

An Unusual Cobalt Complex. Reaction of Cobalt(II) Porphyrin with Iodine in Apolar Solvents

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A new bridged dimer has been obtained upon addition of iodine to cobaltous porphyrins in apolar solvents. Its 2:1 metal:iodine stoichiometry has been characterized by titration and kinetic measurements for its fully reversible formation. The structure of this complex, with I_2 as a bridge between the two cobaltous ions, was further evidenced by its magnetic properties and by its reactivity toward nitrogenous bases. On one hand, an antiferromagnetic coupling of the electron spins of the cobaltous ions in the bridged dimer was demonstrated by electron and proton magnetic resonance. On the other hand, kinetic measurements have shown that the oxidative dissociation of the dimer by imidazole is preceded by the fixation of two bases at the external coordination sites of the bridged complex.

Introduction

Pentacoordinated cobalt(II) porphyrins give reversible 1:1 complexes with molecular oxygen which are stable at room temperature.¹⁻⁵ Warming results in irreversible oxidation, but it is generally accepted that this reaction proceeds via a μ -peroxo intermediate.^{1,4,6-8} Such a binuclear complex has been recently stabilized by Chang⁹ using a cofacial cobalt(II) diporphyrin. A new cobalt(II) diporphyrin complex obtained with molecular iodine and stable at room temperature in apolar solvents²² has been characterized. Its physicochemical properties and its reactivity toward ligand coordination and oxidoreduction may be of interest for the general understanding of binuclear metalloporphyrin complexes, and its stability should favor investigations in the solid state.

Materials and Methods

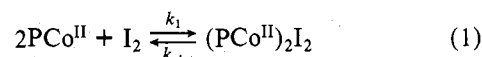
Cobalt(II) deuteroporphyrin IX dimethyl ester ($Co^{II}DPDMe$) and cobalt(II) *meso*- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin ($Co^{II}TPP$) were synthesized and purified according to the procedures of Caughey et al.¹⁰ and Adler, et al.¹¹ Benzene and toluene were of spectral grade. Ethyl acetate was distilled under nitrogen and kept over 4-Å molecular sieve. Doubly sublimated iodine was purchased from Prolabo. Imidazole was recrystallized from water and desiccated under vacuum.

ESR measurements were performed on a Varian V-4502 X-band spectrometer. Proton NMR spectra were recorded at 100 MHz on a Varian XL-100 spectrometer operated in the Fourier transform mode. Stopped-flow experiments were carried out by using a Durrum Instruments apparatus operated under anaerobic conditions when desired and thermostated at 30 °C.

Results

1. Formation of the Iodinated Complex. Addition of iodine to an anhydrous ethyl acetate solution of cobalt(II) deuteroporphyrin IX dimethyl ester results in drastic changes in the optical absorption spectrum; the Soret band broadens and collapses, while the α band grows at the expense of the β band and is blue-shifted by 2 nm (Figure 1). No concomitant absorption appears in the near-infrared range (700–1200 nm). This behavior does not depend on the presence of oxygen, and the iodinated product shows no spectral evolution for 2 months when kept in the dark in a sealed tube. On the other hand, the original PCo^{II} is completely recovered upon heating (60 °C) of a dried sample of the complex for 2 h under high vacuum (10^{-5} torr) as well as by gel filtration on Sephadex LH-20 in toluene. The reaction is thus entirely reversible.

Isosbestic points are observed as long as the concentration of I_2 is lower than that of PCo^{II} (PCo^{II} = cobaltous porphyrin). Further addition of I_2 results in a slight nonisobestic change of the Soret band without measurable evolution of absorption in the visible range. Spectrophotometric titrations in the latter region (480–600 nm) according to the continuous-variation method¹² give well-defined Job curves typical of the reversible formation of a 2:1 $PCo^{II}:I_2$ complex



$K_1 = k_1/k_{-1}$ is ca. $10^{12} M^{-2}$ in ethyl acetate at 30 °C. If the Job curves are drawn from measurements at the Soret band, however, a small deviation from the line shape expected from a pure 2:1 stoichiometry appears at high-molarity fractions of I_2 , which could agree with the formation of minute amounts of polymers of higher order. This is not observed by using benzene or toluene in which the evolution of the Soret band remains isosbestic.

