda, Y. *Tetrahedron Lett.* **2001**, *42*, 4809–4812. (i) Ready, J. M.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2002**, *41*, 1374–1377. (j) Fontecha, J. B.; Goetz, S.; Mckee, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 4553–4556. (k) Shimakoshi, H.; Kaieda, T.; Matsuo, T.; Sato, H.; Hisaeda, Y. *Tetrahedron Lett.* **2003**, *44*, 5197–5199. (l) Ma, C.; Lo, A.; Abdolmaleki, A.; MacLachlan, M. J. *Org. Lett.* **2004**, *6*, 3841–3844. (m) Fontecha, J. B.; Goetz, S.; Mckee, V. *Dalton Trans.* **2005**, 923–929. (n) Glaser, T.; Heidemeier, M.; Fröhlich, R.; Hildebrandt, P.; Bothe, E.; Bill, E. *Inorg. Chem.* **2005**, *44*, 5467–5482. (o) MacLachlan, M. J. *Pure Appl. Chem.* **2006**, *78*, 873–888. (p) Curreli, S.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. W. *J. Org. Chem.* **2007**, *72*, 7018–7021.

- (25) The Nabeshima group reported the oxime-type N_2O_2 ligand: (a) Akine, S.; Taniguchi, T.; Saiki, T.; Nabeshima, T. *J. Am. Chem. Soc.* **2005**, *127*, 540–541. (b) Akine, S.; Taniguchi, T.; Nabeshima, T. *J. Am. Chem. Soc.* **2006**, *128*, 15765–15744. (c) Akine, S.; Sunaga, Shunichi; Taniguchi, T.; Miyazaki, H.; Nabeshima, T. *Inorg. Chem.* **2007**, *46*, 2959–2961. (d) Akine, S.; Kagiya, S.; Nabeshima, T. *Inorg. Chem.* **2007**, *46*, 9525–9527. (e) Akine, S.; Akimoto, A.; Shiga, T.; Oshio, H.; Nabeshima, T. *Inorg. Chem.* **2008**, *47*, 875–885. (f) Akine, S.; Taniguchi, T.; Nabeshima, T. *Inorg. Chem.* **2008**, *47*, 3255.

Scheme 2. Redox Responsive Structural Change in Dicobalt Complex



shown in Figure 2. A scan in the positive direction at 0 V versus Ag/AgCl revealed no oxidative wave, while a scan in the negative direction revealed a first reduction wave at -0.57 V versus Ag/AgCl, which is due to process i.

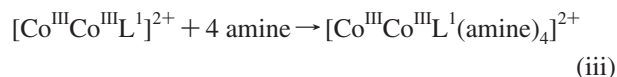


The reduction of the Co(III) complex results in the loss of its axial ligands in weakly coordinating solvents because the electron is added to the antibonding d_{z^2} orbital.²⁶ The second and third reduction potentials due to the Co(II)-Co(II)/Co(II)Co(I) and Co(II)Co(I)/Co(I)Co(I) couples shows reversible behavior at -1.07 and -1.29 V versus Ag/AgCl. In the reversible scan direction, the thus-formed four-coordinate Co(II)Co(II) complex is reoxidized to Co(III)Co(III) at $+0.16$ V versus Ag/AgCl, which has

much higher potentials due to the absence of a donating axial amine at both cobalt centers (process ii).



In a rapid consecutive reaction (coordination of amine, process iii), the six-coordinate complex with a bis-crown structure will then be reformed.



In this way, the irreversible Co(III)/Co(II) redox couple is accompanied by the dissociation of the axial amine in **1**.¹⁶

Next, the CV of **1** was measured in the presence of KClO_4 . The irreversible wave due to process i was positively shifted to -0.49 V versus Ag/AgCl, and all of the other peaks were not changed, as shown in Figure 2. The potassium ion binding site only existed in the initial $[\text{Co}_2\text{L}^1(\text{amine})_4]^{2+}$, and the reduction potential of Co(III) is affected by the axial ligand in the order of changes in its donating ability.²⁷ The binding of the potassium ion at the crown moiety may cause such a perturbation.²⁸ According to the CV study, complex **1** works as a potassium ion receptor using its bis-crown sites and irreversible Co(III)/Co(II) redox couple even in the potassium binding form of **1**, indicating the redox-switchable

