limiting reaction rates were obtained for the first step (oxygen replacement, Figure 4) is consistent with the following mechanism:

$${}^{\delta+}\mathrm{Co^{II}P(CH_3OH)(O_2{}^{\delta-})} + \mathrm{HL^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Co^{III}P(CH_3OH)(O_2H)}]^+ + \mathrm{L} \tag{6}$$

$$[\mathrm{Co^{III}P(CH_3OH)(O_2H)}]^+ + \mathrm{L} \xrightarrow{k_2} [\mathrm{Co^{III}P(CH_3OH)L}]^+ + \mathrm{HO_2\cdot} \tag{7}$$

A similar mechanism was discussed previously[25] for oxidation of a cobalt(II) dioxatetraazaboracyclotetradecatetraene complex. The application of the steady-state approximation to the short-living intermediate $[\mathrm{Co^{III}P(CH_3OH)(O_2H)}]^+$ leads to eq 8 for the $k_{\mathrm{obsd}}{}^{(6)-(7)}$. If the only source of protons is

$$k_{\mathrm{obsd}}{}^{(6)-(7)} = \frac{k_1k_2[\mathrm{HL^+}]}{k_{-1} + k_2} \tag{8}$$

methanol, then eq 9 can be used instead of eq 8, where $K = [\mathrm{HL^+}][\mathrm{CH_3O^-}]/[\mathrm{L}]$.

$$k_{\mathrm{obsd}}{}^{(6)-(7)} = \frac{k_1k_2(K[\mathrm{L}])^{1/2}}{k_{-1} + k_2} \tag{9}$$

Equation 9 explains well the quasi-limiting reaction rates in replacement of oxygen by L (Figure 4, open circles).

The second step (Figure 4, full circles, and Figure 5) is the replacement of the coordinated solvent molecule, eq 10. If

$$[\mathrm{Co^{III}P(CH_3OH)L}]^+ + \mathrm{L} \xrightarrow{k_{\mathrm{obsd}}{}^{(10)}} [\mathrm{Co^{III}PL_2}]^+ + \mathrm{CH_3OH} \tag{10}$$

in ${}^{\delta+}\mathrm{Co^{II}P(CH_3OH)(O_2{}^{\delta-})}$ methanol were replaced by L before oxygen, no limiting rates would have been obtained, since this would be a replacement of a methanol molecule by L in methanol as the solvent. Such a replacement must obey the second-order rate law.[29] Indeed, this is true for the second step, eq 10, which exhibits linear dependence of $k_{\mathrm{obsd}}{}^{(10)}$ on L concentration (Figure 4, full circles, and Figure 5).

The negative entropy of activation ($\Delta S^{\ddagger} = -70$ J K^{-1} mol^{-1}) of the first step, eq 6 and 7, where (6) is considered to be the rate-determining step, is in accordance with the associative nature of this reaction. On the other hand the positive entropy of activation (30 J K^{-1} mol^{-1}) of the second step, eq 10, is to be expected for a dissociative-type process.

It is interesting to note that the rate of the overall reaction (2)–(5), as already discussed, increases with increased ligand-electron-donating ability. On the other hand, the order of reactivity in reaction 10 is reversed. In the overall reaction the entering ligand was also a directing ligand for subsequent reactions, which appears to be a dominating feature, whereas in reaction 10 this is not so. The relatively slow reaction with pip is, most probably, due to steric effects.[7]

Acknowledgment. Thanks are due to Professors H. Hoffmann and H. L. Krauss, University of Bayreuth, Bayreuth, West Germany, who provided facilities for spectral measurements in an oxygen-free atmosphere.

Registry No. $\mathrm{Co^{II}P}$, 14932-10-6; $\mathrm{Co^{II}P(CH_3OH)(O_2)}$, 80285-29-6; py, 110-86-1; pip, 110-89-4; im, 288-32-4; 3CN-py, 100-54-9; 4CN-py, 100-48-1; 4CH$_3$-py, 108-89-4; pyridinium, 16969-45-2.

---

(29) D. Pavlović, D. Šutić, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 2406 (1976).

