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Synthesis, Characterization, and Redox Behavior of New Dicobalt Complexes Having Monoanionic Imine/Oxime-Type Ligands

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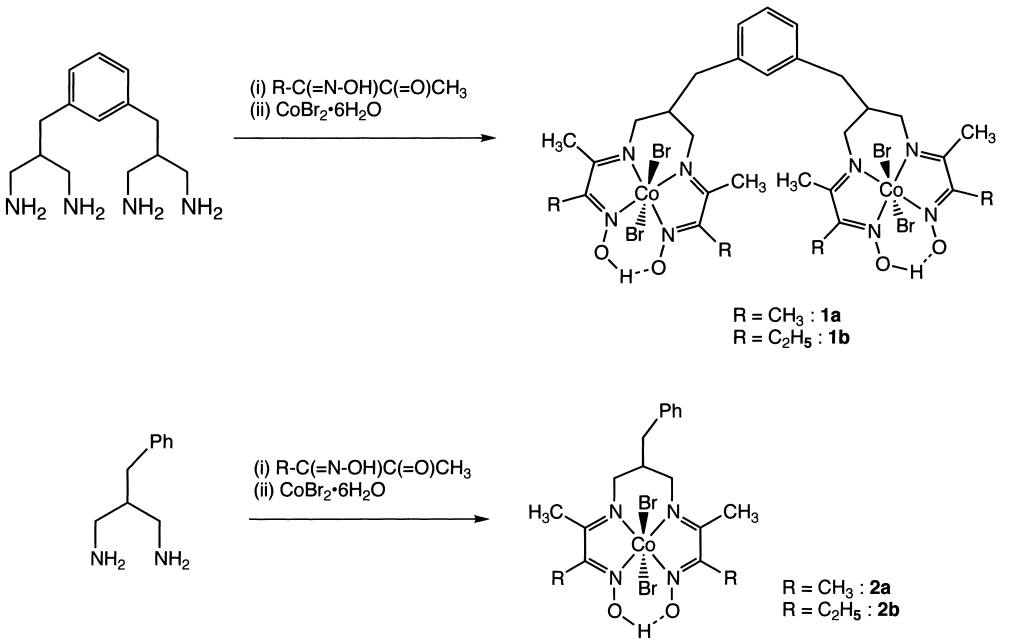
New dicobalt complexes, $[Co^{III}{}_2\mathbf{L}Br_4]$, with monoanionic ligands (**L**) have been synthesized by the reaction of a tetraamine and oximes, followed by an aerobic reaction with $CoBr_2 \cdot 6H_2O$. The complexes were characterized by elemental analyses, IR, ESR, and NMR as well as mass spectroscopies. The redox behavior of the complexes was examined in DMF by means of cyclic voltammetry in comparison with that of the corresponding mononuclear complex. Redox waves identified to Co^{III}/Co^{II} and Co^{II}/Co^{I} for $[Co^{III}{}_2\mathbf{L}]$ were observed at -0.19 V and -0.69 V vs Ag/AgCl, respectively. These potentials are quite similar to those for the corresponding mononuclear complex. An electrogenerated $[Co^{I}{}_2\mathbf{L}]$ species reacts with methyl *p*-toluenesulfonate to give an organocobalt complex. Two-electron reduction of the dinuclear organocobalt compound yields an unstable intermediate that undergoes rapid decomposition by cleavage of the cobalt–carbon bond. The dimethylated complex, which has cobalt–carbon bonds at one axial site of each cobalt, was disproportionated to a tetramethylated complex, involving two cobalt–carbon bonds at both axial sites, and a dicobalt(I) species by two-electron reduction. The tetramethylated cobalt complex was inactive for an electrochemical reduction, but transformed into the dimethylated complex via cleavage of the cobalt–carbon bonds upon electrochemical oxidation.

