Complex III was isolated as a light-yellow crystalline solid stable in the solid state even in air. The rather low, for a copper carbonyl, CO stretching frequency [$\nu_{CO}$ (Nujol) 1926 $cm^{-1}$] suggests the presence in III of a bridging CO,[3] while other unexpected details of the structure of III have been revealed by an X-ray analysis.

**Crystal Data**: $C_{44}H_{57}BCu_2N_4O_3$, $M$ = 827.9, monoclinic, $a$ = 31.875 (3), $b$ = 9.748 (1), $c$ = 14.344 (2) Å, $\beta$ = 95.50 (2)°, $Z$ = 4; $d_{calcd}$ = 1.239 g $cm^{-3}$, space group $I2$ (from systematic absences and structural analysis).[9] Intensity data were collected at the ambient temperature on an "on-line" single-crystal Siemens AED diffractometer using Cu K$\alpha$ radiation ($\lambda$ = 1.54178 Å, 6° < 2$\theta$ < 120°) at a takeoff angle of 6°. The pulse height discriminator was set to accept 90% of the Cu K$\alpha$ peak. For intensities and background the "five-point" technique[10] was used. A total of 3440 independent reflections were measured, of which 2993 were considered observed ($I > 2\sigma(I)$) and used in the structure determination and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques,[11] with anisotropic parameters for nonhydrogen atoms. The final $R$ index was 0.043.[12]

Figure 1 shows a view of the dimeric cation $[Cu_2(tmen)_2(\mu\text{-}CO)(\mu\text{-}PhCO_2)]^+$ with the most relevant bond distances and angles. Each copper has a pseudotetrahedral coordination geometry. The atoms of the two bridging ligands, CO and the carboxylato group, are nearly coplanar with Cu(1) and Cu(2), the dihedral angle between the planes Cu(2), C(13), O(3), Cu(1) and Cu(2), O(2), C(20), O(1), Cu(1) being 169°. The two planes containing copper and the nitrogen donor atoms Cu(1), N(1), N(2) and Cu(2), N(3), N(4) are practically orthogonal to the planes cited above.

The most relevant structural parameters concern (i) the Cu–C bond distances which are the longest so far encountered in copper carbonyl complexes as a consequence of the bridging mode of CO[1]—these distances fall in the range found in some copper alkyls;[13] (ii) the C(13)–O(3) bond distance which is only slightly affected by the bridging bonding mode displayed by CO;[1] (iii) the closeness of the two copper atoms. Such a copper–copper distance exists in a few cases in copper(I) clusters.[14] Whether this distance signifies the existence of a copper–copper direct bond is an open question. We feel that the possible metal–metal interaction responsible for the short interatomic distance is better described in terms of multicentered linkages between the metal and the bridging ligands.

It must be pointed out that the skeleton A in complex III only exists in the solid state and in noncoordinating solvents, such as toluene, in which, however, III is only slightly soluble. When III is dissolved in THF, it displays two CO bands at 2055 and 1930 $cm^{-1}$, ascribable to a partial splitting of the bridging CO by the action of THF.

We would like to stress the relevance of the results presented in the light of the following:

(i) Carbon monoxide displays in a copper(I) complex a bridging bonding mode which is one of the prerequisites for making easier its metal-promoted reduction. This is rather significant in the case of a metal like copper, which has a low oxophilicity and reacts easily with $H_2$. In this context, it must be noticed that, while the presence of copper in various heterogeneous catalysts promoting the reduction of carbon monoxide is very well documented,[15] the information so far available on copper(I) models is very scanty.

(ii) A complex like III may be used as a dinuclear model compound in which CO could be replaced by other small molecules. In this connection, a close relationship could be found between the dinuclear copper unit proposed to be present in naturally occurring systems and the unit A.[16]

**Acknowledgment.** This work has been supported by the Italian National Research Council (CNR).

**Supplementary Material Available:** The final atomic parameters (Tables SI and SII), bond distances and angles (Tables SIII and SIV), molecular structure of $[Cu_2(tmen)_2(\mu\text{-}CO)(\mu\text{-}PhCO_2)]^+$ with the numbering scheme, and a complete listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

(8) When complex II (0.70 g, 1.25 mmol) was added to a methanolic solution (15 mL) of $PhCO_2Na$ (1.0 g, 6.94 mmol) at room temperature, a yellow crystalline solid, which was shown to be III, suddenly formed.

