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Synthesis and redox behavior of dialkylated dicobalt complexes having two discrete salen units

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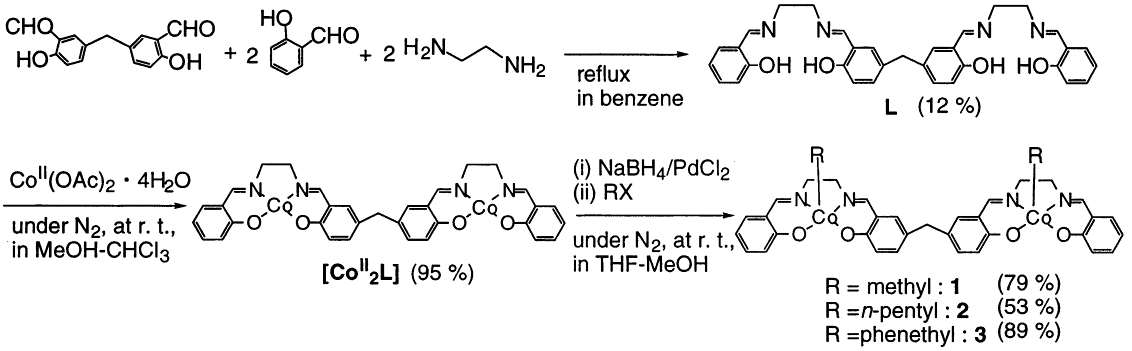
Abstract—Novel dialkylated dicobalt complexes with two discrete salen units have been synthesized and characterized by UV–vis, NMR, and ESI-mass spectroscopies as well as elemental analyses. Redox behavior of the complexes was investigated by means of cyclic voltammetry and ESR spin-trapping techniques. The results indicate that cobalt–carbon bonds cleave homolytically to produce the radical species during the electrolysis. © 2001 Elsevier Science Ltd. All rights reserved.

Formation and cleavage of a metal–carbon σ-bond are important research targets in organometallic chemistry. The application of organometallic compounds to organic syntheses has been of considerable interest.[1] Especially, compounds with a cobalt–carbon bond, found as key intermediates in vitamin B_{12} enzymic reactions, have attracted much attention owing to facile cleavage of the cobalt–carbon bond.[2] A variety of chelated complexes having a cobalt–carbon bond have been synthesized and are used as a versatile radical source for organic syntheses.[3–5] We synthesized a novel dicobalt complex containing [Co(salen)] units, where salen is a dianion of *N*,*N*′-ethylenebis(salicylideneamine), linked with a methylene spacer. It is well known that a [Co(salen)] complex is a vitamin B_{12} model complex and forms a stable cobalt–carbon bond.[6] Therefore, it is expected that the dicobalt complex presented here will form stable cobalt–carbon bonds at each metal center. Such a dicobalt complex could activate two molecules at the same time to form a pair of active species such as radicals, which are expected to selectively form the dimerized compound. In this paper, we report the synthesis, characterization, and redox behavior of novel dialkylated dicobalt complexes.

The dinucleating ligand (**L**) and the corresponding cobalt complexes were prepared as shown in Scheme 1. Dialkylated complexes with cobalt–carbon bonds were synthesized using a procedure similar to that reported by Schrauzer et al.[6] A 50 mg sample of the dicobalt complex [$Co_2{}^{II}L$] was dissolved in 15 mL of THF–MeOH. After the solution was deoxygenated by bubbling nitrogen gas through it, 0.2 g NaOH (in 0.2 mL of



Scheme 1.

Keywords: cobalt–carbon bond; vitamin B_{12} model complex; dinucleating ligand; radical species.

