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Synthesis and Redox Behavior of Dicobalt Complexes Having Flexible and Rigid Linkers

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New dicobalt complexes, [Co^{II}_2**L**], with Schiff-base ligands (**L1**–**L4**) having two discrete metal chelating sites, which are connected to each other by flexible and rigid linkers, have been synthesized. The complexes were characterized by IR, UV–vis, and mass spectroscopy as well as elemental analyses. A magnetic study indicates an antiferromagnetic interaction in **4**. The redox behavior of the complexes was examined by means of cyclic voltammetry compared with those of the corresponding mononuclear complexes. Redox waves, identified to Co^{III}/Co^{II} and Co^{II}/Co^{I}, were clearly observed. Electro-generated [Co^{I}_2**L**]$^{2-}$ reacts with alkyl halide at each metal center to give an organocobalt complex.

The recent growth of studies on multi-metallic compounds involves the areas of homogeneous catalysis, magnetic exchange between paramagnetic centers, and bioinorganic chemistry.[1–7] Molecular systems having two (or more) redox active centers in close proximity, capable of cooperative interactions, are of interest in relation to their potential as catalysts for substrate reduction or oxidation.[8] Considerable effort has thus been directed towards the synthesis of a ligand capable of holding two separated metal ions, either the same or different, which are subject to control by an appropriate modification of the molecular topology.[9,10] Recently, we synthesized a dinucleating ligand in which two H_2salen units, H_2salen is a *N*,*N*′-ethylenebis(salicylideneamine), are covalently linked together so as to bring two bound metal centers into close proximity.[11,12] The corresponding dicobalt complex of this ligand formed a cobalt–carbon bond at each metal center, and cleavage of this bond afforded a coupling product via radical coupling. In this ligand, the connecting linker is limited to methylene, and the distance and geometry of two metal centers are limited. Thus, in this paper, we report on the synthesis of new dicobalt complexes that have a [Co^{II}(saloph)] unit connected to each other with various linkers, as shown in Chart 1. The redox behavior of dicobalt complexes and the reactivities of the electrogenerated $Co^{I}Co^{I}$ species toward alkyl halide were investigated.

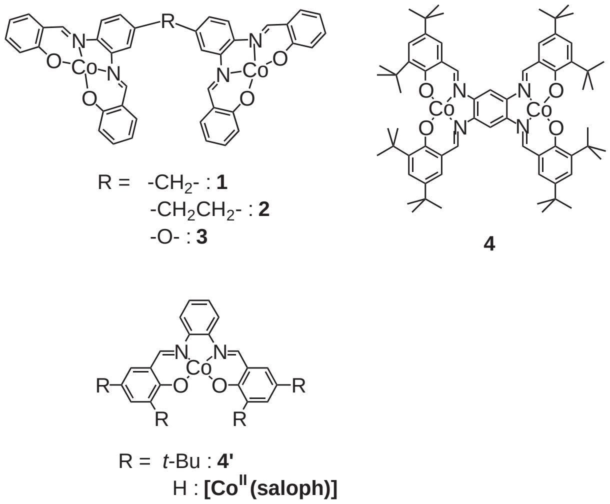

Chart 1.

Experimental

Materials. All solvents and chemicals used in the synthesis were of reagent grade, and were used without further purification. For electrochemical studies, *N*,*N*-dimetylformamide (DMF) was stirred for one day in the presence of BaO under a nitrogen atmosphere, and distilled under reduced pressure. The distillation was performed with the exclusion of light, and thus-purified DMF was stored in a refrigerator under a nitrogen atmosphere in the presence of activated molecular sieves 4A. Care was taken to remove basic impurities that coordinate to the Co^{III} species and cause additional reduction peaks in the voltammograms.[13] Tetrabutylammonium perchlorate (n-Bu_4NClO_4) was purchased from Nakalai tesque (special grade) and dried at room temperature under vacuum before use. 3,3′,4,4′-Tetraaminodiphenylmethane, 1,2-(3,3′,4,4′-tetraaminodiphenyl)ethane, and 3,3′,4,4′-tetraaminodiphenylether were synthesized by a reported method.[14] [Co^{II}(saloph)], saloph, which is a dianion of *N*,*N*′-(*o*-phenylenediamine)bis(salicylideneamine), was synthesized by a reported method.[15]

General Analyses and Measurements. Elemental analyses were obtained from the Service Center of Elementary Analysis of Organic Compounds at Kyushu University. The ^{1}H,^{13}C, and

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2-D COSY-NMR spectra were recorded on a Bruker Avance 500 spectrometer installed at the Center of Advanced Instrumental Analysis in Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. The UV–vis absorption spectra were measured on a Hitachi U-3300 spectrophotometer at room temperature. The FAB-mass spectra were obtained on a JEOL JMS-HX110A using *m*-nitrobenzylalcohol as a matrix. The IR spectra were recorded on a JASCO IR-810 spectrophotometer using KBr discs.

