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# Optical and ESR Studies of the One-Electron Reduction of Alkylcobaloximes in Rigid Matrices

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The reduced species of chloro- and benzyl(pyridine)cobaloximes and methylcobaloximes were produced in 2-methyltetrahydrofuran solutions by $\gamma$ irradiation at 77 K. From the ESR and optical absorption measurements, the reduced chloro- or benzylcobaloximes are concluded to have a structure of the constrained complex in which the unpaired electron occupies the $3d_{z^2}$ orbital of the cobalt atom strongly perturbed by $Cl^-$ or the benzyl anion in the axial position. For the reduced methylcobaloximes, the unpaired electron is considered to occupy the antibonding orbital of the cobalt–carbon bond. When the irradiated samples are warmed, the reduced chloro- or benzyl(pyridine)cobaloxime dissociates into $Cl^-$ or the benzyl anion and (pyridine)cobaloxime, whereas the reduced methyl(pyridine)cobaloxime dissociates into the methyl radical and reduced (pyridine)cobaloxime. The reductive cleavage of the cobalt–carbon bond is discussed on the basis of the concept of dissociative electron attachment.

## Introduction

Cobalt–carbon bonds had been considered to be unstable and reactive before the discovery of the coenzyme vitamin $B_{12}$.[1] In 1963, Schrauzer and Kohle found that alkylcobaloximes have a stable cobalt–carbon bond.[2] Subsequent studies revealed that alkylcobaloximes exhibit similar chemical behavior to that of the coenzyme $B_{12}$.[3,4] The structure determination of an alkylcobaloxime carried out by Lehnhert indicated that the Co–N bond lengths in plane and the Co–C distance are the same as those in the coenzyme $B_{12}$.[5] From these experimental results, alkylcobaloximes have been accepted as model compounds of the coenzyme $B_{12}$.

Reductive cleavage of the Co–C bond in coenzyme $B_{12}$ and methyl-$B_{12}$ has been extensively studied in order to elucidate the coenzymatic reactions in vivo.[6–8] For alkylcobaloximes, polarographic studies showed that the reduced species produced in the first reduction step spontaneously decay owing to the cleavage of the Co–C bond.[3] The bond cleavage of these reduced species is expected to be closely related to the nature of the orbital that an excess electron occupies.[4]

Recently, we studied the one-electron reduction of chloro(tetraphenylporphinato)cobalt(III) in 2-methyltetrahydrofuran solution by $\gamma$-ray radiolysis at 77 K.[9] The optical absorption and ESR spectra of reduced species are distinctly different from those of (tetraphenylporphinato)cobalt(II). This species, termed constrained complex, has a structure of (tetraphenylporphinato)cobalt(II) with $Cl^-$ in the axial position and immediately dissociates into (tetraphenylporphinato)cobalt(II) and $Cl^-$ on warming the solution.

In the present study, the reduced alkylcobaloximes in 2-methyltetrahydrofuran produced by $\gamma$ radiolysis at 77 K were studied with the aims of establishing their electronic structures and of observing their chemical behavior at higher temperatures.

## Experimental Section

**Materials.** Chloro(pyridine)cobaloxime ($ClCo(dmg)_2py$) and benzyl(pyridine)cobaloximes ($BzlCo(dmg)_2py$) were prepared by the method according to Schrauzer and Windgassen.[10] Methyl(pyridine)cobaloxime ($MeCo(dmg)_2py$), methyl(imidazole)cobaloxime ($MeCo(dmg)_2Im$), and methylaquocobaloxime ($MeCo(dmg)_2H_2O$) were synthesized by the method reported by Yamazaki and Hohokabe.[11] Anal. Calcd for $ClCo(dmg)_2py$: C, 38.68; H, 4.74; N, 17.35. Found: C, 38.42; H, 4.72; N, 17.65. Calcd for $BzlCo(dmg)_2py$: C, 52.29; H, 5.70; N, 15.25. Found: C, 51.98; H, 5.40; N, 15.53. Calcd for $MeCo(dmg)_2py$: C, 43.87; H, 5.79; N, 18.27. Found: C, 43.55; H, 5.72; N, 18.23. Calcd for $MeCo(dmg)_2H_2O$: C, 33.55; H, 5.79; N, 17.39. Found: C, 33.56; H, 5.93; N, 17.22. Calcd for $MeCo(dmg)_2Im$: C, 38.72; H, 5.69; N, 22.57. Found: C, 38.51; H, 5.64; N, 22.54.

2-Methyltetrahydrofuran was purified by distillation and stored on Na–K alloy in vacuo in order to remove traces of water.