(9) The unit cell parameters reduced to the standard setting $C2$ (No. 5) are $a$ = 33.677 (3), $b$ = 9.748 (1), $c$ = 14.344 (2) Å, $\beta$ = 109.59 (2)°. The transformation matrix from the $I2$ to $C2$ orientation is (-1 0 -1 // 0 -1 0 // 0 0 1). Coordinates of equivalent positions for the nonstandard $I2$ setting are (0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$)+; $x$, $y$, $z$; $-x$, $-y$, $-z$. Reexamination of cell constants showed no higher simmetry (S. L. Lawton and R. A. Jacobson, "TRACER, The reduced cell and its crystallographic applications" Report IS-1141, 1965, USAEC, Ames Laboratory, Ames, IA).

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(11) Data reduction, structure solution, and refinement were carried out on a CYBER 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale (Casalecchio, Bologna), using the SHELX-76 system of computer programs (G. Sheldrick, University of Cambridge, 1976). Calculations were performed with the financial support of the University of Parma.

(12) In the first stage of the refinement the phenyl rings of the $BPh_4^-$ anion were constrained as "rigid groups" with free isotropic thermal parameters; then the constraints were removed and the phenyl carbons were allowed to vary anisotropically. All the phenyl hydrogen atoms were located in a difference Fourier map while those associated with the tmen carbon atoms could not be clearly found, probably as a consequence of high thermal motion of their parent atoms. Owing to the limitations of SHELX, only 33 out of the 57 hydrogen atoms were introduced in structure factor calculations. They were put in subsequent refinements in idealized positions (recalculated after every second refinement cycle) riding with isotropic thermal parameters on their parent carbon atoms.

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## Reduction of Bis(histidine)hemin; Model for the Proton-Coupled Reduction of Hemoproteins

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One of the main methods by which the proton modifies and controls the activity of hemoproteins is to couple together equilibria involving the Fe atom (e.g., reduction, coordination) with equilibria involving a second site; examples include the "cooperative effects" in hemoglobin[1,2] and the proton-coupled reduction[3-5] of, and coordination of anions[6] to, the Fe(III) ion in peroxidases, which are probably related to the mechansim of activation of $H_2O_2$.[2,7] The coordination of histamine to the Co(III) ion in cyanoaquocobinamide is known[8] to reduce the p$K$ of the pendant amino group

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(7) P. A. Adams, D. A. Baldwin, G. S. Collier, and J. M. Pratt, *Biochem. J.*, **179**, 273 (1979).

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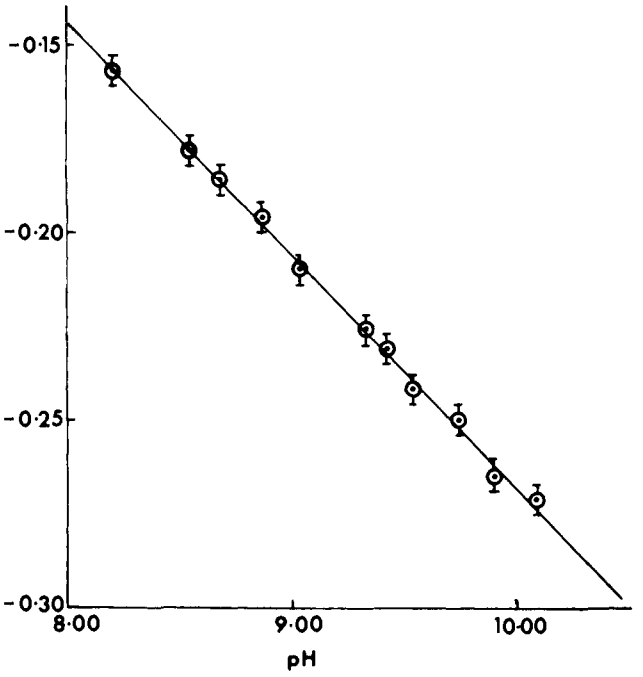


Figure 1. Plot of $E_{1/2}$ in volts (vs. the standard hydrogen electrode) against pH for **2** with HMDE as the working electrode and a scan rate of 100 mV/s.

from 9.5 to 4.5; we have therefore been studying the formation and reduction of Fe(III) hemin complexes in which both axial sites are occupied by derivatives such as histidine (**1**), where the ligand side chains can be used to model neighboring, uncoordinated amino acid side chains in the hemoprotein. We report here that the reduction of the Fe(III) ion in bis(histidine)hemin is accompanied by the uptake of one proton and thereby provides a model for the proton-coupled reduction of hemoproteins.

