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Dimerization of the Octaethylporphyrin *π* Cation Radical Complex of Cobalt(II): Thermodynamic, Kinetic, and Spectroscopic Studies

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Introduction

One electron oxidation of cobalt(II) porphyrins can occur from either the cobalt d or porphyrin π orbitals depending on the choice of porphyrin and reaction media.[1−12] Oxidation of (octaethylporphyrinato)cobalt(II), (OEP)Co^{II} (**1**), in the presence of ligands such as H_2O and CO produces diamagnetic five and six coordinate complexes of cobalt(III).[1−6] In the absence of additional ligands to coordinate with Co(III) the first oxidation of (OEP)Co^{II} occurs from a porphyrin π MO to produce a π cation radical complex of cobalt(II), [(OEP)Co^{II}]$^+$ (**2**).[1,4] Metalloporphyrin π cation radical complexes and dimers of the OEP derivatives have been extensively investigated.[13−30] This article reports on the interconversion of the paramagnetic ($S = 1$) monomer, [(OEP)Co^{II}]$^+$ (**2**), with a diamagnetic dimer, [(OEP)Co^{II}]$_2^{2+}$ (**3**), in dichloromethane solvent. ^{1}H NMR shift and line width studies in CD_2Cl_2 are applied in evaluating the thermodynamic and activation parameters for homolytic dissociation of the diamagnetic dimer (**3**).

Experimental Methods and Analysis

Dichloromethane-d_2 (99.6 atom % D) was placed in a vacuum transfer tube containing P_2O_5 to scavenge for residual water and then degassed by multiple freeze−pump−thaw cycles. (OEP)Co^{II} and (OEP)Zn^{II} were purchased from Aldrich, and anhydrous $AgBF_4$ was purchased from Alfa and stored in an inert-atmosphere box under argon prior to use. Solutions of [(OEP)Co^{II}]$^+BF_4^-$ were prepared by mixing (OEP)Co^{II} and $AgBF_4$ in dicholoromethane using the published procedure for the formation of [(OEP)Co^{II}]$^+ClO_4^-$.[1] Solid samples of (OEP)Co^{II} (1.0−1.7 mg) and a stoichiometric quantity of solid anhydrous $AgBF_4$ were weighed in an inert-atmosphere box and placed in 507 PP Wilmad NMR tubes equipped with a stopcock and then attached to a vacuum line for evacuation. Solution samples were prepared by vacumm transfer of 0.35 mL of dried, degassed dichloromethane-d_2 into the NMR tubes, which were subsequently flame sealed.

Activation parameters for dissociation of the diamagnetic dimer [(OEP)Co^{II}]$_2^{2+}$ into paramagnetic monomers [(OEP)Co^{II}]$^+$ were determined from the temperature dependence of the ^{1}H NMR line width. The expression that relates the ^{1}H NMR line width changes to the rate of dissociation of the diamagnetic dimer is given by eq 1.[31−35]

$$\pi\Delta\nu_{1/2(\mathrm{ex})} = T_{2(\mathrm{ex})}^{\ \ -1} = \tau_\mathrm{d}^{\ -1}[(A\tau_\mathrm{p}/2)^2][1 + (A\tau_\mathrm{p}/2)^2]^{-1} \qquad (1)$$

Equation 1 reduces to $T_{2(\mathrm{ex})}^{\ \ -1} = \tau_\mathrm{d}^{\ -1}$ for nuclei in paramagnetic species where the mean lifetime (τ_p) is long and the electron−nuclear coupling constant (A radians s^{-1}) is large ($(A\tau_\mathrm{p}/2)^2 \gg 1$). The apparent mean lifetime for the diamagnetic species (τ_d) that results from the observed $T_{2(\mathrm{ex})}^{\ \ -1}$ yields the rate constant ($\tau_\mathrm{d}^{\ -1} = k_\mathrm{app}$) for bond homolysis events that result in paramagnetic species that produce efficient nuclear relaxation ($(A\tau_\mathrm{p}/2)^2 \gg 1$).