Much interest has been focused on the synthesis of a dinucleating ligand which can coordinate two metal ions at a suitable distance and geometry, aiming at the cooperative interaction of two metallic sites in metal complexes.[1–4] In such a ligand, the coordination sites of the two metal ions are highly designed and regulated by the coordinating group and ligand framework. *p*-, *m*- , and *o*-Xylene units are available bridging moieties because of their variable conformation.[5,6] As a pendant donor and a coordinating group, cyclam or related tetraazamacrocyclic ligands have been extensively developed in view of their remarkable stability and specificity for metal ions.[7,8] We now consider an imine/oxime skeleton, a so-called Costa-type monoanionic ligand, such as (DO)(DOH)pn. Although (DO)(DOH)pn, which is N^2, $N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime), has been extensively studied in organometallic chemistry, especially in the field of vitamin B_{12} chemistry,[9] little work has been made to extend the use of this ligand toward a dinucleating system. The Costa-type cobalt complex can reproduce the $E_{1/2}$ value for Co^{II}/Co^{I} in base-off aquacobalamin,[10,11] and permits one of the best model complexes for B_{12}-dependent enzymic rearrangements.[12,13] The most remarkable property of this complex is to form a stable cobalt–carbon bond. What happens when a dicobalt complex, bearing two cobalt–carbon bonds, is irradiated with visible light? It would be possible to effect a simultaneous, or near-synchronous, homolytic cleavage of both cobalt–carbon bonds. Therefore, it is expected to activate a pair of substrates via a diorganocobalt complex as an intermediate when we use the dicobalt complex.[14,15] In this paper, we report on the synthesis, characterization, and redox behavior of new dicobalt complexes with monoanionic Costa-type ligands.

Experimental

Materials. Methyl *p*-toluenesulfonate was purified by distillation under reduced pressure. 1,3-Phenylenebis(methylene)bis{2-(1,3-propanediamine)} and 2-benzyl-1,3-diaminopropane were prepared by the same method, reported in the literature.[16] 3-Hydroxyimino-4-pentanone was prepared by a reaction between 2-pentanone and methyl nitrate.[17] [Co(salen)], salen, a dianion of disalicylidene ethylenediamine, and $[Co(Hdmg)_2]$, Hdmg, a monoanion of dimethylglyoxime, were synthesized by a reported method.[18,19] All of the solvents and chemicals used in the syntheses were of reagent grade. For electrochemical studies, *N*, *N*-dimethylformamide (DMF) was stirred for one day in the presence of BaO under a nitrogen atmosphere, and distilled under reduced pressure. Tetra-*n*-butylammonium perchlorate (TBAP) and tetra-*n*-butylammonium bromide (TBABr) were purchased from Nakalai Chemicals (special grade) and dried at 60 °C under a vacuum before use. Dicobalt complexes, **1a** and **1b**, and the reference mononuclear cobalt complexes, **2a** and **2b**, were prepared as follow (refer to Scheme 1).

Synthesis of 1a. To a methanol solution (20 mL) of 1,3-phenylenebis(methylene)bis{2-(1,3-propanediamine)} (249 mg, 1.0 mmol) was added 2,3-butanedione monoxime (1.62 g, 16.0 mmol); the reaction mixture was refluxed for 30 min. After the reaction mixture was cooled to room temperature, $CoBr_2 \cdot 6H_2O$ (719 mg, 2.2 mmol) was added while air was being bubbled through the solution. The reaction mixture was stirred at room temperature for 8 h to give a greenish-brown powder. The powder was collected by suction filtration, and then washed by water and diethyl ether. After being dried in vacuo, the powder was recrystallized from methanol/water to give a green powder. Yield: 86 mg (17%). Found: C, 34.12; H, 4.76; N, 10.14%. Calcd for $C_{30}H_{44}N_8Br_4Co_2$-



Scheme 1.

O_4•$2H_2O$: C, 34.18; H, 4.59; N, 10.63%. IR [KBr; ν/cm^{-1}] 1520 (C=N). ^{1}H NMR [$CDCl_3$] δ 2.50 (s, 12H, -C*H*$_3$), 2.56 (s, 12H, -C*H*$_3$), 2.91(d, 4H, -C*H*$_2$PhC*H*$_2$-), 3.28 (m, 2H, methine), 3.73 (d-d, 4H, -C*H*$_2$N), 4.17 (d-d, 4H, -C*H*$_2$N), 7.17 (d, 2H, Ph), 7.19 (s, 1H, Ph), 7.36 (t, 1H, Ph), 19.25 (s, 2H, O*H*). ^{13}C NMR [$CDCl_3$] δ 13.92 (-*C*H_3), 17.90 (-*C*H_3), 38.38 (*C*H_2N), 39.56 (-CH_2Ph*C*H_2), 55.26 (methine), 127.9, 129.3, 129.5, 138.7 (Ph), 156.1 (oxime), 174.4 (imine). ESI MS *m*/*z* [M$-$Br]$^+$, 937; [M$-$2Br]$^+$, 858; [M$-$3Br]$^+$, 777; [M$-$4Br]$^+$, 697.