**$\gamma$-Ray Irradiation and Measurements of Electronic Absorption and ESR Spectra.** Irradiation was performed with $\gamma$ rays from a 1.2-kCi $^{60}Co$ source at a dose rate of 57.0 krd $min^{-1}$. Sample cells were plunged in a Dewar vessel containing liquid nitrogen during the course of irradiation. The concentrations of solute were approximately $10^{-3}$ M for all the samples.

High-quality quartz cells for the optical measurement of trapped intermediates had optical path lengths of 0.5–1.5 mm. The absorption spectra were recorded on a Cary 14R spectrophotometer. The irradiated samples were photobleached at 77 K prior to the optical measurement by a tungsten lamp incorporated in the spectrophotometer in order to remove absorption due to trapped electrons.

The ESR studies of the irradiated samples were carried out by using specially prepared glass tubes in which no hydrogen atoms are produced by $\gamma$-ray irradiation at 77 K. X-Band ESR spectra were recorded on a JEOL FES-FE3AX spectrometer. Field and frequency were calibrated with use of DPPH powder, Mn(II) in MgO powder, and a Takeda Riken TR-5501 frequency counter.

## Results

**Absorption Spectra.** Figure 1 shows the absorption spectra of the reduced species observed for the $\gamma$-irradiated 2-methyltetrahydrofuran solutions of $ClCo(dmg)_2py$ and $BzlCo(dmg)_2py$ at 77 K. The absorption peaks are located at 500, 620, and 903 nm for the reduced $ClCo(dmg)_2py$, and at 500, 625, and 900 nm for the reduced $BzlCo(dmg)_2py$, respectively. The two spectra closely resemble each other except for an absorption shoulder around 480 nm observed for the reduced $BzlCo(dmg)_2py$. From the *G* value of electrons in the 2-methyltetrahydrofuran matrix at 77 K,[12] the molar extinction coefficients at 500 nm of the reduced $ClCo(dmg)_2py$ and $BzlCo(dmg)_2py$ were roughly estimated to be higher than $2.5 \times 10^3\ M^{-1}\ cm^{-1}$.

Figure 2 shows the absorption spectra of the reduced species observed for the $\gamma$-irradiated 2-methyltetrahydrofuran solutions of $MeCo(dmg)_2py$ and $MeCo(dmg)_2H_2O$ at 77 K. The

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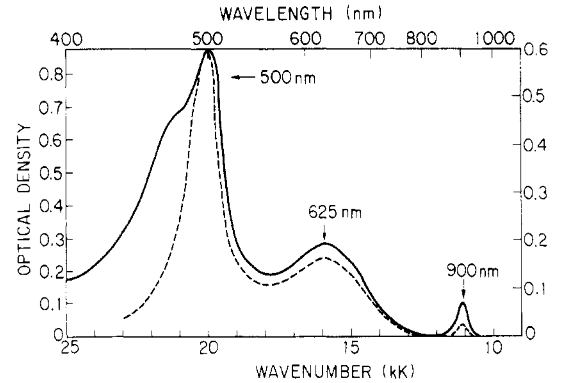

**Figure 1.** Absorption spectra of the reduced BzlCo(dmg)$_2$py (—) and ClCo(dmg)$_2$py (---) in 2-methyltetrahydrofuran obtained with photobleaching for 10 min after $\gamma$ irradiation of the samples for 30 min at 77 K. The left-side scale is for the optical densities of the former, and the right-side scale is for the latter.

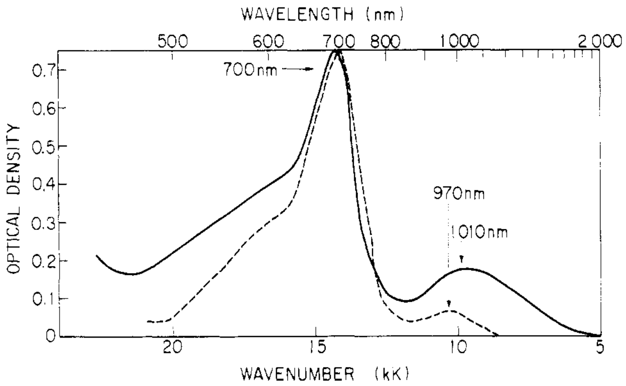

**Figure 2.** Absorption spectra of the reduced MeCo(dmg)$_2$py (—) and MeCo(dmg)$_2$H$_2$O (---) in 2-methyltetrahydrofuran obtained with photobleaching for 5 min after $\gamma$ irradiation of the samples for 10 and 5 min at 77 K, respectively.