Solid State Susceptibility Measurement. The magnetic susceptibilities of powdered samples were measured on a Quantum Design MPMS XL SQUID susceptometer in the temperature range of 2–300 K; the apparatus was calibrated with $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine).[16] Effective magnetic moments (μ_{eff}) were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}}T)^{1/2}$, where χ_{M} is the molar magnetic susceptibility per molecule. The data were corrected for the sample holder contribution and for the diamagnetic contribution estimated through Pascal's constant.[17]

Cyclic Voltammetry. Cyclic voltammograms were obtained using a BAS CV 50 W electrochemical analyzer. A three-electrode cell equipped with a 1.6-mm diameter platinum wire as the working and counter electrodes were used, respectively. An Ag–AgCl (3.0 mol dm^{-3} NaCl) electrode served as a reference. Nonaqueous DMF solutions containing a cobalt complex (5.0×10^{-4} mol dm^{-3}) and *n*-Bu_4NClO_4 (1.0×10^{-1} mol dm^{-3}) were deaerated prior to each measurement, and the inside of the cell was maintained under an argon atmosphere throughout each measurement. All measurements were carried out at 298 K. The scan rate was varied over the range from 10 through 500 mV s^{-1}. The $E_{1/2}$ value of ferrocene/ferrocenium (Fc/Fc^{+}) was +0.56 V vs Ag–AgCl with this setup.

Synthesis of L1. To a solution of 3,3′,4,4′-tetraaminodiphenylmethane (46 mg, 0.2 mmol) in 2 mL of ethanol and 1 mL of chloroform was slowly added a salicylaldehyde (488 mg, 4 mmol) in 1 mL of ethanol; a yellow precipitate appeared during stirring for 3 h, which was allowed to stand in a refrigerator for 1 h. The precipitates were collected by filtration, washed by cold ethanol and dried in vacuo. Yield: 88%. Anal. found: C, 76.11; H, 5.00; N, 8.55%. calcd for $C_{41}H_{32}N_4O_4$: C, 76.38; H, 5.00; N, 8.69%. IR [KBr; ν/cm^{-1}]: 3450 (br, OH), 2950 (s, CH), 1620 (s, C=N), and 1175 (s, C–O). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.12 (2H, s, CH_2), 6.91 (4H, m, Ph), 7.04 (4H, dd, Ph), 7.08 (2H, s, Ph), 7.21 (4H, s, Ph), 7.37 (8H, m, Ph), 8.61 (2H, s, N=C$\underline{\mathrm{H}}$), 8.64 (2H, s, N=C$\underline{\mathrm{H}}$), 13.02 (2H, s, OH), 13.07 (2H, s, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 41.1 (–CH_2–), 117.6, 117.7, 119.0, 119.1, 119.2, 119.3, 119.9, 120.4, 128.1, 132.3, 132.4, 133.3, 133.5, 140.4, 140.8, 142.9 (Ph), 161.3, 161.4 (N=$\underline{\mathrm{C}}$H), 163.4, 164.0 (PhO). HRMS (FAB, *m*/*z*): Calcd for $C_{41}H_{33}N_4O_4$: [MH]$^{+}$, 645.2502. Found: [MH]$^{+}$, 645.2494.

Synthesis of 1. All procedures were carried out using a standard Schlenk apparatus to avoid oxidation by atmospheric dioxygen. To a solution of **L1** (64 mg, 0.1 mmol) in 10 mL of chloroform was dropwise added $Co(OAc)_2 \cdot 4H_2O$ (55 mg, 0.22 mmol) in 10 mL of ethanol. A brown solid was precipitated immediately and the mixture was stirred at 70 °C. After 3 h, the solid was collected by filtration, washed by ethanol and a small amount of chloroform, and dried in vacuo. Yield: 89%. Anal. found: C, 61.59; H, 4.03; N, 7.01%. calcd for $C_{41}H_{28}N_4O_4Co_2 \cdot 2H_2O$: C, 61.98; H, 4.06; N, 7.05%. IR [KBr; ν/cm^{-1}]: 2950 (s, CH), 1580 (s, C=N), and 1180 (s, C–O); HRMS (FAB, *m*/*z*): Calcd for $C_{41}H_{28}N_4O_4Co_2$: [M]$^{+}$, 758.0775. Found: [M]$^{+}$, 758.0787; UV–vis (in DMF): [$\lambda_{\max}$/nm (ε/M^{-1} cm^{-1})], 307 (49300), 341 (33700), 390 (44000).

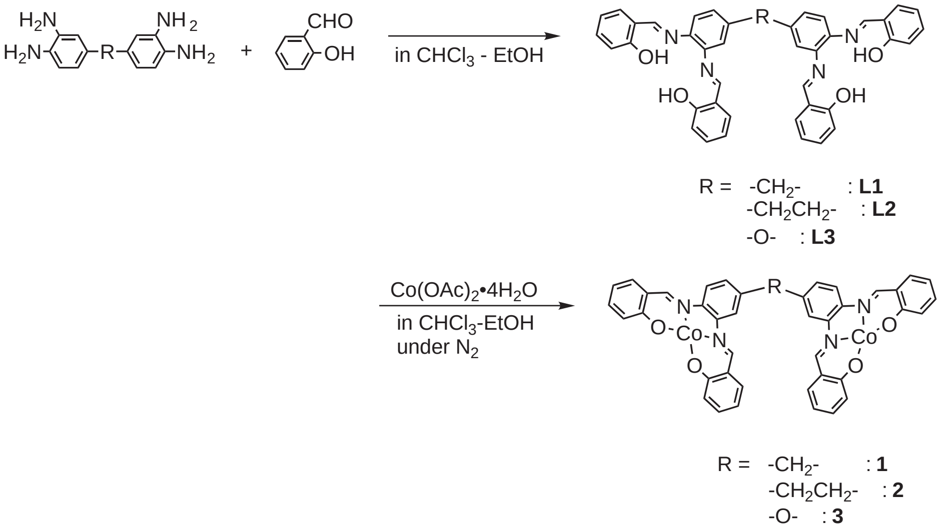
Synthesis of L2. **L2** was synthesized in the same manner as for **L1**, except for use of 3,3′,4,4′-tetraaminodiphenylethane in place of 3,3′,4,4′-tetraaminodiphenylmethane. Yield: 84%. Anal. found: C, 76.51; H, 5.24; N, 8.45%. calcd for $C_{42}H_{34}N_4O_4$: C, 76.58; H, 5.20; N, 8.51%. IR [KBr; ν/cm^{-1}]: 3450 (br, OH), 2950 (s, CH), 1620 (s, C=N), and 1175 (s, C–O); ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ 3.05 (4H, s, –CH_2CH_2–), 6.95 (8H, m, Ph), 7.30 (2H, dd, Ph), 7.39 (8H, m, Ph), 7.63 (4H, dd, Ph) 8.88 (2H, s, N=C$\underline{\mathrm{H}}$), 8.94 (2H, s, N=C$\underline{\mathrm{H}}$), 12.93 (2H, s, OH), 13.06 (2H, s, OH); ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ 36.5 (–CH_2CH_2–), 116.6, 116.7, 119.0, 119.1, 119.4, 119.5, 119.6, 119.8, 127.9, 132.3, 132.4, 133.3, 133.4, 140.0, 141.5, 142.3 (Ph), 160.4, 160.5 (N=$\underline{\mathrm{C}}$H), 163.3, 163.9 (PhO). HRMS (FAB, *m*/*z*): Calcd for $C_{42}H_{35}N_4O_4$: [MH]$^{+}$, 659.2658. Found: [MH]$^{+}$, 659.2662.