Synthesis of 1b. Another dicobalt complex **1b** was synthesized in the same manner as for **1a**, except for using 3-hydroxyimino-4-pentanone in place of 2,3-butanedione monoxime. The product was recrystallized from acetone/water to give a green powder. Yield: 26%. Found: C, 37.59; H, 5.22; N, 10.43%. Calcd for $C_{34}H_{52}N_8Br_4Co_2O_4$•$H_2O$: C, 37.39; H, 4.98; N, 10.26%. IR [KBr; ν/cm^{-1}] 1510 (C=N). ^{1}H NMR [$CDCl_3$] δ 1.15 (t, 12H, -CH_2C*H*$_3$), 2.49 (s, 12H, -C*H*$_3$), 2.91 (d, 4H, PhC*H*$_2$), 2.97 (m, 8H, -C*H*$_2$$CH_3$), 3.26 (m, 2H, methine), 3.73 (d-d, 4H, -C*H*$_2$N), 4.18 (d-d, 4H, -C*H*$_2$N), 7.17 (d, 2H, Ph), 7.19 (s, 1H, Ph), 7.36 (t, 1H, Ph), 19.23 (s, 2H, O*H*). ^{13}C NMR [$CDCl_3$] δ 10.2 (-CH_2*C*H_3), 17.6 (-*C*H_3), 20.9 (-*C*$H_2$$CH_3$), 38.5 (*C*$H_2$N), 39.6 (-$CH_2$Ph*C*$H_2$-), 55.4 *m*/*z* (methine), 127.9, 129.3, 129.6, 138.8 (Ph), 161.5 (oxime), 174.2 (imine). ESI MS *m*/*z* [M$-$Br]$^+$, 993; [M$-$2Br]$^+$, 914; [M$-$3Br]$^+$, 833; [M$-$4Br]$^+$, 753.

Synthesis of 2a. A dry isopropyl ether solution (20 mL) of 2,3-butanedione monoxime (1.3 g, 12.86 mmol) and 2-benzyl-1,3-diaminopropane (520 mg, 3.17 mmol) was heated for 4 h under reflux until 0.1 mL of water was collected in a Dean–Stark trap. The solution was evaporated to give a yellow oil as the target ligand. An acetone solution (20 mL) of the ligand was added dropwise to an aqueous solution (20 mL) of $CoBr_2$•$6H_2O$ (1.04 g, 3.18 mmol) while air was bubbled through the aqueous solution. After the reaction mixture was stirred for 4 h, precipitates were recovered by suction filtration and washed with water and diethyl ether. The resulting cobalt complex was recrystallized from acetone/water to afford light-green needles. Yield: 370 mg(44%). Found: C, 39.70; H, 4.64; N, 10.27%. Calcd for $C_{18}H_{25}N_4Br_2CoO_2$: C, 39.44; H, 4.60; N, 10.22%. IR [KBr; ν/cm^{-1}] 1520 (C=N). ^{1}H NMR [$CDCl_3$] δ 2.51 (s, 6H, -C*H*$_3$), 2.57 (s, 6H, -C*H*$_3$), 2.91 (d, 2H, PhC*H*$_2$-), 3.28 (m, 1H, methine), 3.75 (d-d, 2H, -C*H*$_2$N), 4.17 (d-d, 2H, -C*H*$_2$N), 7.26 (m, 3H, Ph), 7.37 (t, 2H, Ph), 19.28 (s, 1H, O*H*). ^{13}C NMR [$CDCl_3$] δ 13.9 (-*C*H_3), 17.7 (-*C*H_3), 38.3 (*C*H_2N), 39.5 (Ph*C*H_2-), 55.3 (methine), 127.0, 128.9, 129.0, 137.7 (Ph), 156.0 (oxime), 174.3 (imine). ESI MS *m*/*z* [M$-$Br]$^+$, 467; [M$-$2Br]$^+$, 388.