Contribution from the Laboratoire d'Electrochimie et de Chimie Physique de Corps Solide,
ERA au CNRS No. 468, Institute de Chimie, Universite Louis Pasteur, 67000 Strasbourg, France,
the Laboratoire Associe au CNRS No. 31, Institut de Chimie, Universite Louis Pasteur, 67008 Strasbourg Cedex, France,
the Department of Energy and Environment, Brookhaven National Laboratory, Upton, New York 11973,
and the Department of Chemistry, University of Houston, Houston, Texas 77004

Reduction of Copper Tetracyanotetraphenylporphyrin in Nonaqueous Media. Formation of Copper(I)

A. GIRAUDEAU,[1a] A. LOUATI,[1a] M. GROSS,*[1a] H. J. CALLOT,[1b] L. K. HANSON,*[1c] R. K. RHODES,[1d]
and K. M. KADISH*[1d,e]

Received August 21, 1981

The total electrochemical reduction of copper tetracyanotetraphenylporphyrin, (CN)$_4$(TPP)Cu, was investigated in dimethylformamide (DMF) by the techniques of polarography, cyclic voltammetry, thin-layer spectroelectrochemistry, ESR spectroscopy, and extended Hückel calculations. The ESR results establish the existence of a Cu(II) dianion. The electrochemical reactions of (TPP)Cu and (CN)$_4$(TPP)Cu are compared, and the differences in redox behavior can be rationalized by the calculations. Unlike (TPP)Cu, which may be reduced by a total of six electrons in four steps, (CN)$_4$(TPP)Cu is reduced by seven electrons in five steps. This new wave occurs at $E_{1/2} = -1.95$ V in DMF and is attributed to reduction of the Cu(II) dianion to yield a Cu(I) complex. Formation of this species is reversible on the cyclic voltammetry time scale and an electronic spectrum has been obtained. This spectrum consists of a split Soret band at 390.0 and 480.4 nm and a strong band in the visible at 688.2 nm.

Introduction

During the last 15 years a large number of studies have reported oxidation and reduction potentials for metalloporphyrin complexes.[2,3] In nonaqueous media monomeric metalloporphyrins are reduced (usually reversibly) by at least two single electron transfer steps to yield π anions and dianions. This is true for complexes with over 30 different central metals, including copper, and is independent of the charge on the central metal, which may vary from 1+ (in the case of cobalt

---

(1) (a) Laboratoire d'Electrochimie et de Chimie Physique de Corps Solide, Universite Louis Pasteur. (b) Laboratoire Associe au CNRS No. 31, Institut de Chimie, Universite Louis Pasteur. (c) Brookhaven National Laboratory. (d) University of Houston. (e) On leave at the Universite Louis Pasteur, 1980–1981.

(2) D. Dolphin, Ed., "The Porphyrins", Vol. V, Academic Press, New York, 1978.

(3) K. M. Smith, Ed., "Porphyrins and Metalloporphyrins", Elsevier, London, 1975.

0020-1669/82/1321-1581$01.25/0

complexes) to 5+ (in the case of complexes containing Mo as a central ion). Further irreversible reductions of the porphyrin ring are also possible depending on the range of the nonaqueous solvent system. Initial studies suggested that these reactions at negative potentials involved reversible one-electron transfers to form trianions and tetraanions.[4] Later detailed studies, however, showed that these reductions involve a two-electron transfer step with the simultaneous uptake of protons.[5,6] This latter reaction usually occurs in the potential range of −2.0 to −3.0 V vs. SCE and varies little with changes in the type of porphyrin ring or central metal. These reactions have been best characterized by spectroelectrochemical techniques for the reduction of $TPPH_2$ in DMF.[5] Depending on the central metal, metal reduction may also occur in addition to the four reactions at the π system. For complexes containing iron and cobalt as well as almost a dozen other metals, reduction of the metal proceeds *before* reduction of the π system.

For some years two of our laboratories[7,8] have been investigating how changes in porphyrin structures and axially coordinated ligands modify the redox properties of the central metal as well as the porphyrin π ring system. One aim of these studies was to change the energy levels of the porphyrin metal and/or π system so that a π-radical reaction might proceed *before* reduction of the central metal. This has previously been obtained in the case of porphyrin oxidations[9-12] but never in the case of reductions.

We present here electrochemical, spectral, and theoretical evidence for the first metal-centered reduction to occur *after* reduction of the metalloporphyrin π system. Concomitantly, we report the first evidence for reduction at the metal center of a copper(II) porphyrin in solution. Although theoretically predicted for neutral copper(II) porphyrin[13] and perhaps observed in the solid state,[14] direct reduction of Cu(II) to Cu(I) has never been observed for copper porphyrins in solution. The compound which we have investigated is the tetracyano-substituted porphyrin $(CN)_4(TPP)Cu$.