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H_2O) and 15 mg $NaBH_4$ (in 0.15 mL of H_2O) were added, and then 4.0 mg $PdCl_2$ (in 0.2 mL of H_2O containing 1.0 M KCl) was injected to the solution. When the solution color changed to dark-green, 50 mol equivalents of alkyl halides (methyl iodide, *n*-pentyl bromide, and phenethyl bromide) were added to form the corresponding alkylated complexes **1**–**3**. After stirring for 1 h, 5 mL of acetone was added to decompose the excess $NaBH_4$. The solution was filtered to remove an insoluble solid, and the solvent of the filtrate was evaporated to dryness. The residue was washed with H_2O and diethyl ether in order to remove inorganic salts and excess alkyl halide, respectively. The resulting product was dissolved in $CHCl_3$ to filter off an insoluble solid, and evaporated to dryness to afford a dark-brown solid.[7]

The structure of **1** was identified by ^1H NMR (in DMSO-d_6, 500 MHz). The methyl protons attached to the cobalt centers are found at δ 2.01. This peak was not observed for the corresponding deuterium complex ($R=CD_3$). The presence of a cobalt–carbon bond is also corroborated by the electronic spectrum, which shows absorptions at 344, 406(sh), 471(sh), and 650 nm in $CHCl_3$. The absorption maxima at 344 and 650 nm are characteristic of the pentacoordinate alkylcobalt(III) salen complex.[8] These absorption maxima disappeared upon cleavage of the cobalt–carbon bonds by aerobic photolysis. Insight into the nature of the photo-sensitive species has been also obtained from electrospray ionization mass spectrometric (ESI-MS) analysis. ESI-MS has been found to be applicable to the characterization of unstable compounds, including organometallic compounds due to the mildness of the ionization method. Introduction of a MeOH solution of **1** into the ESI mass spectrometer in the dark affords a positive ion mass spectrum with the most prominent peak clusters at *m*/*z* 692 and 677, which have the mass values and isotope patterns consistent with the ions $\{[Co_2\mathbf{L}(CH_3)_2]\}^+$ and $\{[Co_2\mathbf{L}(CH_3)]\}^+$, respectively, as shown in Fig. 1. Complexes **2** and **3** were also identified by the same method. This is the first example of a discrete dicobalt complex having cobalt–carbon bonds.

Redox behavior of the complexes in DMF was investigated by means of cyclic voltammetry (CV) in comparison with the corresponding mononuclear complexes. The cyclic voltammogram of **3** is shown in Fig. 2. The redox behavior was similar in appearance to those for alkylated [Co(salen)] complexes reported by Costa et al.[9] In the course of the initial sweep of CV, a single

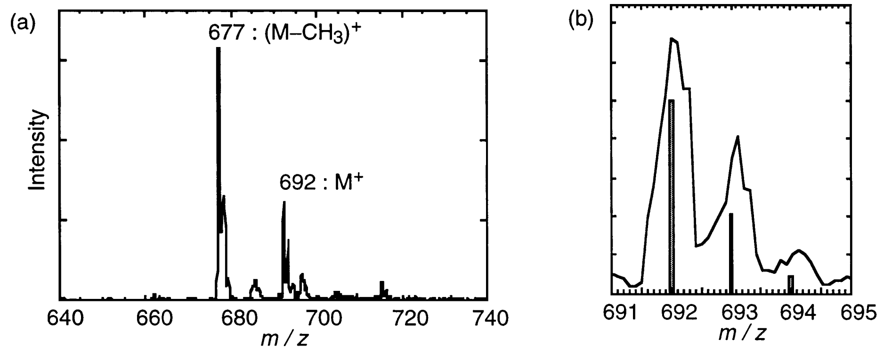

Figure 1. (a) ESI-mass spectrum of complex **1**. (b) Calculated isotope pattern is represented by bars under the peak cluster of the parent ion.