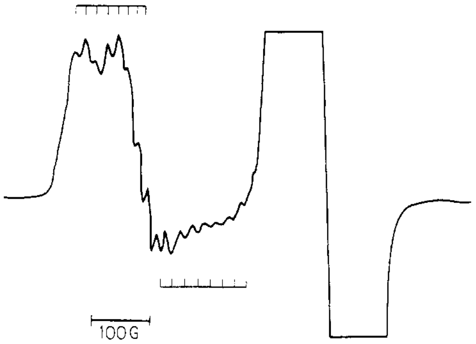

**Figure 3.** ESR spectrum of the reduced BzlCo(dmg)$_2$py in 2-methyltetrahydrofuran obtained with $\gamma$ irradiation of the sample for 30 min at 77 K.

absorption spectrum of the reduced MeCo(dmg)$_2$Im was very similar to that of the reduced MeCo(dmg)$_2$py. The spectra of these three reduced species have absorption peaks around 700 and 1000 nm. No significant differences were observed for these three reduced species. The molar extinction coefficient around 700 nm was estimated to be higher than $10^4$ $M^{-1}$ $cm^{-1}$ for these reduced methylcobaloximes.

**ESR Spectra.** Figure 3 shows the ESR spectrum observed for the $\gamma$-irradiated 2-methyltetrahydrofuran solution of BzlCo(dmg)$_2$py at 77 K. The spectrum shows eight characteristic hyperfine lines due to the interaction of the unpaired electron with the cobalt nucleus ($I = {}^7/_2$) for both parallel and perpendicular components. No superhyperfine (shf) lines due to a nitrogen atom of pyridine in the axial position were resolved. An intense absorption around $g = 2.00$ is ascribed to the solvent radicals produced by $\gamma$ radiolysis.

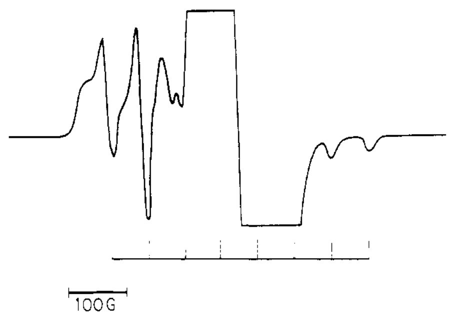

**Figure 4.** ESR spectrum of the reduced MeCo(dmg)$_2$py in 2-methyltetrahydrofuran obtained with $\gamma$ irradiation of the sample for 30 min at 77 K.

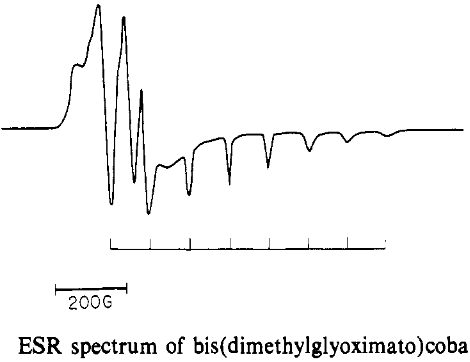

**Figure 5.** ESR spectrum of bis(dimethylglyoximato)cobalt(II) in methanol at 77 K.

The local symmetry of cobaloximes is considered to be $C_{2v}$ but is an effective $C_{4v}$.[13] The g and hyperfine tensors of the reduced BzlCo(dmg)$_2$py were determined to be $g_{\parallel} = 2.14 \pm 0.002$, $g_{\perp} = 2.254 \pm 0.002$, $A_{\parallel}^{Co} = (19.0 \pm 1.0) \times 10^{-4}$ cm$^{-1}$, and $A_{\perp}^{Co} = (18.4 \pm 1.0) \times 10^{-4}$ cm$^{-1}$.

The ESR spectrum observed for the $\gamma$-irradiated 2-methyltetrahydrofuran solution of ClCo(dmg)$_2$py at 77 K was very similar to that shown in Figure 3. No shf structures due to $Cl^-$ and a nitrogen atom of pyridine in the axial position were observed.

Figure 4 shows the ESR spectrum observed for the $\gamma$-irradiated 2-methyltetrahydrofuran solution of MeCo(dmg)$_2$py at 77 K. From the spectrum, one can observe two of eight parallel lines and a part of the perpendicular component. By the assumption that the parallel lines are equally spaced, the values of $g$ and $A^{Co}$ were determined to be $2.002 \pm 0.002$ and $(58.4 \pm 1.0) \times 10^{-4}$ cm$^{-1}$, respectively. The shf structure due to pyridine was not resolved in the spectrum.