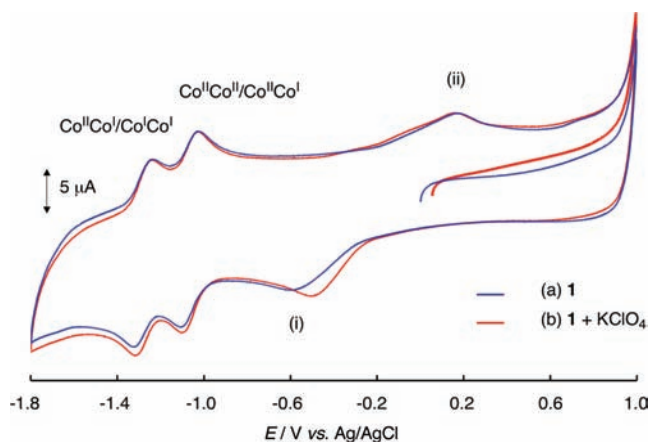


Figure 2. Cyclic voltammogram of **1** (5.0×10^{-4} M) in DMF containing 1×10^{-1} M $n\text{-Bu}_4\text{NClO}_4$ at 25°C (a), $+5 \times 10^{-3}$ M KClO_4 (b); sweep rate = 100 mV s^{-1} .

(26) Böttcher, A.; Takeuchi, T.; Hardcastle, K. I.; Meade, T. J.; Gray, H. B.; Cwikel, D.; Kapon, M.; Dori, Z. *Inorg. Chem.* **1997**, *36*, 2498–2504.

(27) (a) Amirnasr, M.; Vafazadeh, R.; Mahmoudkhani, A. H. *Can. J. Chem.* **2002**, *80*, 1196–1203. (b) Khandar, A. A.; Shrouz, B.; Belaj, F.; Bakhtiari, A. *Polyhedron* **2006**, *25*, 1893–1900.

(28) The shoulder peak in spectrum b around 0 V versus Ag/AgCl may be ascribed to Co(III)Co(III)/Co(II)Co(II) redox couples for amine-coordinated dicobalt complex since binding of the potassium ion changed the monodentate 4-aminomethylbenzo-15-crown-5 into bidentate pseudo-diamine. The binding constant of diamine to the Co(II)Co(II) complex may be increased so that part of complex exists as amine coordinated species.

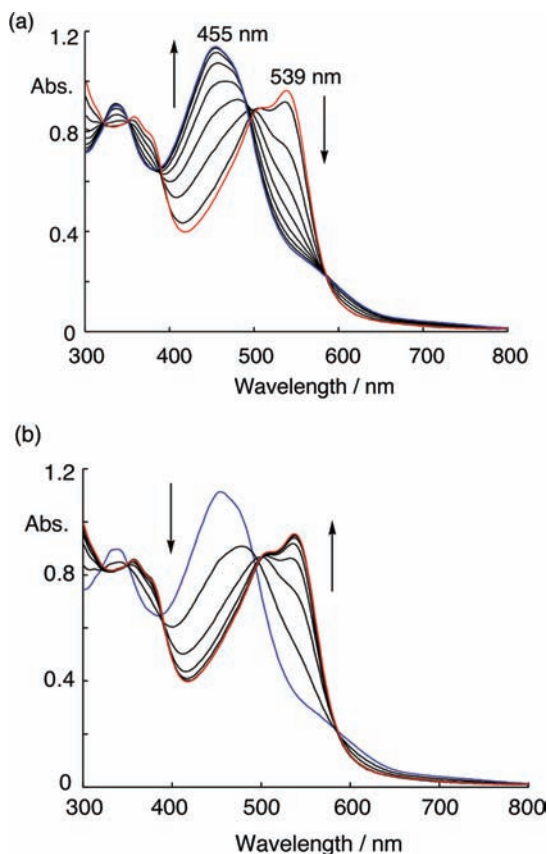


Figure 3. Electronic spectra observed during electrolysis of a DMF solution containing **1** (5.0×10^{-4} M) and $n\text{-Bu}_4\text{NClO}_4$ (1.0×10^{-1} M): at -0.50 V vs Ag/AgCl (a); $+0.20$ V vs Ag/AgCl (b).

structural transformation accompanied by a change in the potassium ion binding behavior, as shown in Scheme 2.