Synthesis of 2b. Another mononuclear cobalt complex **2b** was synthesized in the same manner as for **2a**, except for using 3-hydroxyimino-4-pentanone in place of 2,3-butanedione monoxime. The cobalt complex was recrystallized from acetone/water to give dark-green needles. Yield: 34%. Found: C, 41.87; H, 5.14; N, 9.65%. Calcd for $C_{20}H_{29}N_4Br_2CoO_2$: C, 41.69; H, 5.07; N, 9.72%. IR [KBr; ν/cm^{-1}]: 1510 (C=N). ^{1}H NMR [$CDCl_3$] δ 1.18 (t, 6H, -CH_2C*H*$_3$), 2.50 (s, 6H, -C*H*$_3$), 2.91 (d, 2H, PhC*H*$_2$-), 3.01 (m, 4H, -C*H*$_2$$CH_3$), 3.30 (m, 1H, methine), 3.74 (d-d, 2H, -C*H*$_2$N), 4.17 (d-d, 2H, -C*H*$_2$N), 7.28 (m, 3H, Ph), 7.37 (t, 2H, Ph), 19.26 (s, 2H, O*H*). ^{13}C NMR [$CDCl_3$] δ 10.2 (-CH_2*C*H_3), 17.4 (-*C*H_3), 20.9 (-*C*$H_2$$CH_3$), 38.4 (*C*$H_2$N), 39.5 (Ph*C*$H_2$-), 55.3 (methine), 127.0, 129.0, 129.1, 137.8 (Ph), 161.5 (oxime), 174.0 (imine). ESI MS *m*/*z* [M$-$Br]$^+$, 495; [M$-$2Br]$^+$, 416.

Measurements. Elemental analyses were obtained from the Service Center of Elementary Analysis of Organic Compounds at Kyushu University. The ^{1}H, ^{13}C and 2-D COSY-NMR spectra were recorded on a Bruker AMX 500 spectrometer installed at the Center of Advanced Instrumental Analysis in Kyushu University, and the chemical shifts (in ppm) were referenced relative to $SiMe_4$ as the internal standard. The IR spectra were recorded on a JASCO IR-810 spectrophotometer. Electrospray ionization (ESI) mass spectra were obtained on a PE SCIEX API III. The ESR spectra were obtained on a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter. Cyclic voltammograms were obtained using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with a 1.6-mm diameter platinum wire as the working and counter electrodes was used, and an Ag/AgCl (3.0 M NaCl) electrode served as a reference. DMF solutions containing a cobalt complex (1.0×10^{-3} M), TBAP (1.0×10^{-1} M), and TBABr (2.0×10^{-2} M) were deaerated prior to each measurement, and the inside of the cell was maintained under an argon atmosphere throughout each measurement. All of the measurements were carried out at room temperature. The scan rate was varied over the range from 10 through 500 mV s^{-1}. The $E_{1/2}$ value of ferrocene/ferricinium (Fc/Fc^+) was 0.54 V vs Ag/AgCl with this setup.

Measurements of ESR Spectra. The ESR spectra of divalent cobalt complexes were measured as follows. After complex **1a** or **2a** (1 mM) was dissolved in methanol–benzene (9:1 v/v) and completely degassed by freeze-pump-thaw cycles, 5 equivalent moles of $NaBH_4$ were added to reduce the cobalt complex. ESR spectra of in-situ formed divalent cobalt complexes were obtained at 77 K.

Results and Discussion

Preparation and Characterization of Cobalt Complexes. New dicobalt complexes having monoanionic imine/oxime-type ligands have been synthesized by a one-pot reaction. After a mixture of 2,3-butanedione monoxime and tetraamine was stirred for 30 min in hot MeOH, cobalt(II) bromide was added while air was bubbled through the solution to yield a hexacoordinated cobalt(III) complex. Complexes **1a** and **1b**, isolated as a green solid, gave various satisfactory spectroscopic analyses. Mononuclear analogues, **2a** and **2b**, were prepared in the same manner to give a green crystal, which gives good analytical data. In the IR spectrum, a broad band at 2900 cm^{-1} ($-NH_2$) in the precursor tetraamine disappeared, and new bands assignable to C=N vibration of coordinated azomethine groups appeared at 1520 and 1510 cm^{-1} for **1a** and **1b**, respectively. Diamagnetic cobalt(III) complexes show well-defined proton NMR spectra. The dicobalt complex **1b** has C_{2v} symmetry, and all signals for the mononuclear unit appeared in the same region as shown in Fig. 1. A signal at 19.2 ppm is assigned to the protons in intramolecular hydrogen bonds (see the signal (h) in Fig. 1). The unequivalent methylene hydrogens of the propanediimine chelate ring appear at 3.73 and 4.18 ppm, respectively, and split by each other ($J_{\mathrm{geminal}} = 15.0$ Hz) and by the methine proton ($J_{\mathrm{vicinal}} = 13.5$, 2.5 Hz) (see the signals (f) and (g) in Fig. 1). The proton NMR spectrum and the detailed spectral assignments by 2-D NMR measurements provide conclusive evidence for the structure of **1b**. The formation of **1b** has also been confirmed by ESI-MS. The introduction of a methanol solution of **1b** into an ESI mass spectrometer afforded a positive-ion mass spectrum with the most prominent peak clusters at *m*/*z* 993, 914, 833 and 753, which have mass values and isotope patterns consistent with the ions $[M\text{-}Br]^+$, $[M\text{-}2Br]^+$, $[M\text{-}3Br]^+$, $[M\text{-}4Br]^+$, respectively, as shown in Fig. 2. This is the first example of a Costa-type dicobalt complex linking with a flexible spacer. The formation of another dicobalt complex **1a** and corresponding mononuclear cobalt complexes, **2a** and **2b**, was also supported by similar spectroscopic data.