Similar ESR spectra were obtained with $\gamma$ radiolysis of 2-methyltetrahydrofuran solutions of MeCo(dmg)$_2$H$_2$O and MeCo(dmg)$_2$Im.

Figure 5 shows the ESR spectrum of bis(dimethylglyoximato)cobalt(II) ($Co^{II}$(dmg)$_2$) prepared by mixing dimethylglyoxime and cobalt acetate in methanol. This spectrum is the same as that reported by Rockenbauer et al.,[13] who determined the ESR parameters of $Co^{II}$(dmg)$_2$ in methanol to be $g_{\parallel} = 2.0106$, $g_{\perp} = 2.236$, $A_{\parallel}^{Co} = 102.0 \times 10^{-4}$ cm$^{-1}$, and $A_{\perp}^{Co} = 28.6 \times 10^{-4}$ cm$^{-1}$. When methanol was replaced with 2-methyltetrahydrofuran, the ESR parameters obtained at 77 K were $g_{\parallel} = 2.014 \pm 0.002$, $g_{\perp} = 2.27$ (approximate value), $A_{\parallel}^{Co} = (127.7 \pm 1.0) \times 10^{-4}$ cm$^{-1}$, and $A_{\perp}^{Co} = 47.6 \times 10^{-4}$ cm$^{-1}$ (approximate value).

In Table I are listed the ESR parameters of the reduced alkylcobaloximes and the related compounds. The hyperfine tensors of the reduced ClCo(dmg)$_2$py and alkylcobaloximes

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[13] Rockenbauer, A.; Budó-Záhonyi, E.; Simándi, L. I. *J. Chem. Soc., Dalton Trans.* **1975**, 1792.

**Table I.** ESR Parameters of the Reduced Cobaloximes and Related Compounds at 77 K

| | $g_\parallel$ | $10^4 A_\parallel^{Co}$, cm$^{-1}$ | $g_\perp$ | $10^4 A_\perp^{Co}$, cm$^{-1}$ | solvents |
|---|---|---|---|---|---|
| $[BzlCo(dmg)_2py]^-$ | 2.140 ± 0.002 | 19.0 ± 1.0 | 2.254 ± 0.002 | 18.4 ± 1.0 | 2-MeTHF[c] |
| $[ClCo(dmg)_2py]^-$ | 2.140 ± 0.002 | 19.0 ± 1.0 | 2.252 ± 0.002 | 18.4 ± 1.0 | 2-MeTHF |
| $[MeCo(dmg)_2py]^-$ | 2.002 ± 0.002 | 58.4 ± 1.0 | 2.11[a] | | 2-MeTHF |
| $[MeCo(dmg)_2H_2O]^-$ | 2.002 ± 0.002 | 58.4 ± 1.0 | 2.11[a] | | 2-MeTHF |
| $[MeCo(dmg)_2Im]^-$ | 2.002 ± 0.002 | 58.4 ± 1.0 | 2.11[a] | | 2-MeTHF |
| $Co^{II}(dmg)_2$ | 2.014 ± 0.002 | 127.7 ± 1.0 | 2.27[a] | 47.6 | 2-MeTHF |
| $Co^{II}(dmg)_2$[b] | 2.0106 | 102.0 | 2.236 | 28.6 | MeOH |
| $Co^{II}(dmg)_2py$[b] | 2.0137 | 86.5 | 2.24 | 15 | MeOH |
| $Co^{II}(dmg)_2(py)_2$[b] | 2.0161 | 78.0 | 2.205 | 9.0 | MeOH |
| $Co^{II}(dmg)_2(py)_2$ | 2.015 ± 0.002 | 84.1 ± 1.0 | 2.260[a] | | 2-MeTHF |

[a] Approximate value. [b] Reference 13. [c] 2-Methyltetrahydrofuran.

differ significantly from those of $Co^{II}(dmg)_2$, $Co^{II}(dmg)_2py$, and $Co(dmg)_2(py)_2$.