These structural changes were followed by UV-vis spectroscopy. Complex **1** shows a characteristic UV-vis spectrum at 357, 379, 505, and 539 nm in DMF. During electrolysis at -0.5 V versus Ag/AgCl, the spectrum was changed to a new spectrum with four isobestic points at 322, 349, 388, and 585 nm, as shown in Figure 3a. The final spectrum showed absorption maxima at 336, 455, 477, and 573_{sh} nm, which were characteristic of those of the Co(II)-Co(II) complex **3** in DMF. After electrolysis at -0.5 V versus Ag/AgCl, the potential was subsequently changed to $+0.2$ V versus Ag/AgCl. The spectrum was changed to the starting one with the same isobestic points, as shown in Figure 3b. The recovered species was characterized by a CSI-MS analysis as an original Co(III)Co(III) complex having double bis-crown moieties. These reversible changes were repeated four times without decomposition of the complex, as shown in Figure 4.

NMR and CSI-MS Studies for K^+ Binding. The binding of the potassium ion by **1** was examined using a ^1H NMR spectral titration. The chemical shifts of the various protons in **1** are affected by the addition of KPF_6 , as shown in Figure 5. To clarify the characteristics of this complex formation, we carried out a Job plot experiment. As shown in Figure 6, the Job plot demonstrates the 1:1 complex formation between **1** and the potassium ion. It should be noted that a clear 1:1 stoichiometry is observed, even though the present complex,

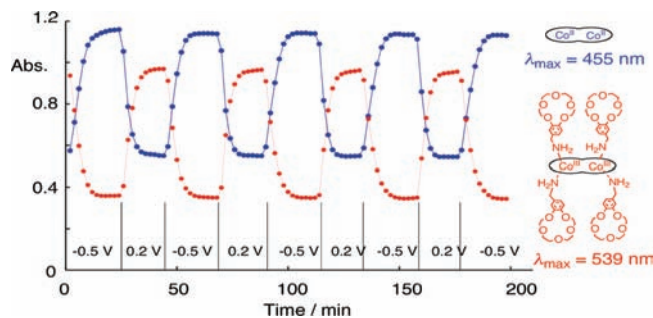


Figure 4. Time course of the absorbance changes in **1** (5.0×10^{-4} M) at 455 and 539 nm in DMF during redox switches between -0.5 V vs Ag/AgCl and $+0.2$ V vs Ag/AgCl.

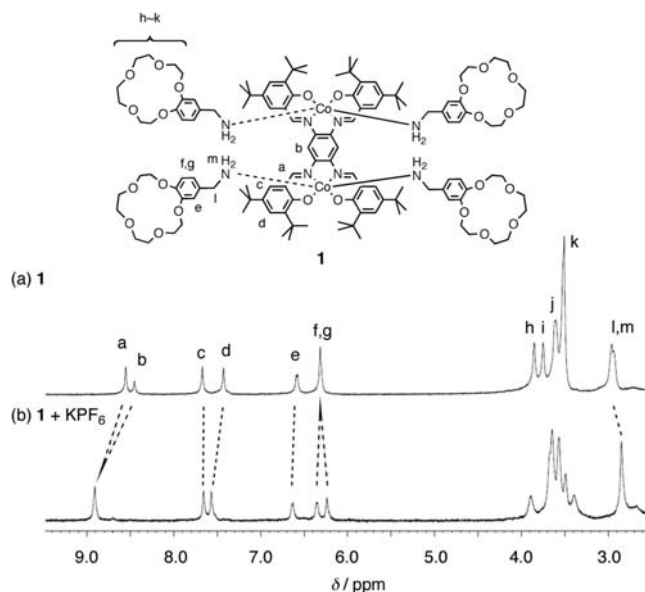


Figure 5. Partial ^1H NMR spectra during titration of **1** (2.0×10^{-3} M) with 100 equiv mol of KPF_6 in CD_3CN at 25°C .