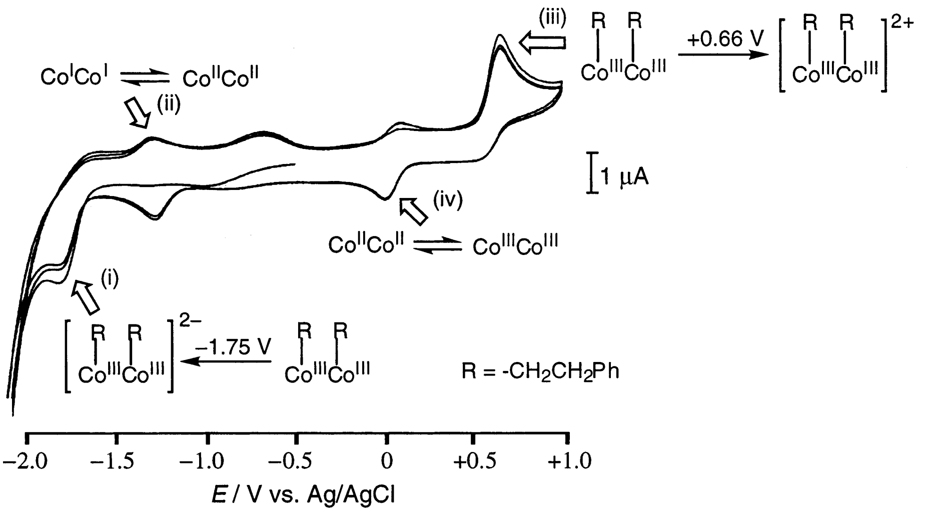

Figure 2. Cyclic voltammogram of **3** (3.0×10^{-4} M) in DMF containing 0.1 M TBAP at room temperature in the dark; sweep rate: 100 mV s^{-1}.

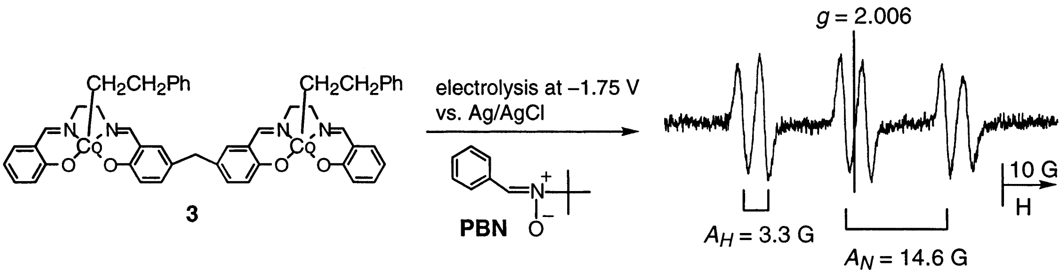

Figure 3. ESR spectrum observed during electrolysis at −1.75 V versus Ag/AgCl of a DMF solution containing **3** (1.0×10^{-3} M), PBN (4.0×10^{-1} M), and TBAP (5.0×10^{-2} M) at room temperature in the dark.

irreversible reduction peak, which is assigned to the one-electron reduction intermediate at each metal site, was observed at ca. −1.75 V versus Ag/AgCl, as shown in Fig. 2(i), while a weak peak at −1.25 V versus Ag/AgCl in the anodic sweep was attributed to the Co(I)/Co(II) oxidation wave (see Fig. 2(ii)). At more anodic potentials, an irreversible oxidation peak, which is assigned to the one-electron oxidation intermediate of **3** at each metal site, was observed at +0.66 V versus Ag/AgCl (see Fig. 2(iii)), and a peak at +0.01 V versus Ag/AgCl, which appeared in the cathodic sweep, is assigned to the Co(III)/Co(II) reduction wave (see Fig. 2(iv)). Redox peaks for (ii) and (iv) in Fig. 2 were not observed during scanning for the potential range from −1.50 V through +0.50 V versus Ag/AgCl.

The above voltammogram indicates that the alkylated complex is decomposed by electrolysis to afford the alkyl radicals in a potential range more cathodic than −1.75 V versus Ag/AgCl and more anodic than +0.66 V versus Ag/AgCl. The redox behavior of the alkylated complex was also followed by an ESR spin-trapping technique with phenyl *N*-*tert*-butylnitrone (PBN). An ESR signal attributable to the PBN spin adduct was observed at $g=2.006$ ($A_N=14.6$ G, $A_H=3.3$ G; 10^4 G = 1 T) in the electrolysis of **3** at −1.75 V, as shown in Fig. 3. The ESR parameter of the spin adduct was almost the same as those for the species formed by photolysis of **3** ($g=2.006$, $A_N=14.6$ G, $A_H=3.5$ G). At this potential, the color of the solution changed to greenish-blue, which is typical for [Co(I)(salen)], and it showed a strong charge-transfer band at ca. 700 nm. These results indicate that the dialkylated complex **3** is reduced to form Co(I) and a radical species at −1.75 V versus Ag/AgCl.