**Thermal Reactions of Reduced Species.** The γ-irradiated samples were warmed from 77 K to room temperature. ESR signals of the reduced $ClCo(dmg)_2py$ and $BzlCo(dmg)_2py$ disappeared completely after recooling the samples to 77 K. The probable reactions are represented as

$$[ClCo(dmg)_2py]^- \rightarrow Cl^- + Co^{II}(dmg)_2py \qquad (1)$$

$$[BzlCo(dmg)_2py]^- \rightarrow C_6H_5CH_2^- + Co^{II}(dmg)_2py \qquad (2)$$

The product, $Co^{II}(dmg)_2py$, changes into a diamagnetic dinuclear cobalt complex at low temperature:[14,15]

$$2Co(dmg)_2py \rightleftarrows [Co^{II}(dmg)_2py]_2 \qquad (3)$$

In order to confirm reactions 1–3, the methyltetrahydrofuran solutions of $ClCo(dmg)_2py$ and $BzlCo(dmg)_2py$ were irradiated in the presence of 1.0 M pyridine at 77 K. The optical absorption and ESR spectra observed at 77 K were identical with those obtained with the irradiated solutions in the absence of pyridine. The irradiated samples were warmed from 77 K to room temperature. After they were recooled to 77 K, the two samples gave the same ESR signal, which has the parallel components of $^{57}Co$ hyperfine structures with well-resolved shf lines (1:2:3:2:1, quintet) due to two nitrogen atoms of two pyridine molecules in the axial positions. This fact evidently indicates the presence of $Co^{II}(dmg)_2(py)_2$[12] in these solutions. The formation of $Co^{II}(dmg)_2(py)_2$ can be interpreted as

$$Co(dmg)_2py + py \rightarrow Co^{II}(dmg)_2(py)_2 \qquad (4)$$

where $Co^{II}(dmg)_2py$ is produced by reactions 1 and 2.

No ESR signal was observed for the reduced methylcobaloximes after warming the irradiated samples to room temperature and recooling them to 77 K. When 2-methyltetrahydrofuran solutions of $CH_3Co(dmg)_2py$ containing 1.0 M pyridine were irradiated at 77 K, the ESR and optical absorption spectra were the same as those obtained with the irradiated solutions in the absence of pyridine. The irradiated sample, contrary to the cases of $ClCo(dmg)_2py$ and $BzlCo(dmg)_2py$, did not show any ESR signal after warming to room temperature and recooling them to 77 K. This implies that $Co^{II}(dmg)_2py$ is not produced from the reduced methylcobaloximes. The probable bond cleavage is shown as

$$[CH_3Co(dmg)_2py]^- \rightarrow CH_3\cdot + Co^{I}(dmg)_2py \qquad (5)$$

Schrauzer and Windgassen[3] have studied the polarographic reduction of methylcobaloximes at room temperature and revealed that the addition of an electron to a methylcobaloxime is accompanied by the cleavage of the Co–C bond:

$$CH_3Co(dmg)_2B + e^- \rightarrow CH_3\cdot + Co^{I}(dmg)_2B \qquad (6)$$

where B is a base component in the axial position. The bond cleavage of the reduced methylcobaloxime, therefore, is confirmingly represented by reaction 5.

## Discussion

**Reduced Species at 77 K.** In radiation chemistry, 2-methyltetrahydrofuran is frequently used as a solvent suitable for producing anion radicals of organic molecules. The radiolytic mechanism is represented as shown in eq 7 and 8,[16]

$$\text{2-MeTHF} \rightsquigarrow \text{2-MeTHF}^{+}\cdot + e^- \qquad (7)$$

$$\text{2-MeTHF}^{+}\cdot + \text{2-MeTHF} \rightarrow \text{2-MeTHFH}^{+} + \text{2-MeTHF}\cdot \qquad (8)$$

where 2-MeTHF, 2-MeTHF$^{+}\cdot$, 2-MeTHFH$^{+}$, and 2-MeTHF· are the 2-methyltetrahydrofuran molecule, cation radical, protonated molecule, and neutral radical, respectively.[17] The cation radicals, 2-MeTHF$^{+}\cdot$, react rapidly with 2-MeTHF to produce stable 2-MeHTFH$^{+}$ and 2-MeTHF· at 77 K (reaction 8). On the other hand electrons are less reactive toward 2-MeTHF, and in the presence of solute molecules (S), they react with S to produce the anion radicals ($S^{-}\cdot$). In glassy solutions at 77 K, these anion radicals are trapped stably and are subject to conventional spectral measurements:

$$e^- + S \rightarrow S^{-}\cdot \qquad (9)$$

This low-temperature matrix technique can be applied to the observation of one-electron reduced species of metal complexes. In a previous study of chloro(tetraphenylporphinato)cobalt(III) ($ClCo^{III}TPP$), the structure of the reduced species was described as $Cl^-\cdots Co^{II}TPP$ in which $Cl^-$ is forced to be confined in the axial position due to the solvent rigidity at 77 K and this transient complex was termed constrained complex.[9] The ESR parameters of the constrained complex have rather larger $g_\parallel$ and smaller $A_\parallel^{Co}$ than those of $Co^{II}TPP$ free from $Cl^-$. On the basis of the theory proposed by McGarvey,[18] these ESR parameters were interpreted by assuming that the $A_1^2$ state of $Co^{II}TPP$ is mixed with the higher excited states by strong electrostatic perturbation due to $Cl^-$ in the axial position.