Thermodynamic values for the dissociation of [(OEP)Co^{II}]$_2^{2+}$(BF_4^-)$_2$ were obtained from analysis of ^{1}H NMR chemical shift measurements at a series of temperatures (300−360 K) where **2** and **3** are in limiting fast interchange. Nonlinear least squares curve fitting of the measured δ_obs values at a series of temperatures to eq 2 gives the best fit values

$$\begin{aligned}\delta_\mathrm{obs} = \delta_\mathrm{D} + \delta_\mathrm{D}/(4[\mathrm{M}]_\mathrm{i})[\mathrm{e}^{-\Delta H°/RT}\mathrm{e}^{\Delta S°/R} - (\mathrm{e}^{-2\Delta H°/RT}\mathrm{e}^{2\Delta S°/R} + \\ 8[\mathrm{M}]_\mathrm{i}\mathrm{e}^{-\Delta H°/RT}\mathrm{e}^{\Delta S°/R})^{1/2}] + 1/(4[\mathrm{M}]_\mathrm{i})[-\mathrm{e}^{-\Delta H°/RT}\mathrm{e}^{\Delta S°/\mathrm{R}} + \\ (\mathrm{e}^{-2\Delta H°/RT}\mathrm{e}^{2\Delta S°/R} + 8[\mathrm{M}]_\mathrm{i}\mathrm{e}^{-\Delta H°/RT}\mathrm{e}^{\Delta S°/R})^{1/2}](C_\mathrm{M}T^{-1} + \delta_\mathrm{Mo}) \quad (2)\end{aligned}$$

for $\Delta H°$ and $\Delta S°$ for dissociation of the dimer (D) and the slope of the temperature dependence (C_M) for the contact shift of the paramagnetic monomer (M).

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Results and Discussion

Oxidation of (OEP)Co^{II} by AgBF$_4$ in CH$_2$Cl$_2$. Reaction of AgBF$_4$ with (OEP)Co^{II} (**1**) in rigorously dried dichloromethane results in the one-electron oxidation of **1** to produce [(OEP)-Co^{II}]$^+$BF$_4^-$ (**2**), which is formulated as a porphyrin π cation radical complex of cobalt(II) on the basis of prior studies.[1] Large downfield ^{1}H NMR paramagnetic shifts are observed for the methylene (CH$_2$) and methine (═CH) protons in **2**. Assuming that the paramagnetic shifts are dominated by contact terms from π spin density, the paramagnetic shifts indicate that there is positive π spin density on the pyrrole carbons and negative π spin density on the methine carbons. Negative π spin density on the methine carbons is a clear indication that the π molecular orbital that contains the unpaired electron has a node at the methine carbon which is a defining characteristic for the a$_{1u}$ porphyrin π MO.[14,36,37] ^{1}H NMR contact shifts for **2** thus support the assignment of an unpaired electron to the a$_{1u}$ porphyrin π MO of [(OEP)Co^{II}]$^+$BF$_4^-$ [16] rather than the a$_{2u}$.[5] The most probable electron configuration for **2** places an unpaired electron in both the a$_{1u}$ porphyrin π and a$_{1g}$ cobalt (II) d$_{z^2}$ orbitals, which corresponds to an ^{3}A$_{1u}$ ground state.

Dimerization of [(OEP)Co^{II}]$^+$BF$_4^-$ in CH$_2$Cl$_2$. Dichloromethane solutions of [(OEP)Co^{II}]$^+$BF$_4^-$ (**2**) experience changes in the electronic spectrum as the temperature is lowered that are indicative of the dimerization of **2** to [(OEP)Co^{II}]$_2^{2+}$ (**3**). A multiplicity of peaks including two prominent bands in the Soret region (391 nm, 352 nm) and at least one new broad transition in the near-IR region centered at 870 nm are particularly characteristic features for the electronic spectrum of **3** (see Supporting Information). Similar electronic spectral changes are observed in the dimerization of Zn(II) and Mg(II) octaethylporphyrin π cation radical complexes.[14,15] Near-IR bands at 920 and 950 nm, respectively, in the cation radical dimers [(OEP)-Zn]$_2^{2+}$ (**4**)[15] and [(OEP)Mg]$_2^{2+}$ (**5**)[14] have been assigned to transitions from the filled bonding to the empty antibonding molecular orbitals that result from interporphyrin cation radical $\pi-\pi$ interactions. This assignment has also been suggested for the near-IR bands observed for a series of cationic metalloporphyrin dimers[17] and is the probable origin for the 793 and 870 nm bands in [(OEP)Rh]$_2^{2+}$(BF$_4^-$)$_2$ (**6**)[18] and [(OEP)Co^{II}]$_2^{2+}$-(BF$_4^-$)$_2$, respectively.

The methine hydrogen NMR chemical shifts for [(OEP)Zn]$_2^{2+}$ (δ = 3.49) and [(OEP)Rh]$_2^{2+}$ (δ = 4.70) are dramatically changed from a typical aromatic OEP position ($\delta \sim 10$). The methine ^{1}H NMR shift positions in **4** and **6** approach the values for localized olefins ($\delta \sim 3-5$), which is a consequence of interruption of the porphyrin aromaticity and associated π electron ring current by cation dimer formation.[15,18] The methine hydrogens of **3** experience a large upfield shift (δ = 7.22) relative to normal aromatic porphyrin complexes such as (OEP)-Co−I (δ = 10.47). However, the magnitude of the shift for [(OEP)Co^{II}]$_2^{2+}$ (**3**) is only about half that observed for [(OEP)-Rh]$_2^{2+}$ (**6**) and [(OEP)Zn]$_2^{2+}$ (**4**) (Table 1), which indicates that **3** retains more aromaticity and ring current than **4** or **6**.