Experimental Section

The porphyrins (TPP)Cu and $(CN)_4(TPP)Cu$ were prepared according to known procedures.[15] ESR and polarographic measurements were performed in DMF or pyridine containing 0.1 M supporting electrolyte. Thin-layer spectroelectrochemistry was done with 0.2 M supporting electrolyte. Supporting electrolytes were either tetrabutylammonium perchlorate (TBAP) or tetra-*n*-hexylammonium perchlorate (THAP) and, along with DMF, were purified according to earlier reported methods.[15] Pyridine (Aldrich Puriss product) was used without further purification.

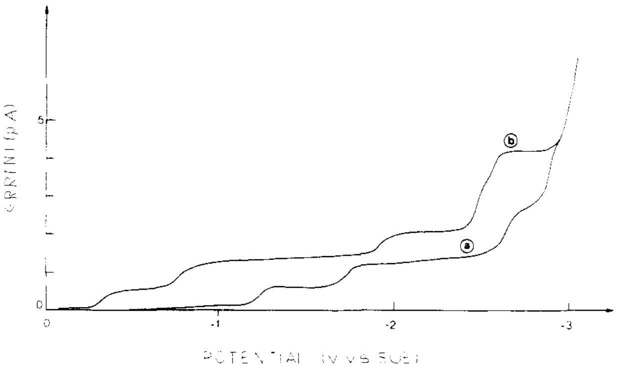


Figure 1. Polarogram of (a) 1.03 × 10^{-3} M (TPP)Cu and (b) 1.00 × 10^{-3} M $(CN)_4(TPP)Cu$ in DMF and 0.1 M THAP.

Table I. Half-Wave Potentials (V vs. SCE) for Reduction of (TPP)Cu and $(CN)_4(TPP)Cu$ in DMF and 0.1 M THAP

	reversible reaction[a]			irreversible reaction[b]	
complex	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^3$	$E_{1/2}^4$	$E_{1/2}^5$
TPP(Cu)	−1.24	−1.70	NR	−2.65	∼−2.90
$(CN)_4(TPP)Cu$	−0.34	−0.76	−1.95	−2.48	−2.57

[a] One-electron transfers. [b] Two-electron transfers. NR = no reaction.

All electrochemical measurements have been carried out under argon or nitrogen. Experiments at a dropping-mercury electrode (DME) were performed with a classical three-electrode potentiostatic device (Solea-Tacussel), comprising a potentiostat (PRT 20 - 2X), a voltage pilot unit (Servovit 2), a millivoltmeter with a high-impedance input (S 6 B), and a potentiometric recorder (EPL 2). For cyclic voltammetric measurements, a signal generator (GSATP from Solea-Tacussel) was associated with the above units. The working electrode utilized was mercury for the polarographic measurements and a gold minigrid electrode for the spectroelectrochemical measurements. Coulometric measurements were performed on a large mercury-pool electrode (area 6 cm^2). The reference electrode utilized was a saturated calomel electrode that was electrically connected with the studied solution by a junction bridge of the corresponding solvent-supporting electrolyte solution.

The spectrophotometric analyses were carried out in situ in a thin-layer cell containing a gold minigrid electrode. The path length of the thin-layer cell was found to be 0.006 cm by both spectrophotometric and electrochemical calibration. The design of this cell has been presented in a recent publication.[16] Scan rates for cyclic voltammetry in the thin-layer cell were 4 mV/s. The spectroelectrochemical measurements were made with a Tracor Northern 1710 optical spectrometer/multichannel analyzer, which provided time-resolved spectra. The spectra result from the signal averaging of 100 5-ms spectral acquisitions. Each acquisition represents a single spectrum from 325 to 950 nm, simultaneously recorded by a diode-array detector with a resolution of 1.2 nm/channel. Values of λ are accurate to ±0.5 nm while ϵ is good to ±5% on the absolute value presented. Solutions were electrolysed at potentials cathodic of each wave in order to ascertain the ESR properties of each electrogenerated species. ESR experiments were performed under a nitrogen atmosphere after exhaustive electrolysis on an X-band Brucker spectrometer.