Synthesis of 2. **2** was synthesized in the same manner as for **1**, except for use of **L2** in place of **L1**. Yield: 94%. Anal. found: C, 62.87; H, 3.94; N, 6.92%. calcd for $C_{42}H_{30}N_4O_4Co_2 \cdot 2H_2O$: C, 62.39; H, 4.24; N, 6.93%. IR [KBr; ν/cm^{-1}]: 2950 (s, CH), 1580 (s, C=N), and 1180 (s, C–O). HRMS (FAB, *m*/*z*): Calcd for $C_{42}H_{30}N_4O_4Co_2$: [M]$^{+}$, 772.0931. Found: [M]$^{+}$, 772.0955. UV–vis (in DMF): [$\lambda_{\max}$/nm (ε/M^{-1} cm^{-1})], 307 (42800), 337 (32600), 391 (39800).

Synthesis of L3. **L3** was synthesized in the same manner as for **L1**, except for use of 3,3′,4,4′-tetraaminodiphenylether in place of 3,3′,4,4′-tetraaminodiphenylmethane. Yield: 91%. Anal. found: C, 74.02; H, 4.67; N, 8.50%. calcd for $C_{40}H_{30}N_4O_5$: C, 74.29; H, 4.68; N, 8.66%. IR [KBr; ν/cm^{-1}]: 3450 (br, OH), 1615 (s, C=N), and 1180 (s, C–O). ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ 6.95 (8H, m, Ph), 7.12 (2H, dd, Ph), 7.29 (2H, d, Ph), 7.40 (4H, q, Ph), 7.56 (2H, d, Ph), 7.66 (4H, t, Ph), 8.94 (2H, s, N=C$\underline{\mathrm{H}}$), 8.95 (2H, s, N=C$\underline{\mathrm{H}}$), 12.75 (2H, s, OH), 12.98 (2H, s, OH); ^{13}C NMR (DMSO-*d*$_6$, 125 MHz): δ 110.2, 116.6, 116.7, 117.6, 119.1, 119.2, 119.5, 119.6, 120.9, 132.4, 132.5, 133.3, 133.6, 138.0, 144.0, 156.0 (Ph), 160.3, 160.4 (N=$\underline{\mathrm{C}}$H), 163.2, 164.7 (PhO). HRMS (FAB, *m*/*z*): Calcd for $C_{40}H_{31}N_4O_5$: [MH]$^{+}$, 647.2294. Found: [MH]$^{+}$, 647.2313.

Synthesis of 3. **3** was synthesized in the same manner as for **1**, except for use of **L3** in place of **L1**. Yield: 88%. Anal. found: C, 62.11; H, 3.41; N, 7.23%; calcd for $C_{40}H_{26}N_4O_5Co_2 \cdot 1H_2O$: C, 61.71; H, 3.62; N, 7.20%. IR [KBr; ν/cm^{-1}]: 2950 (s, CH), 1580 (s, C=N), and 1180 (s, C–O). HRMS (FAB, *m*/*z*): Calcd for $C_{40}H_{26}N_4O_5Co_2$: [M]$^{+}$, 760.0567. Found: [M]$^{+}$, 760.0568. UV–vis (in DMF): [$\lambda_{\max}$/nm (ε/M^{-1} cm^{-1})], 307 (45500), 338 (35000), 393 (44500).