**1** reacts with dimeric iron(III) hematin (alkaline hemin) above pH 8 to form a complex (**2**) with a spectrum (Soret band at 410 nm) very similar to those of the monomeric bis(*N*-ethyl- and -methyl-imidazole) complexes ($\lambda$ 411 nm) in aqueous alkali.[9] A study of the equilibrium between hematin and **1** at pH 8.5–12[10] where **1** exists as the zwitterionic $^{+}H_3NCHRCO_2^{-}$ and anionic $H_2NCHRCO_2^{-}$ with a p$K$ of 9.2[11] identified **2** as a monomer with two molecules of anionic **1** over the whole range; i.e., the p$K$ of the amino group of **1** has been shifted to $\leq$8.[12] Another product can be detected at low concentrations of **1** by relatively small changes in the spectrum; the equilibrium corresponds to one **1** per hematin dimer, and the product is probably a donor–acceptor adduct of **1** with hematin. **2** can be reduced by $Na_2S_2O_4$ to give a new complex, **3** which has the same spectrum (maxima at 421, 525, and 555 nm) as that formed by the reaction of **1** with the dimeric iron(II) heme (421, 526, and 556 nm) and also that of reduced cytochrome $b_5$ (423, 527, and 556 nm), where both axial ligands are histidine residues;[15] a quantitative study of the equilibrium between **1** and Fe(II) to determine the charge on the ligands was unfortunately prevented by background changes in spectra, presumably due to aggregation.

The reduction of **2** was studied by cyclic voltammetry at 25 °C under $N_2$ from pH 8 to 10 using freshly prepared $0.5 \times 10^{-3}$ M solutions of hematin in 0.2 M ligand and 0.1 M $NaHCO_3$, $\mu$ = 0.3 ($NaNO_3$), and raising the pH by the addition of 6 N NaOH. Initial experiments at varying pH and with varying concentrations of **1** and hematin showed that the peak due to hematin,[16] which was observed in the complete absence of **1**, became replaced at low concentrations of **1** by a second peak at more positive potentials, which could be ascribed to the adduct of hematin with **1**, and at higher concentrations of **1** by a third peak at the same potential as the first, but obviously due to **2**. The second peak, which became more noticeable relative to the third at high pH and high hematin concentration and at low concentrations of **1**, could be suppressed by using a scan rate of $\geq$100 mV/s, while no significant concentration of free hematin would be present in 0.2 M **1** at pH 8–10. This enabled the third peak due to **2** to be studied on its own. The variation of $E_{1/2}$ with pH in the presence of 0.2 M **1** (see Figure 1) gives a slope of $-0.060 \pm 0.001$ V per pH unit, corresponding to the uptake of one proton per electron. Further experiments showed that the same pH dependence was obtained if the working HMDE was replaced by either a platinum, gold, or carbon paste electrode (all with SCE as the reference electrode) or if $NaNO_3$ was replaced by $LiNO_3$ or NaCl, that the value of $E_{1/2}$ was independent of the hematin concentration (from $10^{-5}$ to $2 \times 10^{-3}$ M at pH 9.02), the concentration of **1** (from $10^{-3}$ to $2 \times 10^{-1}$ M at pH 8.57), and the sweep rate (up to 1.0 V $s^{-1}$ at pH 8.25, 8.55, and 9.06), and that the ratio of the anodic to the cathodic current $i_p^A/i_p^C$ remains unity within experimental error up to the sweep rate of 1.0 V $s^{-1}$ with $\Delta E_p = 60 \pm 5$ mV, which indicates[17] that both the electrode reaction and the protonation step are fast.

The reduction of **2** is therefore accompanied by the virtually simultaneous uptake of one proton over at least two pH units without the liberation of free **1** or changes in any accompanying ions and is unaffected by the nature of the electrode surface. If we make the reasonable assumptions (i) that electrochemical reduction gives the same product **3** (where both axial ligands are **1**) as does chemical reduction by $Na_2S_2O_4$, (ii) that other possible, if unlikely, products with different structures (e.g., where one of the coordinated histidines has been converted into a carbene ligand[18] or become dissociated from the metal to form a donor–acceptor complex with the porphyrin ring) would have significantly different spectra from that of reduced cytochrome $b_5$, and (iii) that none of the carboxylate groups of either the coordinated **1** or the porphyrin side chains can be protonated at such a high pH, then the only possible conclusion is that the proton is taken up by the pendant $NH_2$ group of a coordinated **1**. Our results show that the uptake of an electron by an iron(III) porphyrin can be coupled to the uptake of a proton by a neighboring group (with no direct "electronic" interaction) even in a protein-free complex in an aqueous medium, due to the greater relative stabilization of the conjugate base and acid by the higher and lower valency, respectively. The stabilization mechanism probably involves a combination of Coulombic, steric, and hydrogen-bonding effects.