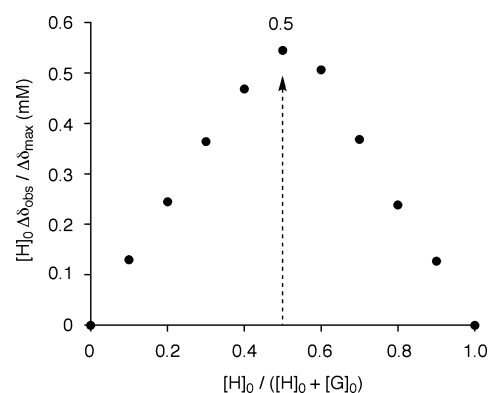


Figure 6. Job plot for **1**· K^+ complex formation in CD_3CN at 25°C .

1, has two binding sites of bis-crown moieties. The association constant (K) was determined by NMR titration using the nonlinear curve fitting method, as shown in Figure S3 (Supporting Information). The bis-crown moieties of **1** worked as potassium ion binding sites, with the high association constant ($K_{1:1}$) of $1.97 \times 10^5 \text{ M}^{-1}$ ($\log K = 4.29$) probably caused by the preorganized bis-crown structure. The K value is considerably greater than those of the reported crown compounds such as benzo-15-crown-5 and 4-acetylbenzo-15-crown-5 in the same solvent at 25°C as $\log K$

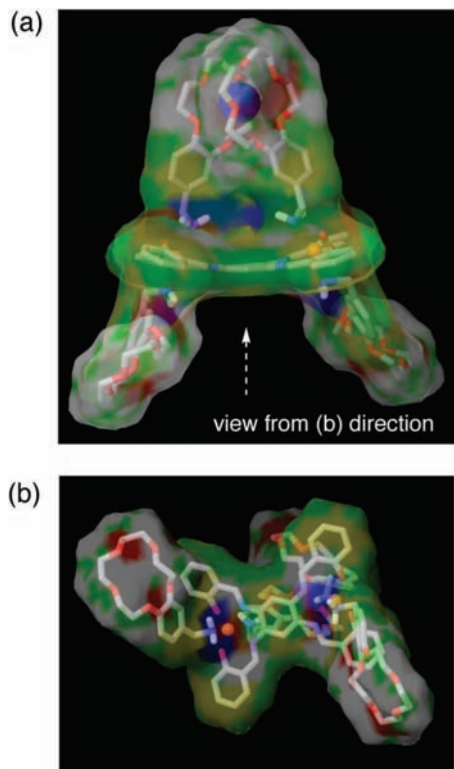


Figure 7. Energy-optimized structure (MM2 force field) of potassium ion binding of **1** with simulated electrostatic potentials. The negative and positive regions are red and blue, respectively, and the neutral region is white.

values of 2.77 and 2.96, respectively.²⁹ Preorganization of the cleftlike structure of the bis-crown moiety should be suitable for guest binding. The CSI-MS analysis also supported the 1:1 binding with **1**. The CSI-MS showed an intense peak at m/z 781.38 ascribed to $[\text{Co}_2\text{L}^1(\text{amine})_4\text{K}]^{3+}$ with satisfied isotope patterns, as shown in Figure S2 (Supporting Information).

On the basis of the molecular mechanics study of the potassium ion binding structure of **1**, followed by a molecular dynamics simulation,³⁰ the 1:1 complex showed a warp structure with platform L^1 bending in the same direction for the potassium binding site. Due to this structural change with the first potassium ion binding, the opposite bis-crown moiety may be opened to its cleft structure, as shown in Figure 7; hence, it may depress the second ion binding.

Solvent Extraction of K^+ with **1.** The binding ability of **1** was also examined by the solvent extraction of potassium picrate from water to chloroform. An absorbance at 356 nm ascribed to the picrate ion in water decreased with three equivalent moles of **1** in the chloroform layer after solvent extraction, as shown in Figure S4 (Supporting Information). Presumably, one of the three picrates was extracted by complexation with **1** at the bis-crown site as potassium picrate, and two of the three picrates were extracted into the chloroform layer by anion exchange of the complex, as shown in Figure 8. Indeed, the IR bands at 845 and 558 cm^{-1} ascribed to the PF_6^- counteranion of **1** disappeared,