Activation Parameters for Dissociation of Diamagnetic Dimers into Paramagnetic Monomers from ^{1}H NMR Relaxation Studies. ^{1}H NMR spectra for the methine hydrogens in the diamagnetic dimer, [(OEP)Co^{II}]$_2^{2+}$ (**3**), in dichloromethane for the temperature range of 230−260 K manifest exchange broadening that results from dissociation of the diamagnetic dimer (**3**) into paramagnetic monomers [(OEP)Co^{II}]$^+$ (**2**) (Figure 1). Apparent activition parameters for dissociation of [(OEP)-Co^{II}]$_2^{2+}$ in CD$_2$Cl$_2$ were obtained from the temperature dependence of k_{app} for **3** and the use of transition state theory ($\Delta H^{\ddagger}_{app}$ = 18.7± 0.8 kcal mol^{-1} and $\Delta S^{\ddagger}_{app}$ = 27 ± 3 cal K^{-1} mol^{-1}) (Figure 2).

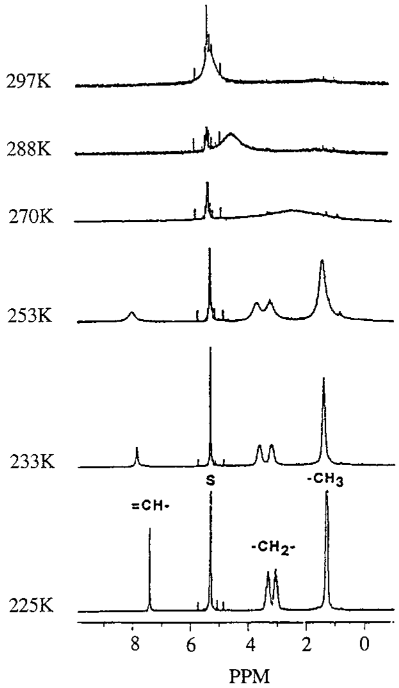

Figure 1. Temperature dependence of the ^{1}H NMR of [(OEP)-Co^{II}]$_2^{2+}$(BF$_4^-$)$_2$ in CD$_2$Cl$_2$ (225−297 K).

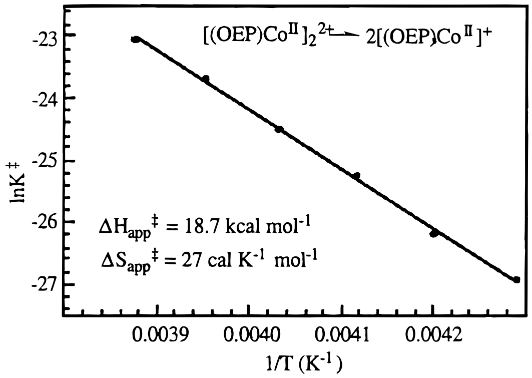

Figure 2. Determination of the activation parameters for dissociation of the diamagnetic dimer [(OEP)Co^{II}]$_2^{2+}$ into paramagnetic (S = 1) monomers [(OEP)Co^{II}]$^+$ in CD$_2$Cl$_2$ from the methine ^{1}H NMR line broadening.

Table 1. ^{1}H NMR Shifts (δ ppm) for [(OEP)M] Complexes in CD$_2$Cl$_2$

compound	T (K)	−CH═	−CH$_2$	−CH$_3$
[(OEP)Zn]$_2^{2+}$	219	3.49	1.42	0.56
[(OEP)Rh]$_2^{2+}$	293	4.70	1.93, 1.52	0.98
[(OEP)Co^{II}]$_2^{2+}$	200	7.22	3.16, 2.99	1.26
(OEP)Co−I	293	10.47	4.11	1.92
(OEP)Rh−I	293	10.31	4.18	1.98

The ^{1}H NMR line broadening method was also used to evaluate the kinetics for dissociation of the diamagnetic zinc dimer [(OEP)Zn]$_2^{2+}$(BF$_4^-$)$_2$ (**4**) in CD$_2$Cl$_2$. Analysis of the temperature dependence of the methine hydrogen line broadening yields activation parameters of $\Delta H^{\ddagger}$ = 17.7 ± 0.8 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 23 ± 3 cal K^{-1} mol^{-1} for dissociation of **4** into the