The coupling of proton with electron (or anion) uptake in hemoproteins obviously requires the presence of some acid–base group whose p$K_{III}$ in the Fe(III) form is lower than and whose p$K_{II}$ in the Fe(II) form (or with the anion) is higher than the operating range of pH. If, however, p$K_{II}$ and p$K_{III}$ are both either (a) lower or (b) higher than the operating pH, than any necessary compensation of the added negative charge can only occur through (a) the uptake of a cation or (b) the loss of an anion, respectively. In agreement with this, the reduction of cytochrome $c_2$ involves protonation of the anion of a weakly acidic tyrosine,[19] while the reduction of cytochrome $b_5$ involves the binding of a cation next to a more strongly acidic propionate side chain of the porphyrin[15] and the reduction of cytochrome $c$ involves the loss of an anion located next to a strongly basic (and protonated) lysine.[19] The

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sixth coordination position in cytochrome *c* peroxidase is surrounded by tryptophan, histidine, and arginine;[20] the last is an obvious candidate for the site of protonation in reduction, coordination of anions, and activation of $H_2O_2$. The most likely sites for coupled proton uptake in the physiological range are therefore the side chains of lysine and arginine ($RNH_2$, as in our model and possibly peroxidase), serine, threonine, and tyrosine ($RO^-$, as in cytochrome $c_2$); less likely are cysteine ($RS^-$, too readily oxidized), histidine, and tryptophan (heterocyclic anions, charge too diffuse; neutral histidine, p*K* too low).

Further work with other substituted imidazoles will be reported elsewhere.

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## Formation of Superoxide Ion from Singlet Oxygen. On the Use of a Water-Soluble Singlet Oxygen Source

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An electron-transfer mechanism giving rise to a radical cation–superoxide ion pair or charge-transfer complex has been proposed in the singlet oxygenations of electron-rich substrates (D) and the quenching process of singlet oxygen ($^1O_2$) by certain quenchers.[1] These examples include (1) [2 + 2] cycloaddition of $^1O_2$ to enamines proposed by Foote,[2] (2) reactions with phenols,[3] sulfides,[4] and azines,[5] and (3) quenching of $^1O_2$ by phenols,[3a] sulfides,[4] amines,[1a,6] and NADH.[7] Schaap et al.[8] have reported that [2 + 2] cycloaddition of $^1O_2$ to vinyl ethers does not seem to involve electron transfer. However, the evidence for the formation of superoxide ion ($O_2^{-}\cdot$) from $^1O_2$ has not been obtained so far in either the reaction or the quenching process.[9] The radical

$$D + {}^1O_2 \rightleftharpoons (D^{+}\cdot + O_2^{-}\cdot) \begin{cases} \rightarrow DO_2 \\ \rightarrow D + {}^3O_2 \end{cases}$$

(1) For reviews, see: (a) Bellus, D. *Adv. Photochem.* **1979**, *11*, 105. (b) Foote, C. S. In "Singlet Oxygen", Wasserman, H. H.; Murray, R. W., Eds.; Academic Press: New York, **1979**; p 139. (c) Foote, C. S. In "Singlet Oxygen-Reactions with Organic Compounds and Polymers", Rånby, B., Rabek, J. F., Eds.; Wiley: New York, **1978**; p 135.

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(9) Hematoporphyrin sensitized photooxidation of NADH has been reported to produce $O_2^{-}\cdot$.[10] However, the interaction between photoexcited sensitizer and oxygen resulting in production of $O_2^{-}\cdot$ directly[11] could contribute to confusion in such experiments.[7]

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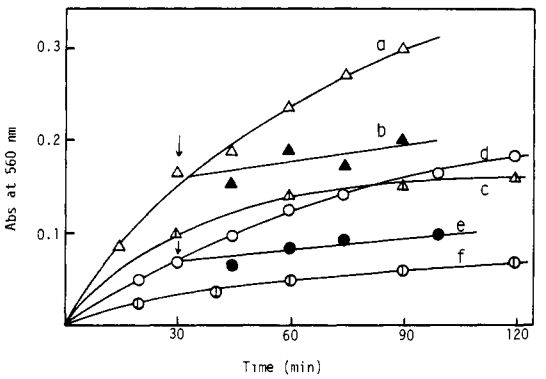