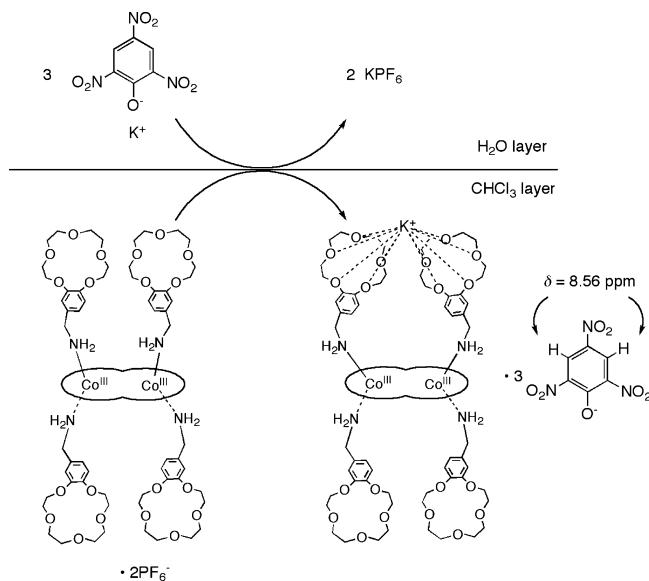


Figure 8. Schematic representation of potassium extraction with **1**.

Table 1. Extraction of Potassium Salts by Various Extracting Reagents^a

extracting reagent (concentration, mM)	$[\text{K}^+]_{\text{after}}/\text{mM}^b$	K^+ extracted (% Ex) ^c
1 (0.65)	3.39	94
2 (0.65)	3.92	12
3 (0.65)	3.93	11
benzo-15-crown-5 (2.60)	3.86	21

^a [potassium picrate] = 4.0 mM; solvent, 1 mL of 1:1 CHCl_3 – H_2O v/v at 20 °C. ^b Concentration of K^+ in H_2O layer after extraction. ^c Calculated by the equation, $\text{Ex} = \{(4.0 - [\text{K}^+]_{\text{after}})/0.65\} \times 100$.

and new bands at 1312 and 1268 cm^{-1} assignable to the $\text{N}=\text{O}$ vibrations of the picrate appeared after the solvent extraction, as shown in Figure S5 (Supporting Information). From the UV–vis and IR studies, one equivalent mole of potassium ions was extracted by **1**.

The amount of potassium ions was also directly determined using an atomic absorption/flame emission spectrophotometer. These results are summarized in Table 1. Referenced complexes **2** and **3** (Chart 2) without the crown moiety extracted few if any potassium ions. The benzo-15-crown-5 extracted only 21% of the potassium ions reflected by its small association constant²⁹ compared to that of **1**, where 94% of the potassium ions assuming a 1:1 complexation were extracted in the organic layer.

Conclusions

The redox-switchable dicobalt complex having double bis-crown moieties consisting of the 4'-aminomethylbenzo-15-crown 5-ether has been prepared in high yield. The CV and UV–vis spectroelectrochemical experiments showed the reversible coordination/dissociation of the 4'-aminomethylbenzo-15-crown 5-ether to the cobalt centers in response to an external stimulus, that is, electrical energy, when the applied potential was changed between -0.5 V and $+0.2$ V versus Ag/AgCl . Due to the geometric change in the cobalt complex caused by changing the cobalt oxidation state at the above potentials, a redox-switchable supramolecular complex having the double bis-crown moieties was constructed. The ^1H NMR, UV–vis, IR, and CSI-MS studies

(29) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721–2085.

(30) The calculations were carried out using the MacroModel 9.1 software.

revealed that the complex binds one equivalent mole of potassium ions with a high binding constant (K) due to its preferable bis-crown structure. The concept for this crown-assembled approach to molecular recognition is demonstrated for the first time. We are presently exploring this concept in regard to various applications, such as carriers, sensors, and catalysts.

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Note Added after Print Publication. Due to a production error, Scheme 1 was a duplicate of Scheme 2 in the version posted on the Web January 9, 2009 (ASAP) and published in the February 2, 2009, issue (Vol. 48, No. 3, pp 1045–1052); the correct electronic version of the paper was published on March 30, 2009, and an Addition & Correction appears in the April 6, 2009, issue (Vol. 48, No. 7).

Supporting Information Available: Additional graphs, UV–vis, CSI-mass, and IR spectra for the potassium binding of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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