Results

The well-known polarogram of (TPP)Cu is illustrated in Figure 1a. As has been reported for the same complex in dimethyl sulfoxide (Me_2SO), the first two steps are reversible, one-electron reductions to form the π anion radical and dianion.[17] The last two steps, not investigated in Me_2SO, are irreversible and involve proton uptake. Coulometric measurements in DMF confirm that one electron is transferred

---

(4) D. W. Clack and N. S. Hush, *J. Am. Chem. Soc.*, **87**, 4238 (1965).
(5) J. G. Lanese and G. S. Wilson, *J. Electrochem. Soc.*, **119**, 1039 (1972).
(6) G. Peychal-Heiling and G. S. Wilson, *Anal. Chem.*, **43**, 550 (1971).
(7) (a) A. Louati, M. Gross, and J. Jordan, *J. Electroanal. Chem. Interfacial Electrochem.*, **86**, 301 (1978); (b) A. Louati, E. Schaeffer, H. J. Callot, and M. Gross, *Nouv. J. Chim.*, **2**, 163 (1978).
(8) (a) L. A. Bottomley and K. M. Kadish, *Inorg. Chem.*, **20**, 1348 (1981); (b) K. M. Kadish and L. A. Bottomley, *ibid.*, **19**, 832 (1980); (c) K. M. Kadish, L. R. Shiue, R. K. Rhodes, and L. A. Bottomley, *ibid.*, **20**, 1274 (1981); (d) K. M. Kadish, M. M. Morrison, L. A. Constant, L. Dickens, and D. G. Davis, *J. Am. Chem. Soc.*, **98**, 8387 (1976); (e) K. M. Kadish, L. A. Bottomley, and J. S. Cheng, *ibid.*, **100**, 1731 (1978).
(9) K. M. Kadish and M. M. Morrison, *Inorg. Chem.*, **15**, 980 (1976).
(10) G. M. Brown, F. R. Hopf, J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **95**, 5939 (1973).
(11) J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *Inorg. Chem.*, **11**, 2767 (1972).
(12) C. K. Chang, L. K. Hanson, P. F. Richardson, R. Young, and J. Fajer, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 2652 (1981).
(13) (a) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966); (b) B. Roos and M. Sundbom, *J. Mol. Spectrosc.*, **36**, 8 (1970); (c) D. A. Case and M. Karplus, *J. Am. Chem. Soc.*, **99**, 6182 (1977); (d) A. Antipas, D. Dolphin, M. Gouterman, and E. C. Johnson, *ibid.*, **100**, 7705, (1978); (e) D. E. Ellis and Z. Berkovitch-Yellin, *J. Chem. Phys.*, **74**, 2427 (1981).
(14) Y. Niwa, *J. Chem. Phys.*, **62**, 737 (1975).
(15) A. Giraudeau, H. J. Callot, J. Jordan, I. Ezahr, and M. Gross, *J. Am. Chem. Soc.*, **101**, 3857 (1979).
(16) R. K. Rhodes and K. M. Kadish, *Anal. Chem.*, **53**, 1539 (1981).
(17) R. H. Felton and M. Linschitz, *J. Am. Chem. Soc.*, **88**, 1113 (1966).

Table II. Electronic Spectra of Various Copper Complexes Electrochemically Generated in DMF and 0.1 M TBAP from $(CN)_4(TPP)Cu$ in a Thin-Layer Cell

species	λ,[a] nm ($10^{-4}\epsilon$[b])						
$(CN)_4TPP)Cu^{II}$	441.3 (13.9)	447.4 sh (13.7)		590.4 sh (0.95)	646.0 (3.42)		
$[(CN)_4(TPP)Cu^{II}]^-$	448.6 (7.34)	467.0 sh (5.9)	507.9 (2.42)	566.0 (0.95)	619.7 (2.56)	822.8 (1.20)	861.7 (1.49)
$[(CN)_4(TPP)Cu^{II}]^{2-}$	446.2 (4.62)			573.9 (3.35)	627.1 (6.41)		
$[(CN)_4(TPP)Cu^{I}]^{3-}$	390.0 (4.30)	480.4 (4.76)		636.8 sh (3.40)	688.2 (5.02)		

[a] λ ±0.5 nm. [b] ϵ ±5% (absolute); sh = shoulder.

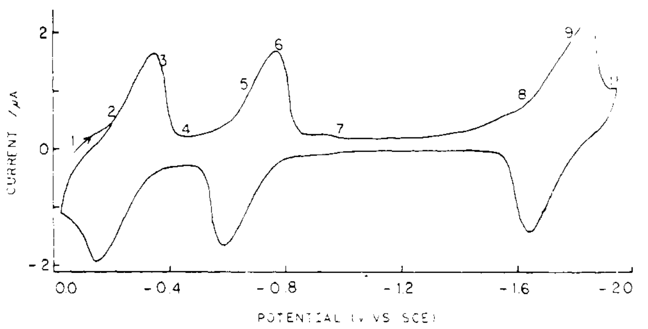


Figure 2. Thin-layer cyclic voltammogram of 1.0×10^{-3} M $(CN)_4(TPP)Cu$ in DMF and 0.1 M TBAP. Numbers 1–11 correspond to potentials at which electronic spectra were obtained. Scan rate = 4 mV/s.

in each of the first two steps while two are transferred in each of the last two reductions.