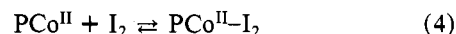
The kinetics of reaction of $Co^{II}DPDMe$ with I_2 in ethyl acetate have been investigated at 538 nm by using the stopped-flow technique and by varying the concentrations of I_2 or PCo^{II} (Table I). The complex appears without pre-equilibrium or side reaction. When there is a large excess of I_2 over PCo^{II} , the absorbance of the porphyrin follows a purely hyperbolic time dependence. This indicates that complex formation is second order in PCo^{II} , in agreement with the stoichiometry of reaction 1 which obeys the rate equation

$$dx/dt = k_1([I_2]_0 - x)([PCo^{II}]_0 - 2x)^2 - k_{-1}x \quad (2)$$

where x is the amount of complex produced at time t after mixing and $[I_2]_0$ and $[PCo^{II}]_0$ are the initial concentrations. Due to the high value of k_1 relative to k_{-1} , $k_{-1}x$ can be deleted from eq 2 provided $[I_2]_0 \geq 5[PCo^{II}]_0$. Under these conditions, integration of eq 2 results in the expression

$$\frac{1}{(2[I_2]_0 - [PCo^{II}]_0)^2} \left[\frac{2[I_2]_0 - [PCo^{II}]_0}{[PCo^{II}]_0} + \ln \frac{2[I_2]_0}{4[I_2]_0 - [PCo^{II}]_0} \right] = k_1 t_{1/2} \quad (3)$$

which permits an experimental determination of k_1 ($2.83 \times 10^9 M^{-2} s^{-1}$) and provides a check for the order in I_2 and PCo^{II} (Figure 2). Complex formation appears indeed to be a single-step process. However, the kinetic equation (3) still applies for a two-step reaction



in which the formation of the labile 1:1 intermediate is not rate limiting.

The substitution of $Co^{II}TPP$ for $Co^{II}DPDMe$ does not significantly alter the reaction at equilibrium. The former compound was preferred, owing to its higher solubility, for the investigation of the magnetic properties of the iodinated complex by ESR and proton NMR measurements. The ESR spectrum of $Co^{II}TPP$ in benzene at 77 K disappears as I_2 is added, and no residual paramagnetism remains if the amount

Table I. Kinetic Data for the Formation of the Iodinated Complex of $\text{Co}^{\text{II}}\text{DPDMe}$ in Ethyl Acetate at 30 °C

	$[\text{PCo}^{\text{II}}]_0 = 18 \mu\text{M}$					$[\text{PCo}^{\text{II}}]_0 = 24 \mu\text{M}$					
	12.5	25	50	125	250	0.125	0.25	0.375	0.50	1.00	1.50
$[\text{I}_2]_0, \text{mM}$	12.5	25	50	125	250	0.125	0.25	0.375	0.50	1.00	1.50
$10^{-6}L, \text{M}^{-2}$	28.57	12.40	5.90	2.25	1.10	1.72	0.847	0.559	0.419	0.209	0.141
$t_{1/2}, \text{ms}$	1100	440	200	75	40	62	34	21.5	14.0	7.2	5.0

^a L represents the left-hand side of eq 3.

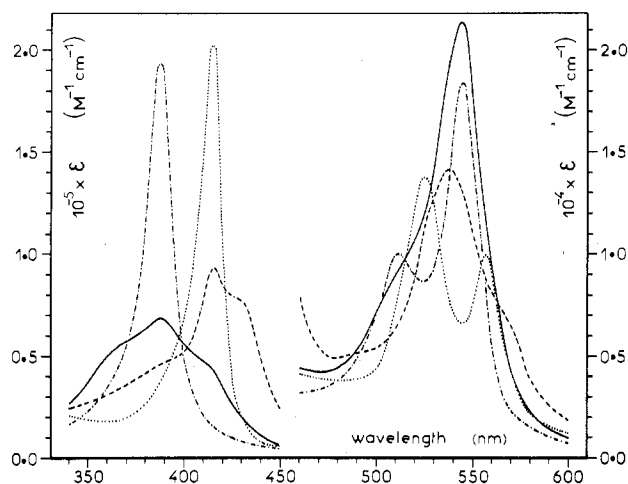


Figure 1. Absorption spectra of CoDPDMe derivatives in ethyl acetate: (---) PCo^{II} (λ_{max} 388, 513, 547 nm); (—) $\text{PCo}^{\text{II}}\text{-I}_2\text{-PCo}^{\text{II}}$ (λ_{max} 388, 545 nm); (-·-) $\text{Im-PCo}^{\text{II}}\text{-I}_2\text{-PCo}^{\text{II}}\text{-Im}$ (λ_{max} 416, 539 nm); (···) $(\text{Im-PCo}^{\text{II}}\text{-Im})^+\text{I}^-$ (λ_{max} 415, 525, 556 nm).