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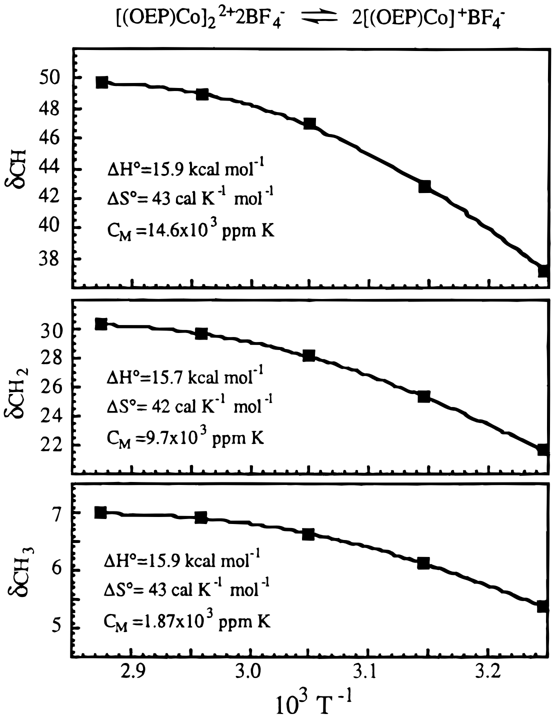

Figure 3. Points are observed chemical shifts (δ) for the methine (CH) and ethyl (CH_2 and CH_3) resonances for the limiting fast interchange of **3** and **2** as a function of temperature. The solid lines are calculated from eq 2 using the best fit $\Delta H°$ and $\Delta S°$ for dissociation of **3** and the slope (C_M) of the paramagnetic shift for **2**.

paramagnetic π cation radical monomer, $[(OEP)Zn]^+BF_4^-$ (see Supporting Information).

Thermodynamics of Dimerization of $[(OEP)Co^{II}]^+$ by ^1H NMR Shift Measurements. At temperatures greater than 300 K the 200 MHz ^1H NMR for a CD_2Cl_2 solution of **2** and **3** results from the limiting fast interchange of **2** and **3**. Thermodynamic values for the dissociation of $[(OEP)Co^{II}]_2^{2+}(BF_4^-)_2$ ($\Delta H° = 15.9 \pm 0.5$ kcal mol^{-1}; $\Delta S° = 43 \pm 3$ cal K^{-1} mol^{-1}) have been evaluated from the temperature dependence of the observed fast exchange averaged ^1H NMR shifts using eq 2 (Figure 3). The difference of ~2.8 kcal mol^{-1} between the enthalpy of dissociation ($\Delta H° = 15.9 \pm 0.5$ kcal mol^{-1}) and the activation enthalpy for dissociation ($\Delta H^{\ddagger} = 18.7 \pm 0.8$ kcal mol^{-1}) for **3** is in the range (2−3 kcal mol^{-1}) frequently observed for bond homolysis reactions of neutral molecules in low-viscosity media.[38] The very large positive entropy change observed for dissociation of **3** into the monocation **2** ($\Delta S° = 43$ cal K^{-1} mol^{-1}) probably results from the dication unit having larger interactions with the anions and solvent than occur for the monocationic monomers.

The activation enthalpy for dissociation of $[(OEP)Co^{II}]_2^{2+}$ ($\Delta H^{\ddagger} = 18.7 \pm 0.8$ kcal mol^{-1}) is comparable to that for $[(OEP)Zn]_2^{2+}$ ($\Delta H^{\ddagger} = 17.7 \pm 0.8$ kcal mol^{-1}) but substantially smaller than that for $[(OEP)Rh]_2^{2+}$.[18] The monomer units in $[(OEP)Zn]_2^{2+}$ (**4**) are held together in the dimer exclusively by interporphyrin cation radical $\pi-\pi$ interactions, but the bonding in $[(OEP)Rh]_2^{2+}$ (**6**) consists of a $Rh^{II}-Rh^{II}$ ($4d_{z^2}-4d_{z^2}$) bond in addition to interporphyrin $\pi-\pi$ bonding.[18] The diamagnetism, electronic spectrum, and ^1H NMR of $[(OEP)Co^{II}]_2^{2+}$ are consistent with the presence of both interporphyrin and intermetal bonding, but the $Co^{II}-Co^{II}$ ($3d_{z^2}-3d_{z^2}$) bonding is substantially smaller than in $[(OEP)Rh]_2^{2+}$ and the disruption of the porphyrin aromaticity through interporphyrin cation radical $\pi-\pi$ bonding is also less than that in either **4** or **6**.

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Supporting Information Available: Text giving experimental details and supporting electronic and ^1H NMR spectra for **2**−**4** are deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

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