Synthesis of L4. To a suspension of 1,2,4,5-tetraaminobenzene$\cdot$4HCl (224 mg, 0.8 mmol) in 20 mL of pyridine was slowly added 3,5-di-*tert*-butylsalicylaldehyde (1.48 g, 6.3 mmol) in 10 mL of ethanol; the reaction mixture was stirred for 1 h. The precipitates were collected by filtration, washed by cold ethanol and dried in vacuo to give a yellow solid. Yield: 66%. Anal. found: C, 78.90; H, 9.08; N, 5.56%. calcd for $C_{66}H_{90}N_4O_4$: C, 79.00; H, 9.04; N, 5.58%. IR [KBr; ν/cm^{-1}]: 3450 (br, OH), 2950 (s, CH), 1610 (s, C=N), and 1170 (s, C–O). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.34(36H, s, *t*-butyl), 1.45 (36H, s, *t*-butyl), 7.26 (2H, s, Ph), 7.32 (4H, d, Ph), 7.49 (4H, d, Ph), 8.83 (4H, s, N=C$\underline{\mathrm{H}}$), 13.54 (4H, s, OH); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 29.7 (–C($\underline{\mathrm{C}}H_3$)), 31.7 (–C($\underline{\mathrm{C}}H_3$)), 34.6 (–$\underline{\mathrm{C}}$($CH_3$)), 35.5 (–$\underline{\mathrm{C}}$($CH_3$)), 111.4, 119.0, 127.6, 129.1, 137.6, 141.3, 142.2 (Ph), 159.0 (N=$\underline{\mathrm{C}}$H), 165.3 (PhO). HRMS (FAB, *m*/*z*): Calcd for



Scheme 1.

$C_{66}H_{91}N_4O_4$: $[MH]^+$, 1003.7040. Found: $[MH]^+$, 1003.7026.

Synthesis of 4. All procedures were carried out using a standard Schlenk apparatus to avoid oxidation by atmospheric dioxygen. To a solution of **L4** (150 mg, 0.15 mmol) in 20 mL of chloroform was added dropwise $Co(OAc)_2 \cdot 4H_2O$ (92 mg, 0.37 mmol) in 10 mL of ethanol. A brown solid was precipitated immediately, and the mixture was stirred at room temperature. After 1 h, the solid was collected by filtration, washed by a small amount of cold methanol, chloroform, and dried in vacuo. A microcrystal was obtained by recrystallization from diethylether/acetonitrile. Yield: 84%. Anal. found: C, 70.73; H, 7.63; N, 4.99%. calcd for $C_{66}H_{86}N_4O_4Co_2$: C, 70.95; H, 7.76; N, 5.01%. IR [KBr; ν/cm^{-1}]: 2950 (s, CH), 1580 (s, C=N), and 1180 (s, C–O). HRMS (FAB, *m*/*z*): Calcd for $C_{66}H_{86}N_4O_4Co_2$: $[M]^+$, 1116.5313. Found: $[M]^+$, 1116.5311. UV–vis (in $CHCl_3$): [λ_{max}/nm (ε/M^{-1} cm^{-1})], 337 (46200), 348 (44700), 464 (70700), 481 (69900), 573 (sh, 15300).

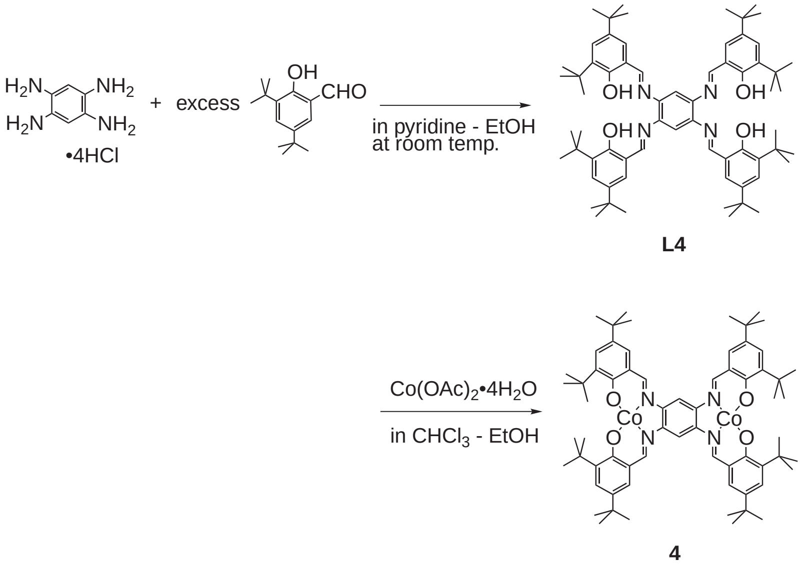
Synthesis of L4′. To a solution of *o*-phenylenediamine (246 mg, 1.05 mmol) in 5 mL of ethanol was slowly added 3,5-di-*tert*-butylsalicylaldehyde (54 mg, 0.5 mmol) in 5 mL of ethanol; a yellow precipitate appeared during stirring for 1 day, which was then allowed to stand in a refrigerator for 6 h. The precipitates were collected by filtration, washed by cold ethanol and dried in vacuo. Yield: 50%. Anal. found: C, 79.79; H, 8.86; N, 5.22%. calcd for $C_{36}H_{48}N_2O_2$: C, 79.96; H, 8.95; N, 5.18%. IR [KBr; ν/cm^{-1}]: 3450 (br, OH), 2950 (s, CH), 1620 (s, C=N), and 1175 (s, C–O). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.34 (36H, s, *t*-butyl), 1.45 (36H, s, *t*-butyl), 7.26 (2H, s, Ph), 7.32 (4H, d, Ph), 7.49 (4H, d, Ph), 8.83 (4H, s, N=C$\underline{H}$), 13.54 (4H, s, OH); ^{13}C NMR(CD_2Cl_2, 125 MHz): δ 29.7 ($-C(\underline{C}H_3)_3$), 31.7 ($-C(\underline{C}H_3)_3$), 34.6 ($-\underline{C}(CH_3)_3$), 35.5 ($-\underline{C}(CH_3)_3$), 111.4, 119.0, 127.6, 129.1, 137.6, 141.3, 142.2 (Ph), 159.0 (N=$\underline{C}$H), 165.3 (PhO). MS (FAB, *m*/*z*): $[MH]^+$, 541.7.