ESR Study of Cobalt(II) Complexes. To elucidate the existence of a metal–metal interaction in the molecule, ESR spectra were measured in its divalent state. The ESR spectrum of a dicobalt(II) complex, which was prepared by the reduction of **1a**, is shown in Fig. 3. The complex shows a typical axial-type ESR spectrum (d_{z^2} ground state, $g_\perp = 2.28$, $g_\parallel = 2.01$, $A_\parallel^{Co} = 109$ G),[20] and is almost similar to that for a corresponding mononuclear complex which was prepared by the reduction of **2a** ($g_\perp = 2.30$, $g_\parallel = 2.02$, $A_\parallel^{Co} = 112$ G). Therefore, we concluded that no metal-metal interaction exists in the dicobalt complex. The following electrochemical measurements also supported that there was no interaction between the two cobalt centers.

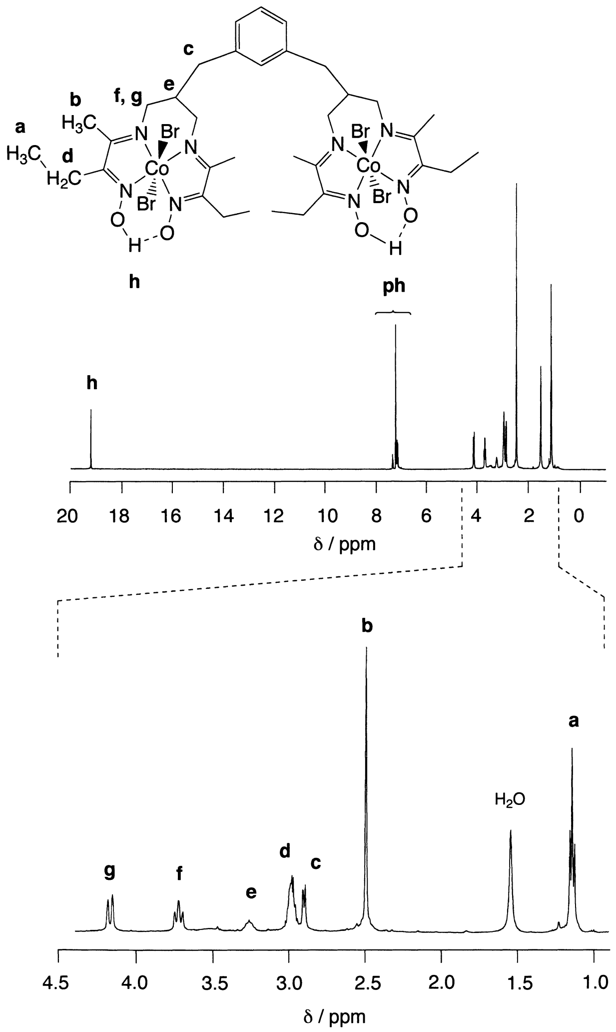


Fig. 1. ^1H NMR (500 MHz) spectra of the complex **1b** in $CDCl_3$. The assignments are shown in the figure.