The ESR parameters of the reduced $ClCo(dmg)_2py$ and $BzlCo(dmg)_2py$ determined in the present study indicate that these species have the constrained complex structure. The hyperfine splitting due to the axial ligand is frequently observed for cobaloximes having the electronic state of $A_1^2$.[13,15] The two constrained complexes, however, do not show the shf splitting due to a nitrogen atom of pyridine in the axial position. This result is explained by the decrease in contribution of $A_1^2$ to the electronic state of $Co^{II}(dmg)_2py$ resulting from mixing of it with the higher excited states. The probable structures of the two reduced species are represented as

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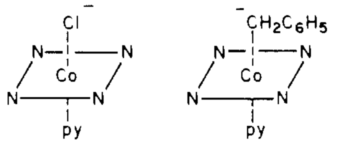
(14) Rockenbauer, A.; Budő-Záhonyi, E.; Simándi, L. I. *J. Coord. Chem.* **1972**, *2*, 53.

(15) Schrauzer, G. N.; Lee, L.-P. *J. Am. Chem. Soc.* **1968**, *90*, 6541.

(16) Kevan, L. *Actions Chim. Biol. Radiat.* **1971**, *15*, 81.

(17) Hoshino, M.; Arai, S.; Imamura, M. *Radiat. Phys. Chem.* **1980**, *15*, 377.

(18) McGarvey, B. R. *Can. J. Chem.* **1975**, *53*, 2498.



The fact that no shf splittings due to Cl are observed for the ESR spectrum of the reduced $ClCo(dmg)_2py$ is interpreted by considering dissociation of the Co–Cl bond as in the case of the reduced $ClCo^{III}TPP$.[9] The distance, $Co–Cl^-$, in the reduced $ClCo(dmg)_2py$ is considered to be short enough for $Cl^-$ to exert strong effects on the $d_{z^2}$ orbital of the cobalt atom.

Manov and his co-workers[19] studied the ESR spectrum of $[Co^{II}(dmg)_2Cl_2]^{2-}$ produced in alcohol solutions of $Co^{II}(dmg)_2$ containing high concentrations of $Cl^-$ at low temperatures. The spectrum shows a weak interaction of the cobalt atom with the two $Cl^-$. Presumably, the distance, $Co–Cl^-$, in $[Co^{II}(dmg)_2Cl_2]^{2-}$ is much longer than that of the reduced $ClCo(dmg)_2py$.

The ESR and optical absorption spectra of the reduced $BzlCo(dmg)_2py$ are very similar to those of the reduced $ClCo(dmg)_2py$, indicating that the Co–C bond is also dissociated. It is noted that the absorption spectra of these constrained complexes resemble those of $Co^{II}(dmg)_2$ and its homologues.[13]

For the reduced methylcobaloximes, the ESR parameters are distinctly different from those of the constrained complexes and cannot be interpreted by assuming the structure as $CH_3^- \cdots Co^{II}(dmg)_2B$ (B = $H_2O$, py, or Im). In fact, the absorption spectra of the reduced methylcobaloximes differ clearly from those of the reduced $ClCo(dmg)_2py$ and $BzlCo(dmg)_2py$. Green et al.[20] explained the stable Co–C bond in alkylcobaloximes in terms of the energy diagram of the cobalt 3d orbitals. From the bonding scheme of the alkylcobaloximes, the excess electron captured by them is expected to occupy the antibonding orbital of the Co–C bond or $3d_{x^2-y^2}$ of the cobalt atom. The former assumption is plausible from the following reasons: (1) No shf structures due to four nitrogen atoms in plane were observed for the parallel and perpendicular components in the ESR spectra of the reduced methylcobaloximes.[21] (2) The features of the ESR spectra observed for the reduced methylcobaloximes are very similar to those for $Co^{II}(dmg)_2$. (3) The values of $A_{\parallel}^{Co}$ of the reduced methylcobaloximes are nearly 67% of that of $Co^{II}(dmg)_2py$,[22] indicating that the unpaired electron should be spread partly outside the cobalt atom.