**Figure 1.** Reduction of NBT during incubation of the endoperoxide (**2**) and *N*,*N*-dimethyl-*p*-anisidine (**5**) in the presence and absence of SOD. A solution containing **2** (2 mM), **5** (1 mM), and NBT (1 mM) was shaken at 35 °C. After incubation dimethylformamide was added to dissolve the precipitated diformazan, and absorbance change at 560 nm was measured: curve (a) △, (b) ▲, and (c) ▲ in $NaHCO_3$ saturated aqueous solution (pH 8.3); curve (d) ○, (e) ●, and (f) ⊖ in phosphate buffer (pH 7.5). SOD (32 μg/mL) was added at the point indicated by arrow (b, e) or prior to the incubation (c, f).

cation–$O_2^{-}\cdot$ pair would be short-lived because of the rapid reverse electron transfer and chemical reaction within a cage. One of the most effective methods for detecting such short-lived $O_2^{-}\cdot$ would be an enzymic assay utilizing superoxide dismutase (SOD), owing to its highly specific and rapid ($k = 2 \times 10^9$ $M^{-1}$ $s^{-1}$) reaction with $O_2^{-}\cdot$.[12] A highly polar aqueous solvent would also be preferable for such an electron-transfer reaction. For this purpose, a water-soluble chemical source[13] that can generate $^1O_2$ under mild conditions (up to 40 °C) and gives no significant effect on the enzyme activity is highly desirable. Photochemical methods can be used as $^1O_2$ sources only with special precaution, since illumination of dye photosensitizers in the presence of oxygen may often produce $O_2^{-}\cdot$ with the intervention of photoreduced dyes.[11] We report herein the first observation of $O_2^{-}\cdot$ from the reaction of $^1O_2$ with aromatic amines by using SOD and a newly developed water-soluble $^1O_2$ source.

Methylene blue sensitized photooxygenation of 3-(4-methyl-1-naphthyl)propionic acid[14] (**1**, 0.15 M) in dichloromethane–methanol (8:5) at 0 °C followed by rapid column chromatography (silica gel, $CHCl_3$) gave the naphthalene 1,4-endoperoxide **2**[15] (80%) (Scheme I). The endoperoxide **2** was soluble in phosphate buffer or $NaHCO_3$ saturated aqueous solution.[16] Warming the solution to 35 °C produced **1** quantitatively with the liberation of $^1O_2$.[17,18] In phosphate buffer at pH 7.5, **2** reverted with a half-life of 23 min ($E_a$ = 17 kcal/mol) at 35 °C to **1** and $^1O_2$. The formation of $^1O_2$ was confirmed by the reaction of α-lipoic acid[13] or imidazole–nitrosodimethylaniline,[19] both of which are known to react with $^1O_2$ in water. The effectiveness of **2** in singlet oxygenation in aqueous solvent is also illustrated by the successful isolation of *N*-formylkynurenine (**3**, 23%) and **4**[20] (42%) from the

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(15) KI-starch test, positive; $^1H$ NMR ($CDCl_3$) δ 1.9 (s, 3 H, Me), 2.70–2.85 (m, 4 H, $CH_2CH_2$), 6.7 (s, 2 H, CH=CH), 7.2–7.4 (m, 4 H, aromatic H), 9.2 (br, s, 1 H, COOH); $^{13}C$ NMR ($CDCl_3$–$CD_3OD$) δ 14.8, 24.2, 27.2, 77.8, 79.3, 119.3, 119.4, 125.8, 125.9, 136.0, 139.2, 139.6, 140.2, 174.5.

(16) **2** was soluble up to 10 mM in 0.26 M phosphate buffer (pH 7.5) and up to 40 mM in $NaHCO_3$ saturated aqueous solution (pH 8.3) at 25 °C.

(17) Wasserman, H. H.; Larsen, D. L. *J. Chem. Soc., Chem. Commun.* **1972**, 253. See also: Saito, I.; Matsuura, T., ref 1b, p 511.

(18) A trapping experiment with the singlet oxygen acceptor, diphenylisobenzofuran, in methanol has shown that $^1O_2$ is formed in more than 82% yield.

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