Electrochemistry of Cobalt Complexes. The cyclic voltammogram of the dinuclear cobalt complex **1b** in DMF is shown in Fig. 4a, which also displays a cyclic voltammogram of the mononuclear cobalt complex **2b** under the same conditions. The Co^{II}/Co^{I} and Co^{III}/Co^{II} redox couples ($E_{1/2}$) for **1b** were observed at -0.69 V and -0.19 V vs Ag/AgCl, respectively. The redox behavior for **1b** was very similar to that for the corresponding mononuclear complex **2b**, as shown in Fig. 4b. In order to provide an unambiguous assignment of the redox couples, coulometry studies were carried out at -1.0 V and -0.5 V vs Ag/AgCl. The charge passed corresponded to two electrons and one electron at each potential for **1b** and **2b**, respectively. The redox potentials for complex **1a** are listed in Table 1. Modifications of the peripheral moieties provided no

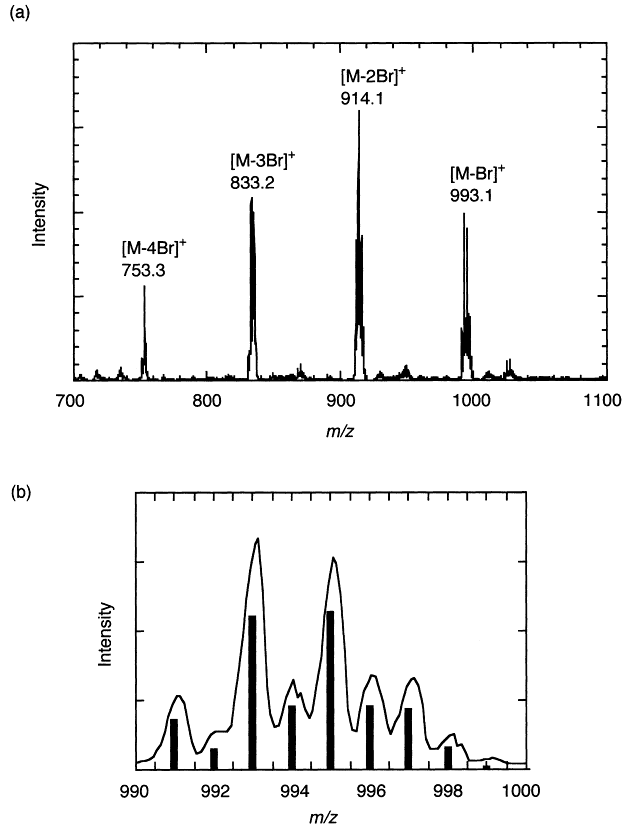


Fig. 2. (a) ESI-mass spectrum of complex **1b**. (b) Calculated isotope pattern is represented by bars under a peak cluster of the parent ion.

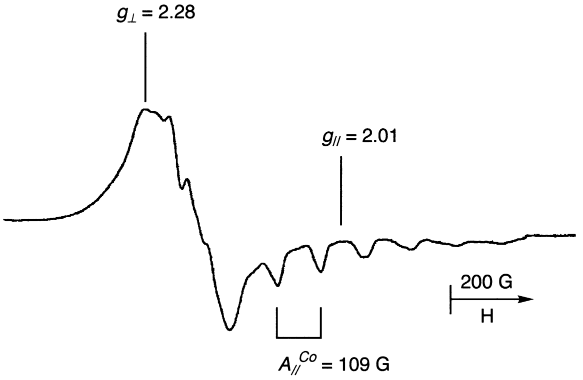


Fig. 3. ESR spectrum of dicobalt(II) complex, which was prepared by the reduction of **1a**, in methanol–benzene (9:1 v/v) at 77 K.