Synthesis of 4′. All procedures were carried out using a standard Schlenk apparatus to avoid oxidation by atmospheric dioxygen. To a solution of **L4′** (43 mg, 0.08 mmol) in 10 mL of chloroform was added dropwise $Co(OAc)_2 \cdot 4H_2O$ (22 mg, 0.09 mmol) in 10 mL of ethanol. A brown solid was precipitated immediately, and the mixture was stirred at room temperature. After 3 h, the precipitates were collected by filtration, washed by a small amount of ethanol and dried in vacuo. Yield: 76%. Anal. found: C, 72.40; H, 7.73; N, 4.68%. calcd for $C_{36}H_{46}N_2O_2Co_1$: C, 72.34; H, 7.76; N, 4.69%. IR [KBr; ν/cm^{-1}]: 2950 (s, CH), 1580 (s, C=N), and 1180 (s, C–O). MS (FAB, *m*/*z*): $[M]^+$, 597.3. UV–vis (in $CHCl_3$): [λ_{max}/nm (ε/M^{-1} cm^{-1})], 312 (23700), 411 (18900), 457 (sh, 14200), 542 (5800), 587 (3400).

Results and Discussion

Syntheses of Ligands and Dicobalt Complexes. Dinucleating ligands, (**L1**, **L2**, and **L3**) were effectively synthesized by similar methods reported previously, as shown in Scheme 1.[18] The dinucleating ligand **L4** was also synthesized by the reaction of commercial 1,2,4,5-tetraaminobenzene and 3,5-di-*tert*-butylsalicylaldehyde in pyridine, as shown in Scheme 2.[19] The free-base form of 1,2,4,5-tetraaminobenzene was very sensitive to air, and was used as a hydrochloride salt. A desirable product was obtained under aerobic condition within 1 h when pyridine was used as a solvent. These ligands afforded a stable dicobalt complex in the reaction of cobalt acetate under a nitrogen atmosphere at high yields. Satisfactory elemental analyses and high-resolution FAB-mass spectra were obtained for these complexes.

Magnetic Properties of Dicobalt Complexes. The magnetic susceptibilities of complexes **2** and **4** were determined over the temperature range of 2 K–300 K. Plots of the molar susceptibility (χ_M) and the effective magnetic moment (μ_{eff}), per Co atom, as a function of the temperature for **2** and **4** are shown in Figs. 1a and 1b, respectively. The dicobalt complex **2**, which contains a flexible ethylene linker, has a magnetic moment of 2.85 μ_B at 300 K. This value is in the range of values expected for a non-interacted low spin Co^{II} ion. The moment monotonously decreased with decreasing temperature to 2.46 μ_B at 2 K, due to temperature-independent paramagnetism (N_α) associated with the Co^{II} ion. In the case of **4**, the susceptibility curves showed rounded maxima at 18 K, whereas those of μ_{eff} exhibited a continuous decrease upon cooling from $\mu_{eff} = 2.28$ μ_B/Co at 300 K, as shown in Fig. 1b. The occurrence of maxima in χ_M is indicative of the existence of antiferromagnetic coupling between the paramagnetic cobalt centers.[20] The variable temperature data was thus fitted



Scheme 2.

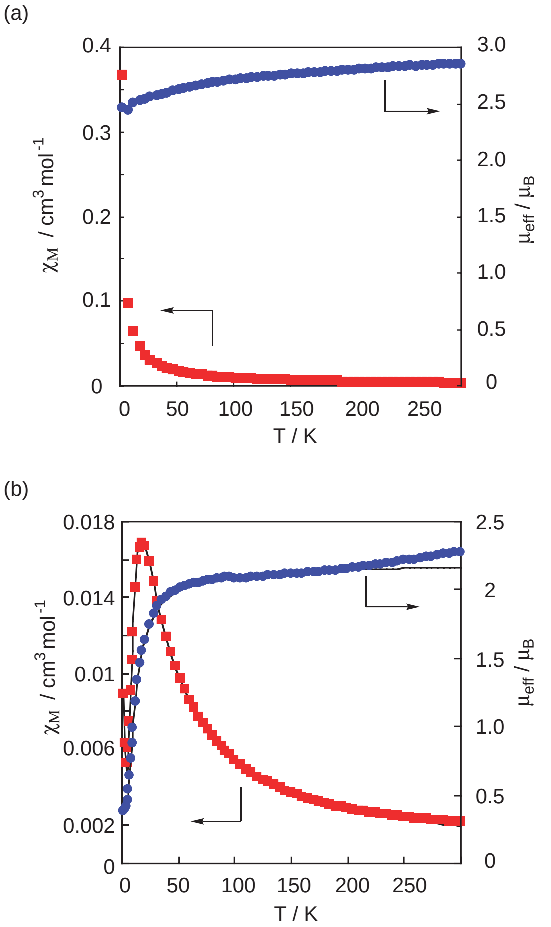


Fig. 1. Temperature dependences of the magnetic susceptibility (■) and effective magnetic moment (●) of (a) **2** and (b) **4** under 500 G.

to the Bleaney–Bowers equation[21] (Eq. 1), using the Heisenberg (isotropic) exchange Hamiltonian ($H = -2JS_1 \cdot S_2$) for two interacting $S = 1/2$ centers, where $-2J$ is the energy difference between the singlet and triplet states, χ_M is expressed per mole of cobalt atoms, N is Avogadro's number, β is the Bohr magneton, k is the Boltzmann constant, T is the absolute temperature, N_α is the temperature-independent paramagnetism, and ρ is the fraction of paramagnetic impurity.