The shf structure due to $CH_3$ was not resolved in the ESR spectrum of the reduced $CH_3Co(dmg)_2py$. It is likely that the shf structure is hidden within the line width of the spectrum because of a small density of the unpaired electron located on $CH_3$. No shf structure due to a nitrogen atom of pyridine was observed for the two parallel lines of the reduced $CH_3Co(dmg)_2py$. This may be due to the increase in the line width on going to higher fields.[13]

Extensive studies carried out by Schrauzer[4] on the reductive cleavage of the Co–C bond of methylcobaloximes under various reducing conditions support the view that the excess electron occupies the antibonding molecular orbital of the Co–C bond ($\sigma^*$). The intense absorption peaks of a reduced methylcobaloxime and $Co^{II}(dmg)_2$ are located around 700 and 475 nm, respectively. Because of their strong intensities the former is assumed to be due to an electronic transition from $\sigma^*$ and the latter from $d_{z^2}$ to ligand $\pi$ orbitals. The orbital energy level of $\sigma^*$ is considered to be higher than that of $d_{z^2}$. The absorption peak of the reduced methylcobaloxime, therefore, is deduced to be located at a wavelength longer than that of $Co^{II}(dmg)_2$.

**Chemical Reactions of the Reduced Species.** The reductive cleavage of the chemical bonds in organic molecules has frequently been observed.[12]

$$R–X + e^- \rightarrow R\cdot + X^- \qquad (10)$$

This dissociative electron attachment occurs whenever

$$A(X) > D(R–X) \qquad (i)$$

and

$$A(X) > A(R) \qquad (ii)$$

where $D(R–X)$ is the bond dissociation energy of the R–X bond and $A(X)$ and $A(R)$ are the electron affinities of X and R, respectively.[12] The relationship between the electron affinity and the bond dissociation energy is also represented by eq i and ii for the reductive cleavage of the cobaloximes in the present study.

The reduced $ClCo(dmg)_2py$ dissociates into $Cl^-$ and $Co^{II}(dmg)_2py$. This result implies

$$A(Cl) > D(Cl–Co) \qquad (iii)$$

and

$$A(Cl) > A(Co) \qquad (iv)$$

where $D(Cl–Co)$ and $A(Co)$ are the dissociation energy of the Co–Cl bond and the electron affinity of $Co(dmg)_2py$, respectively. For $BzlCo(dmg)_2py$, similar to $ClCo(dmg)_2py$

$$A(Bzl) > D(Bzl–Co) \qquad (v)$$

and

$$A(Bzl) > A(Co) \qquad (vi)$$

where $D(Bzl–Co)$ is the dissociation energy of the Bzl–Co bond.

The electron affinities of Cl and a benzyl radical are reported to be 3.7 and 1.8 eV, respectively.[23] From eq iv–vi and from $A(Cl)$ and $A(Bzl)$ it is deduced that

$$A(Co) < 1.8 \text{ eV} \qquad (vii)$$

and

$$D(Bzl–Co) < 1.8 \text{ eV} \qquad (viii)$$

The reduced $CH_3Co(dmg)_2py$ dissociates into a methyl radical and $Co^I(dmg)_2py$. Therefore

$$A(Co) > D(Me–Co) \qquad (ix)$$

and

$$A(Co) > A(Me) \qquad (x)$$

where $D(Me–Co)$ is the dissociation energy of the $CH_3$–Co bond. From eq vii and ix and from the electron affinity of the methyl radical (1.08 eV),[23] one obtains

$$1.8 \text{ eV} > A(Co) > 1.08 \text{ eV} \qquad (xi)$$

By the substitution of eq xi into ix, $D(Me–Co)$ is estimated as

$$D(Me–Co) < 1.8 \text{ eV} \qquad (xii)$$

From eq viii and xii, the dissociation energy of the Co–C bond

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is concluded to be lower than 1.8 eV for BzlCo(dmg)$_2$py and CH$_3$Co(dmg)$_2$py.

Recently, Halpern et al.[24] estimated the Co–C bond dissociation energy of C$_6$H$_5$(CH$_3$)CHCo(dmg)$_2$py to be 19.9 kcal. This value is in a range of the estimated one in the present study.

In 1974, Seki et al.[25] studied the reductive cleavage of vitamin B$_{12}$ and coenzyme B$_{12}$. They reported that the reduced vitamin B$_{12}$ dissociates into vitamin B$_{12r}$ and CN$^-$, whereas the reduced coenzyme B$_{12}$ dissociates into B$_{12s}$ and an organic radical. According to the present results, the difference in the dissociation reaction between the reduced vitamin B$_{12}$ and coenzyme B$_{12}$ is interpreted by the larger electron affinity of CN (3.8 eV)[23] and smaller one of the organic radical than that of vitamin B$_{12r}$. The dissociation energy of the Co–C bond in the coenzyme should be smaller than the electron affinity of vitamin B$_{12r}$.