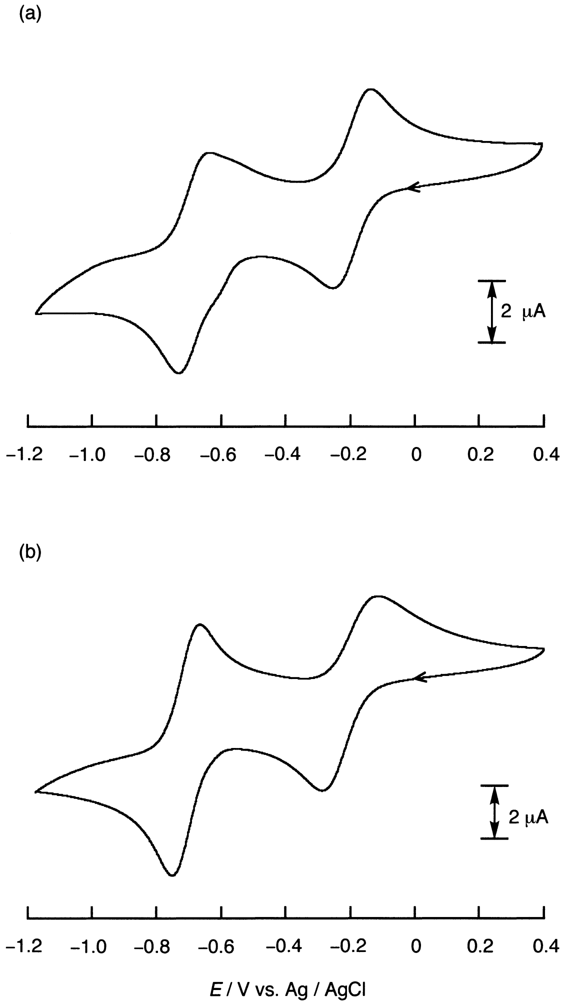


Fig. 4. Cyclic voltammograms of (a) **1b** (5.0×10^{-4} M) and (b) **2b** (1.0×10^{-3} M) in DMF containing 0.1 M TBAP and 0.02 M TBABr. Scan rate, 100 mV sec^{-1}.

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}
1a[b)]	−0.19	−0.71
1b[b)]	−0.19	−0.69
2a[b)]	−0.21	−0.74
2b[b)]	−0.20	−0.71
[Co^{II}(salen)]	+0.10	−1.21
[$Co^{II}(Hdmg)_2$]	+0.12	−1.02
Vitamin B_{12}[c)]	*ca.* +0.3	−0.74
Hydrophobic B_{12}[d)]	*ca.* +0.4	−0.61

a) Working and counter electrodes: Pt, [**1a**] = [**1b**] = 5.0×10^{-4} M, [**2a**] = [**2b**] = 1.0×10^{-3} M, [TBAP] = 0.1 M, [TBABr] = 2.0×10^{-2} M, under Ar atmosphere at room temperature. Scan rate 100 mV/s. b) In the presence of 2.0×10^{-2} M TBABr. c) Ref. 24. d) Ref. 25.

remarkable change in the redox potentials in comparison to **1a** with **1b**, in which the oxime methyl groups of **1a** are replaced by ethyl groups. The ratios between the anodic and cathodic peak currents of **1a** and **1b**, 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. The plots of i_p ($= i_{pa} + i_{pc}$) vs $\nu^{1/2}$(ν is the scan rate, mV s^{-1}) were linear, and the potential separation between the anodic and cathodic peaks varied from 160 to 60 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. Therefore, the present redox reactions in DMF are consistent with reversible one-electron transfer processes for each metal.[21]

Comparisons with the redox potentials for other cobalt com-

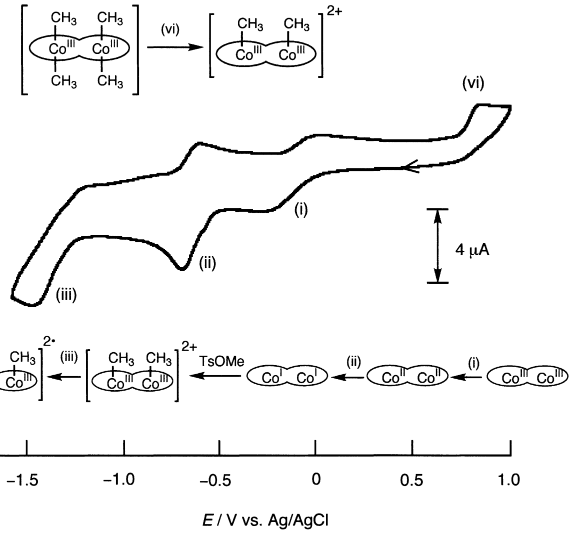
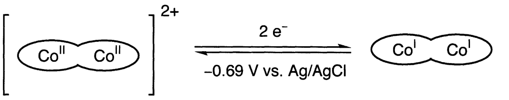


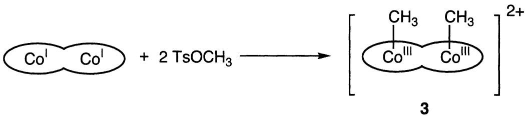
Fig. 5. Cyclic voltammogram of **1b** in the presence of methyl *p*-toluenesulfonate in DMF. Initial concentration: **1b**, 1.0×10^{-3} M; methyl *p*-toluenesulfonate, 3.0×10^{-2} M; TBAP, 0.1 M. Scan rate, 100 mV sec^{-1}.