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\left[\frac{1-\rho}{3+\exp(-2J/kT)}\right] + \frac{0.45\rho}{T} + N_\alpha. \quad (1)$$

This procedure treats a complex as a ground-state singlet with a low-lying triplet state. A simple curve-fitting routine was used to determine the parameters g and $-2J$. The best data fit to Eq. 1 gave $g = 2.50$, $-2J = 20\ \mathrm{cm}^{-1}$, $N_\alpha = 100 \times 10^{-6}\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$, $\rho = 0.030$, and a least-squares error (R) of 2.20×10^{-2}. These data indicate an intramolecular antiferromagnetic interaction in complex **4**.

Redox Behavior of Dicobalt Complexes. Cyclic voltammograms of dicobalt complexes **1**, **2**, and **3** in DMF are shown in Fig. 2, which also display a cyclic voltammogram of the monocobalt complex [Co^{II}(saloph)] under the same conditions. The Co^{III}/Co^{II} and Co^{II}/Co^{I} redox couples ($E_{1/2}$) for **1** were observed at +0.14 vs Ag–AgCl and −1.06 V vs Ag–AgCl, respectively. The redox potentials were very similar to those of the corresponding mononuclear complex [Co^{II}(saloph)], as shown in Table 1. The ratios between the anodic and cathodic peak currents, i_{pa}/i_{pc}, were almost unity and independent of the scan rate (from 10 to 500 mV s^{-1}) for the two redox couples in DMF. Plots of i_p ($= i_{pa} + i_{pc}$) vs $v^{1/2}$ (v is the scan rate, mV s^{-1}) were linear, and the potential separation between the anodic and cathodic peaks varied from 100 to 80 mV for the two redox couples, while the $E_{1/2}$ values remained constant within an accuracy of 5% regardless of the scan-rate variation. The present electrochemical redox reactions in DMF are consistent with reversible one-electron transfer processes.[22] The redox behaviors of **2** and **3** were almost similar to those of **1**. Both Co^{III}/Co^{II} and Co^{II}/Co^{I} redox couples appeared at almost the same potentials, and no significant change was observed due to the type of linkers. In this way, electron transfers of **1**, **2**, and **3** occur independently at each cobalt center with no

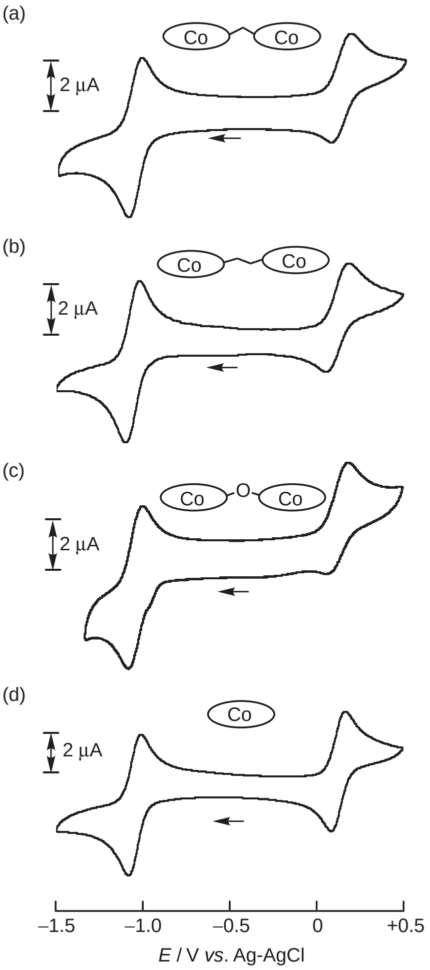


Fig. 2. Cyclic voltammograms of (a) **1** (5×10^{-4} mol dm^{-3}), (b) **2** (5×10^{-4} mol dm^{-3}), (c) **3** (5×10^{-4} mol dm^{-3}), and (d) [Co^{II}(saloph)] (1×10^{-3} mol dm^{-3}) in DMF containing 0.1 mol dm^{-3} n-Bu$_4$NClO$_4$. Scan rate is 100 mV s^{-1}.

Table 1. Redox Potentials for the Various Cobalt Complexes in DMF[a)]

Complex	$E_{1/2}$/V vs Ag–AgCl	
	Co^{III}/Co^{II}	Co^{II}/Co^{I}
1	+0.14	−1.06
2	+0.12	−1.06
3	+0.13	−1.06
4[b)]	+0.37	−1.22
		−1.41
4′[b),c)]	+0.52	−1.22
[Co(saloph)][c)]	+0.14	−1.05

a) Working and counter electrode: Pt, [complex] = 5.0×10^{-4} M, [n-Bu$_4$NClO$_4$] = 0.1 M, under Ar atomosphere at room temperature. Scan rate, 100 mV/s. b) Solvent, THF. c) [complex] = 1.0×10^{-3} M

interaction between two metal centers.

In the case of **4**, redox pairs, corresponding to the Co^{III}Co^{III}/Co^{II}Co^{II}, Co^{II}Co^{II}/Co^{II}Co^{I}, and Co^{II}Co^{I}/Co^{I}Co^{I} couples, were observed at +0.37 V, −1.22 V (E_1), and −1.41 V (E_2) vs Ag–AgCl, respectively, as shown in Fig. 3a.