**Registry No.** [BzCo(dmg)$_2$py]$^-$, 54388-32-8; [ClCo(dmg)$_2$py]$^-$, 79391-64-3; [MeCo(dmg)$_2$py]$^-$, 54388-33-9; [MeCo(dmg)$_2$H$_2$O]$^-$, 79391-65-4; [MeCo(dmg)$_2$Im]$^-$, 79391-66-5; Co$^{II}$(dmg)$_2$, 36451-49-7.

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# Electron Transfer between a Cobalt Clathrochelate and Ferrocene in Acetonitrile

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The kinetics of electron transfer between the clathrochelate Co(dmg)$_3$(BF)$_2$BF$_4$ (dmg is the deprotonated dimethylglyoxime ligand) and ferrocene has been studied in acetonitrile as a function of concentration, temperature, and added *n*-Bu$_4$NBF$_4$. With no added electrolyte, the reaction is second order with a rate constant of $(1.6 \pm 0.1) \times 10^4$ M$^{-1}$ s$^{-1}$ (25 °C), a $\Delta H^{\ddagger}$ of 8.4 kcal/mol, and a $\Delta S^{\ddagger}$ of −11 cal/(mol deg). In the presence of 0.5 M *n*-Bu$_4$NBF$_4$ the rate constant is decreased by a factor of 1.8 and the activation parameters found are a $\Delta H^{\ddagger}$ of 8.2 kcal/mol and $\Delta S^{\ddagger}$ of −13 cal/(mol deg). The equilibrium constant measured for the reduction of the Co(III) complex by ferrocene at 25 °C and 0.05–0.5 M salt determined from pulse polarography measurements is 0.33. For 0.1 M electrolyte, $\Delta H^\circ$ was found to be 5.0 kcal/mol and $\Delta S^\circ$ to be 15 cal/(mol deg). From the above information and literature data, the Marcus theory was used to calculate an electron self-exchange rate constant for the cobalt complex of $1.1 \times 10^2$ M$^{-1}$ s$^{-1}$ ($\Delta H^{\ddagger} = 7.3$ kcal/mol; $\Delta S^{\ddagger} = -25$ cal/(mol deg)). This value is similar to the value of the self-exchange of Co(phenanthroline)$_3{}^{3+/2+}$. This system is a prototype for further detailed studies of nonaqueous electron transfer and theoretical analysis of the special case of electron transfer without the involvement of electrostatic work in precursor or successor complex formation.

The study of electron-transfer reactions has long been an active area of research. This activity has expanded during the last decade, with extensive experimental studies of bioinorganic systems[1,2] as well as classical inorganic[3,4] and some organometallic reactions.[5] Theoretical work has also been pursued, especially with reference to the distance dependence of electron-transfer efficiency and the quantum-mechanical details of the electron-transfer process.[6] There are also predictions[7,8] of the dependence of rate constants on the properties of solvents, although most studies have been done in aqueous solution.

Outer-sphere electron-transfer reactions, in which no bonds are made or broken, are the easiest to analyze mechanistically and theoretically, and the most complete theory has been developed for these reactions. The theoretical treatment most often applied to experimental data is that of Marcus as promulgated by Sutin.[7] In order to ensure that the reactions are limited to an outer-sphere pathway, it is sufficient to work with complexes that are substitution inert in the oxidation states used. It is also helpful if the complexes can be modified to change their size and structure so that aspects such as electrostatic interaction, solvation, electron-transfer distance, and ligand conjugation can be studied. The clathrochelates, ligands that form three-dimensional cages, are ideal for such studies.

The system chosen for this initial work involves the clathrochelate Co(dmg)$_3$(BF)$_2$BF$_4$, where dmg is the doubly deprotonated dimethyglyoxime ligand. This complex, initially synthesized by Rose and co-workers,[9] is formed by capping the N-bonded tris-chelate form of the tris(dimethylglyoxime)cobalt(III) ion with BF$_3$. This links the three free oxygen atoms on each of two opposite faces and forms a symmetric and stable complex. The Co–N bond is only 0.08 Å longer in the low-spin Co(II) complex than in the Co(III) complex.[10] The electron-transfer partner should have a similar electrochemical potential and should have well-known electron-transfer reactivity. The requirement for a similar potential arises from the need for a relatively low driving force. Highly exergonic reactions may be too rapid and also may deviate from theory because of the high-energy paths that are available to them.[11,12] Ferrocene meets these requirements well, and its electron-transfer reactivity has recently been carefully studied by Wahl and co-workers, who measured the electron

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