plexes with dianionic ligands, [$\mathrm{Co^{II}}$(salen)] and [$\mathrm{Co^{II}(Hdmg)_2}$] are also listed in Table 1. The $\mathrm{Co^{II}/Co^{I}}$ redox couples for [Co(salen)] and [$\mathrm{Co(Hdmg)_2}$] in DMF were observed at −1.21 V and −1.02 V vs Ag/AgCl, respectively. The $\mathrm{Co^{II}/Co^{I}}$ couple is sensitive primarily to the basicity of the equatorial ligand.[22,23] The complexes synthesized here have less negative $\mathrm{Co^{II}/Co^{I}}$ redox couples because they have monoanionic ligands. A natural vitamin $\mathrm{B_{12}}$ and a modified vitamin $\mathrm{B_{12}}$ having a monoanoinic corrin ligand afford similar redox potentials, as shown in Table 1.[24,25]

Costa-type dicobalt complexes are easily reduced to the corresponding cobalt(I) species, as shown in Eq. 1. Square-planar cobalt(I) complexes are strong nucleophiles and react with various electrophiles, such as organic halide or alkyl *p*-toluenesulfonate, to give organocobalt complexes.[26] The addition of methyl *p*-toluenesulfonate as an electrophile significantly changed the voltammetric pattern of **1b**, as shown in Fig. 5. In the presence of an excess methyl *p*-toluenesulfonate, a new irreversible peak appeared at ca. −1.50 V vs Ag/AgCl and the $\mathrm{Co^{II}/Co^{I}}$ redox wave became somewhat irreversible. A methylated Costa-type complex was reduced at ca. −1.50 V vs Ag/AgCl in DMF, as we previously reported.[27] The decrease on the oxidation peak for $\mathrm{Co^{I}/Co^{II}}$ suggests that the cobalt(I) species reacts with methyl *p*-toluenesulfonate to give [$\mathrm{(CH_3\text{-}Co^{III})_2}$**L**], **3**, with a cobalt–carbon bond on both metal centers, as shown in Eq. 2, where **L** represents the corresponding ligand. The new peak at ca. −1.50 V vs Ag/AgCl is assigned to the reduction of **3**.



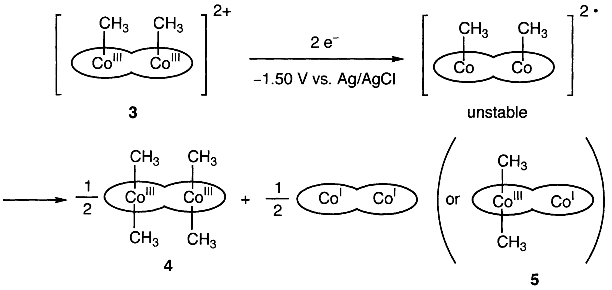
(1)



3

(2)

The two-electron reduction intermediate of **3** was unstable and disproportionated to a dicobalt(I) species and the tetramethylated cobalt complex **4** at the above potential, as shown in Eq. 3. Another possibility is that it intramolecularly disproportionates to form **5**. The electrochemical behavior of a Costa-type mononuclear cobalt complex with a cobalt–carbon bond was previously proved by us.[12,27] We have also prepared a Costa-type cobalt complex bearing two methyl groups at both axial sites, which is inactive for electrochemical reduction, and oxidized at +0.73 V vs Ag/AgCl to form a methylated complex and a methyl radical.[12] Although complex **4** was inactive for electrochemical reduction, an irreversible oxidation peak was observed at +0.80 V vs Ag/AgCl, when scanned to the anodic direction. The similarity of the cyclic voltammogram to that of the mononuclear complex suggests that the cobalt–carbon bond of complex **4** is cleaved to afford the dimethylated complex **3** and methyl radicals by the electrochemical oxidation, as shown in Eq. 4.



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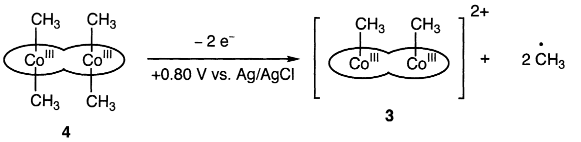

(4)

In conclusion, new dicobalt complexes having monoanionic imine/oxime-type ligands have been synthesized and characterized by various spectroscopic methods as well as elemental analyses. The metal sites of the complexes, which are linked by a *m*-xylene spacer, are completely discrete. Such dicobalt complexes could activate two molecules at the same time to form a pair of active species, such as radicals, which are expected to selectively form dimerized compounds.[15] If we used a dicobalt complex having monoanionic ligands, it is expected to work as a catalyst under very mild reduction conditions. Further work on the reactivities of the complexes with multi-reaction sites is in progress in our laboratory.

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