In this paper, we have reported the synthesis and redox behavior of novel dialkylated dicobalt complexes having two discrete salen units. Further work on reactions of these dialkylated complexes is currently in progress in our laboratory.

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7. Compound **1**: ^{1}H NMR (DMSO-d_6, 500 MHz): $\delta=2.01$ [s, 6H, C$\underline{H}_3$], 3.43 [m, 4H, -NC$\underline{H}_2$C$\underline{H}_2$N-], 3.56 [s, 2H, -PhC$\underline{H}_2$Ph-], 3.64 [m, 4H, -NC$\underline{H}_2$C$\underline{H}_2$N-], 6.36 [s, 2H, Ph], 6.70 [d, 2H, Ph], 6.76 [d, 2H, Ph], 6.93 [s, 4H, Ph], 7.06 [t-d, 2H, Ph], 7.12 [d-d, 2H, Ph], 7.90 [s, 2H, N=C$\underline{H}$], 7.95 [s, 2H, N=C$\underline{H}$]; ESI-MS: *m*/*z* 692 (M$^+$), 677 ((M−CH$_3$)$^+$); UV–vis: [λ_{max}/nm (ε/M^{-1} cm^{-1})], 650 (2350). Anal. found: C, 57.95; H, 5.39; N, 7.77%. Calcd for $C_{35}H_{34}Co_2N_4O_4\cdot2H_2O$: C, 57.70; H, 5.26; N, 7.69%. Compound **2**: ^{1}H NMR (DMSO-d_6, 500 MHz): $\delta=0.65$ [t, 6H, C$\underline{H}_3$-], 0.76 [m, 4H, C$\underline{H}_2$], 1.11 [m, 4H, C$\underline{H}_2$], 1.20 [m, 4H, C$\underline{H}_2$], 3.19 [m, 4H, C$\underline{H}_2$], 3.44 [m, 4H, -NC$\underline{H}_2$C$\underline{H}_2$N-], 3.57 [s, 2H, -PhC$\underline{H}_2$Ph-], 3.67 [m, 4H, -NC$\underline{H}_2$C$\underline{H}_2$N-], 6.36 [t, 2H, Ph], 6.73 [d, 2H, Ph], 6.78 [d, 2H, Ph], 6.93 [m, 4H, Ph], 7.06 [t-d, 2H, Ph], 7.12 [d-d, 2H, Ph], 7.94 [s, 2H, N=C$\underline{H}$], 8.00 [s, 2H, N=C$\underline{H}$]; ESI-MS: *m*/*z* 804 (M$^+$), 733 ((M−C$_5$H$_{11}$)$^+$); UV–vis: [λ_{max}/nm (ε/M^{-1} cm^{-1})], 658 (1620). Anal. found: C, 61.43; H, 6.47; N, 6.66%. Calcd for $C_{43}H_{50}Co_2N_4O_4\cdot2H_2O$: C, 61.31; H, 6.23; N, 6.21%. Compound **3**: ^{1}H NMR (DMSO-d_6, 500 MHz): $\delta=2.07$ [t, 4H, Co-C$\underline{H}_2$], 3.17 [m, 4H, PhC$\underline{H}_2$], 3.47 [m, 4H, -NC$\underline{H}_2$C$\underline{H}_2$N-], 3.56 [s, 2H, -PhC$\underline{H}_2$Ph-], 3.66 [m, 4H, -NC$\underline{H}_2$C$\underline{H}_2$N-], 6.36 [t, 2H, Ph], 6.79 [d, 2H, Ph], 6.84 [d, 2H, Ph], 6.94 [m, 8H, Ph], 7.09 [m, 10H, Ph], 7.93 [s, 2H, N=C$\underline{H}$], 8.01 [s, 2H, N=C$\underline{H}$]; ESI-MS: *m*/*z* 872 (M$^+$), 767 ((M−PhCH$_2$CH$_2$)$^+$); UV–vis: [λ_{max}/nm (ε/M^{-1} cm^{-1})], 657 (2270). Anal. found: C, 64.88; H, 5.60; N, 6.19%. Calcd for $C_{49}H_{46}Co_2N_4O_4\cdot2H_2O$: C, 64.76; H, 5.55; N, 6.16%.
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