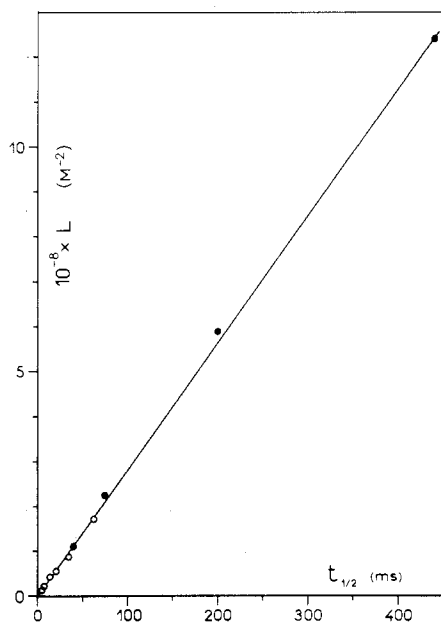


Figure 2. Effect of the concentration of $\text{Co}^{\text{II}}\text{DPDMe}$ (●, 18 μM ; ○, 24 μM) and I_2 on the half-formation time of the bridged diporphyrin complex. The conditions and the concentration function L are defined in Table I.

of I_2 is sufficient for a complete formation of the binuclear product. The absence of ESR absorption at $g = 2$ further indicates that no free radical due to porphyrin-ring oxidation¹³ is present. On the other hand, the proton NMR spectrum of paramagnetic $\text{Co}^{\text{II}}\text{TPP}$ in benzene- d_6 at 34 °C¹⁴ is modified upon addition of 1 equiv of I_2 ; then, the pyrrolic and phenyl proton resonances lie in a range characteristic of diamagnetic porphyrin complexes (Table II). In addition, the line widths of the resonances suggest a very slow rate of exchange due to dissociation of the complex, in agreement with the backward rate constant deduced from stopped-flow and equilibrium

Table II. ^1H NMR Chemical Shifts (ppm from Me_4Si , δ Positive for Low-Field Shifts) of CoTPP Complexes in Benzene- d_6 at 34 °C

	$\text{Co}^{\text{II}}\text{TPP}$	$(\text{Co}^{\text{II}}\text{TPP})_2\text{I}_2$	$(\text{TPP})\text{H}_2$
pyrrole H	15.95	9.13	8.75
phenyl H, ortho	12.98	8.12	8.30
phenyl H, meta	9.60	7.48	7.80
phenyl H, para	9.41	7.48	7.80

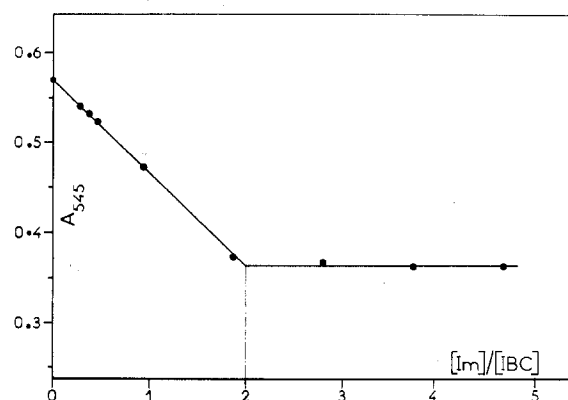


Figure 3. Imidazole concentration dependence of absorbance (545 nm) at the extrapolated dead-time of the stopped flow (2.2 ms) upon mixing of imidazole solutions with a fixed amount (10.7 μM) of the iodinated binuclear complex (IBC, preformed with the stoichiometric amount of I_2) of CoDPDMe in ethyl acetate.

measurements ($k_{-1} = 2.8 \times 10^{-3} \text{ s}^{-1}$).

2. Reaction of Imidazole with the Iodinated Complex. The addition of a 50-fold excess of imidazole (Im) to the iodinated complex of $\text{Co}^{\text{II}}\text{DPDMe}$ in ethyl acetate results in the rapid formation of a product characterized as the hexacoordinated cobaltic porphyrin^{15,16} $(\text{Im-PCo}^{\text{III}}\text{-Im})^+\text{I}^-$ in view of its spectral similarity (Figure 1) to bis(pyridine)¹⁷ and bis(histidine)¹⁸ cobaltic complexes. Exchange experiments show that I^- is the counterion in the complex. In fact, in ethyl acetate the addition of tetrabutylammonium iodide to the $(\text{Im-PCo}^{\text{III}}\text{-Im})^+\text{OH}^-$ complex (λ_{max} 416, 528, 559 nm), prepared by air-oxidation of PCo^{II} with excess imidazole and 50 mM H_2O , results in the formation of the same spectrally characterized complex as that obtained by reaction of imidazole with the iodinated adduct (λ_{max} 415, 525, 556 nm). Nearly identical spectra are obtained in benzene or toluene solution, agreeing with little or no solvent interaction at this stage.