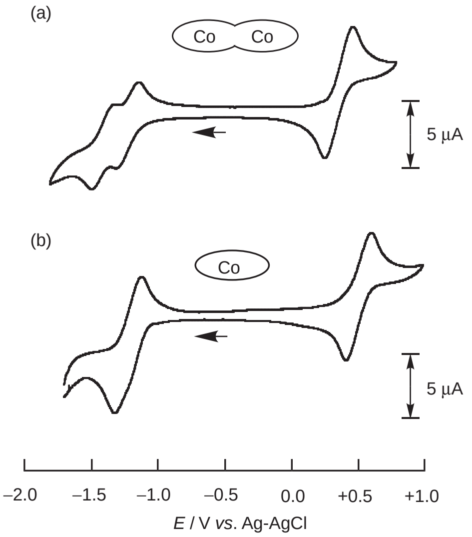
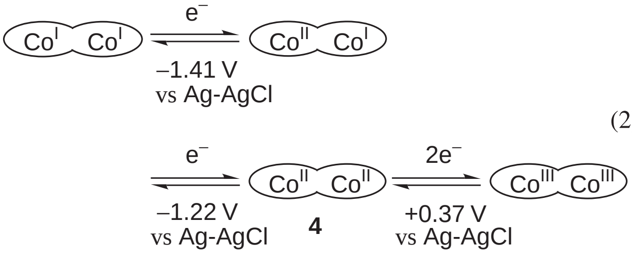
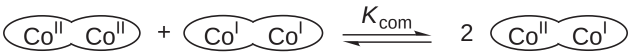


Fig. 3. Cyclic voltammograms of (a) **4** (5×10^{-4} mol dm^{-3}), (b) **4′** (1×10^{-3} mol dm^{-3}) in tetrahydrofuran (THF) containing 0.1 M n-Bu$_4$NClO$_4$. Scan rate is 100 mV s^{-1}.



(2)

In order to provide an unambiguous assignment of these redox couples, coulometry studies were carried out. The charge passed corresponded to one electron at −1.30 V and −1.50 V, and the charge passed corresponded to two electrons at +0.60 V vs Ag–AgCl. In this way, the dicobalt complex **4** shows two sequential reduction, E_1 and E_2, separated by an amount $E = E_1 - E_2 = 0.190$ V. The thermodynamic significance of E can be illustrated by the comproportionation equilibrium (K_{com}) shown in Eqs. 3 and 4.



(3)

$$E = RT/nF \ln K_{\mathrm{com}}. \tag{4}$$

The value is $K_{\mathrm{com}} = 1630$, indicating that the present mixed valence state (Co^{II}Co^{I}) was somewhat stabilized.

Reactivity of Co^{I} Species. Square–planar Co^{I} complexes are strong nucleophiles that react with various organic halides to give organocobalt complexes.[23] As a consequence, the addition of alkyl halides to cobalt complexes generally leads to changes in the cyclic voltammetric pattern of the complex. In the case of **2**, the addition of excess benzyl bromide gives rise to a new irreversible redox wave at the more cathodic potential for the Co^{II}/Co^{I} reduction peak, as shown in Fig. 4. The Co^{II}/Co^{I} redox wave became irreversible, and shifted to the more anodic side. The disappearance of the oxidation peak

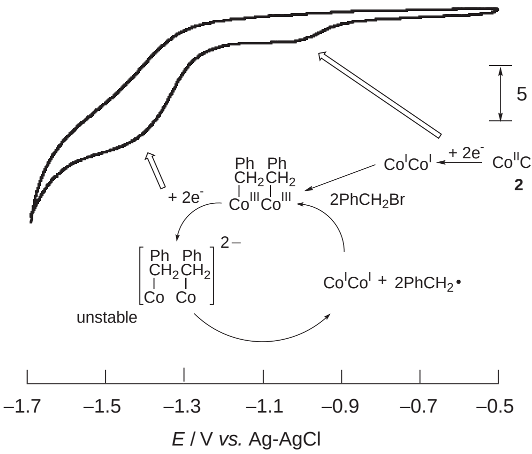
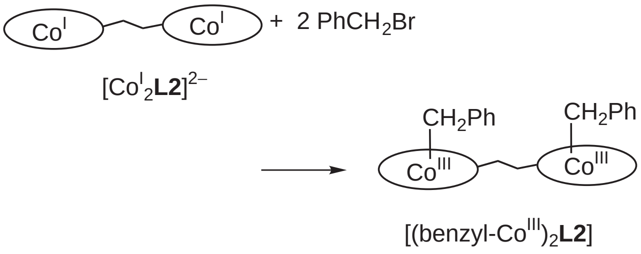


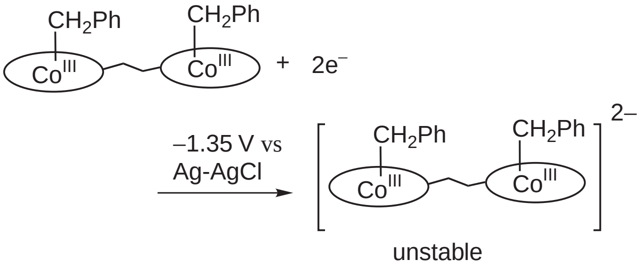
Fig. 4. Cyclic voltammogram of **2** in the presence of benzyl bromide in DMF. Initial concentrations: **2**, 5.0×10^{-4} mol dm^{-3}; benzyl bromide, 1.0×10^{-2} mol dm^{-3}; n-Bu$_4$NClO$_4$, 1.0×10^{-1} mol dm^{-3}. Scan rate: 100 mV s^{-1}.

for Co^{I}/Co^{II} suggests that the reaction of $[\mathrm{Co^{I}}_2\mathbf{L2}]^{2-}$ with benzyl bromide gives [(benzyl–Co^{III})$_2$**L2**] with a cobalt–carbon bond on both metal centers, as shown in Eq. 5.



(5)

Indeed, a controlled potential electrolysis of **2** at −1.15 V vs Ag–AgCl in the presence of benzyl bromide was carried out and followed by electronic spectroscopy. The starting spectrum of **2** was changed to a new spectrum having absorption maxima at 387, 568, and 613 nm, as shown in Fig. 5(b). The spectrum then changed to Fig. 5(c) by irradiation with visible light. The spectrum (c) is ascribed to Co^{III} species for auto-oxidized product of Co^{II} species, which is formed by the homolytic cleavage of cobalt–carbon bond. These absorption maxima and the photochemical behavior are characteristic of those for the complex with a cobalt–carbon bond.[24] Therefore, the new peak at ca. −1.35 V vs Ag–AgCl is caused by the reduction of [(benzyl–Co^{III})$_2$**L2**], as shown in Eq. 6.



(6)

A similar redox behavior was observed in the cases of **1**, **3**, and **4** as well as [Co^{II}(saloph)].

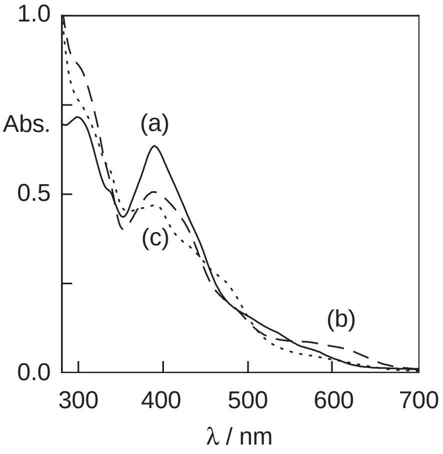


Fig. 5. Electronic spectral changes observed during the controlled potential electrolysis of a DMF solution containing **2** (5.0×10^{-4} mol dm^{-3}), benzyl bromide (1.0×10^{-2} mol dm^{-3}), and n-Bu$_4$NClO$_4$ (1.0×10^{-1} mol dm^{-3}) at −1.15 V vs Ag-AgCl; (a) before electrolysis, (b) after electrolysis and (c) after irradiation with visible light.

In conclusion, all of the dicobalt complexes synthesized in this study showed the reversible Co^{III}/Co^{II} and Co^{II}/Co^{I} redox couple. Cyclic voltammograms of the complexes in the presence of alkyl halide exhibited the formation of a cobalt–carbon bond at both cobalt centers. Further work on the reactivity of dialkylated cobalt complexes with various linkers is currently in progress in our laboratory.

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References

1 “Bioinorganic Catalysis,” ed by J. Reedijk, Marcel Dekker, New York (1999).

2 C. J. Cairns and D. H. Busch, *Coord. Chem. Rev.*, **69**, 1 (1986).

3 K. S. Murray, *Adv. Inorg. Chem.*, **43**, 261 (1995).

4 K. D. Karlin, *Science*, **261**, 701 (1993).

5 M. W. Göbel, *Angew. Chem., Int. Ed. Engl.*, **33**, 1141 (1994).

6 L. Que, *Dalton Trans.*, **1997**, 3933.

7 N. Kitajima, *Adv. Inorg. Chem.*, **39**, 1 (1992).

8 B. Bosnich, *Inorg. Chem.*, **38**, 2554 (1999).

9 P. A. Vigato and S. Tamburini, *Coord. Chem. Rev.*, **106**, 25 (1990).

10 P. Zanello, S. Tamburini, P. A. Vigato, and G. A. Mazzocchin, *Coord. Chem. Rev.*, **77**, 165 (1987).

11 H. Shimakoshi, W. Ninomiya, and Y. Hisaeda, *Dalton Trans.*, **2001**, 1971.

12 H. Shimakoshi, A. Goto, Y. Tachi, Y. Naruta, and Y. Hisaeda, *Tetrahedron Lett.*, **42**, 1949 (2001).

13 E. Eichhorn, A. Rieker, B. Speiser, and H. Stahl, *Inorg. Chem.*, **36**, 3307 (1997).

14 V. L. Bell and R. A. Jewell, *J. Polymer. Sci.*, **5**, 3043 (1967).

15 B. O. West, *J. Chem. Soc.*, **1954**, 395.

16 N. F. Curtis, *J. Chem. Soc.*, **1961**, 3147.

17 E. A. Boudreaux and L. N. Mulay, "Theory and Applications of Molecular Paramagnetism," Wiley, New York (1976), p. 491.

18 H. Chen, J. A. Cronin, and R. D. Archer, *Inorg. Chem.*, **34**, 2306 (1995).

19 K. Chichak, U. Jacquemard, and N. R. Branda, *Eur. J. Inorg. Chem.*, **2002**, 357.

20 O. Kahn, "Molecular Magnetism," Wiley-VCH, New York (1992).

21 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

22 R. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York (1969), p. 143.

23 G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, **91**, 3341 (1969).

24 H. Shimakoshi, T. Kaieda, T. Matsuo, H. Sato, and Y. Hisaeda, *Tetrahedron Lett.*, **44**, 5197 (2003).