However, the reaction of imidazole (up to 50 mM) with the preformed iodinated complex appears from stopped-flow measurements at 545 nm to be a three-step process. The first step is apparently diffusion controlled and corresponds to the irreversible chelation of two ligand molecules per mole of complex (Figure 3). The resulting compound (Figure 1) shows no evolution for several minutes when the $[\text{Im}]:[\text{PCo}^{\text{II}}\text{-I}_2\text{-PCo}^{\text{II}}]$ ratio does not exceed a 2:1 stoichiometry, but it is irreversibly oxidized into the cobaltic bis(imidazole) monomer through a biphasic reaction if the imidazole concentration is further increased (the whole kinetics is independent of the presence of oxygen; I_2 should thus be considered as the electron acceptor in the complex). The relative rates of these last two phases are nearly independent of the imidazole concentration, and the absorbance change involved in the

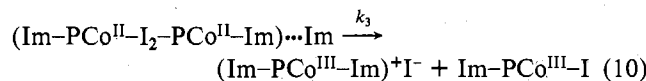
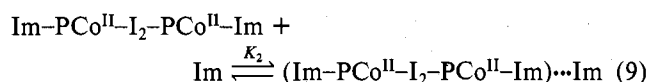
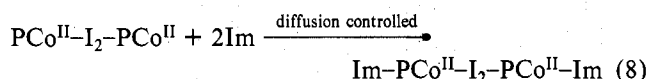
second phase remains ca. 4 times as large as that in the final step. This indicates that both steps are first order in imidazole; the apparent rate constant k_1 for the initial reaction fits linearly to the first power of the imidazole concentration through a Lineweaver-Burk double-reciprocal plot; i.e., k_1 obeys the equation

$$1/k_1 = a + b/[Im] \quad (6)$$

where a is 0.53 s and b is 29 mM s. In other words, the oxidoreductive splitting of the intermediate follows the initial rate equation

$$v_i = [IBC]_0[Im]/(b + a[Im]) \quad (7)$$

where $[IBC]_0$ is the "initial" concentration of the iodinated binuclear complex ($Im-PCo^{II}-I_2-PCo^{II}-Im$) which binds two imidazole molecules in the primary step. v_i tends to $[IBC]_0[Im]/b$ and $[IBC]_0/a$ as $[Im]$ goes to zero and to infinity, respectively. These saturation kinetics indicate that the irreversible splitting of the binuclear intermediate starts with the rapid and reversible attack by a third imidazole molecule. The last phase agrees well with the exchange of I^- for imidazole at the sixth coordination site of the cobaltic ion. These reactions therefore follow the scheme



Reaction 10 being the rate-limiting step, the initial rate of formation of the monomeric cobaltic species is

$$v_i = k_3 K_2 [IBC]_0 [Im] / (1 + K_2 [Im]) \quad (12)$$

with $k_3 = 1/a = 1.9 \text{ s}^{-1}$ and $K_2 = a/b = 18 \text{ M}^{-1}$.

Discussion

The formation of a stable 1:1 complex of cobalt(II) porphyrins with molecular iodine has not been observed, in contrast with the well-characterized superoxo complexes obtained with molecular oxygen.¹⁹ On the contrary, the reaction of iodine with cobalt(II) porphyrins results in the formation of a stable diporphyrin complex. The stoichiometry of this adduct has been demonstrated by titration and kinetic measurements which already suggest a bridged structure similar to that of the μ -peroxo dimers.^{4,9}

The "sandwiched" structure is further supported by the antiferromagnetic coupling of the cobaltous ion electron spins

and by the kinetic analysis of the dissociation by imidazole. A large alteration of the electronic properties of cobalt(II) in the iodinated adduct is revealed by the dramatic increase in affinity for imidazole compared to that for bare cobalt(II) porphyrin.⁶ The kinetic analysis also indicates the cooperative binding of two imidazole molecules at both external coordination sites, resulting in the formation of a bis(imidazole) diporphyrin intermediate (Figures 1 and 3). Covalent binding of a single base to each porphyrin ring²⁰ should permit one to obtain also a stabilized cobaltous dimer in the solid state. These iodinated bridged porphyrin dimers may exhibit unusual electrical conductivity as recently reported by Mertes and Ferraro²¹ for related tetraaza complexes of palladium crystallized in stoichiometric amount with iodine.

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Registry No. $PCo^{II}-I_2-PCo^{II}$, 70713-63-2; $(Co^{II}TPP)_2I_2$, 70713-64-3; $Im-PCo^{II}-I_2-PCo^{II}-Im$, 70713-62-1; $(Im-PCo^{III}-Im)^+ I^-$, 70713-61-0; $Co^{II}DPDMe$, 15892-11-2; $Co^{II}TPP$, 14172-90-8; $(TPP)H_2$, 917-23-7.

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- (22) The experiments reported herein have been performed in anhydrous ethyl acetate ($\epsilon_r = 6.02$), unless otherwise stated. In polar solvents, irreversible oxidoreduction occurs rapidly following addition of iodine to cobalt(II) porphyrins, and the product iodide may act as a counterion of the cobalt(III) porphyrins formed concomitantly.