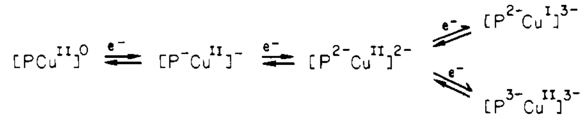
In contrast to the electrode reactions of (TPP)Cu, the β-substituted complex $(CN)_4(TPP)Cu$ shows a seven-electron reduction in five steps (Figure 1b) of which the first three have a reversible, diffusion-controlled shape of $E_p - E_{p/2} = 0.06 \pm 0.003$ V. The fact that three reversible reductions are observed suggests the possibility of a metal ion reduction although from the polarogram alone it is not clear with which, if any, of the three steps metal reduction might be associated.

The potentials for both (TPP)Cu and $(CN)_4(TPP)Cu$ in DMF are listed in Table I. The first and second waves of $(CN)_4(TPP)Cu$ are shifted to potentials 0.90 and 0.94 V less negative than those of (TPP)Cu. These values compare favorably with those of other metallo complexes of $(CN)_4(TPP)^{2-}$ and TPP^{2-}, which show an ~240-mV anodic shift/CN group when the π system is reduced. These shifts are due to the electron-withdrawing substituents (see discussion of the theoretical calculations). The potential difference between the first and the second waves is 420 mV, in agreement with differences found for a number of other complexes in which reduction is known to occur at the π system.[17,18]

So that the products of the electrode reactions could be further investigated, thin-layer optical spectra and ESR spectra were obtained after each reduction. Figure 2 shows the thin-layer cyclic voltammogram obtained in DMF. Reversibility was maintained for a number of cycles with only slight loss of current occurring after cycling for 30 min or more. Spectra were obtained at a number of points both on the rising part of the wave and on the plateau of each reduction step. These were taken at the points numbered 1–11 in Figure 2.

At the first reduction step in the thin-layer cell, the intense Soret band of $(CN)_4(TPP)Cu$ decreases and a new spectrum with an absorption band in the near-IR region appears (Figure 3a and Table II). This spectrum is characteristic of a monoanion species in solution.[6,19] Clear isosbestic points are observed, indicating the presence of only two species in solution. ESR spectra, measured after controlled-potential reduction at −0.7 V, show the disappearance of the starting signal (Figure 4a). This lack of ESR signal could be due either to reduction to Cu(I), which is ESR silent, or to reduction at the ring with coupling between the unpaired electrons on the Cu(II) and the anion. Such a coupling has been observed upon oxidation of $(TPP)Cu^{II}$ to the corresponding Cu(II) π cation radical.[20]

Scheme I



On controlled-potential reduction at the second step, (points 5–7, Figure 2) the near-infrared bands disappear, and a spectrum with two intense visible bands appears. Again, clear isosbestic points are obtained, indicating only two species in solution (Figure 3b and Table II). The product is paramagnetic and exhibits an ESR signal analogous to the starting material. This is shown in Figure 4b. The fact that a Cu(II) signal is still observed clearly indicates formation of the $[(CN)_4(TPP)Cu^{II}]^{2-}$ dianion. An analogous Cu(II) dianion has also been observed for the case of the two-electron reduction of a sulfonated copper phthalocyanine complex.[21]

Finally, thin-layer spectra on the third step (points 8–11, Figure 2) yield, reversibly, a new electronic spectrum unlike any previously observed for complexes of copper porphyrins. Isosbestic points are again obtained, indicating the presence of only two species in solution. Similar spectra were obtained in DMF (Figure 3c and Table II) and pyridine although there exists a slight difference between the relative heights of the split Soret band, possibly due to differences in axial coordination between the two species. All attempts to isolate the products of the third step for further characterization have proven unsuccessful. Bulk coulometry on a longer time scale yields a value of 3.0 electrons but gives a species that cannot be reoxidized and whose spectrum is unlike that obtained on the time scale of the cyclic voltammogram. The species obtained by controlled-potential electrolysis at −2.0 V is ESR silent, suggesting either a Cu(II) trianion or a Cu(I) dianion.

On the basis of the results in this study, as well as data in the literature, the initial reduction sequence of $(CN)_4(TPP)Cu$ can be written as shown in Scheme I where P = $(CN)_4(TPP)^{2-}$. In this scheme, the first and second reduction products have been characterized as having reduction occur at the conjugated π system. In contrast, the third reduction will yield a species which can be formally characterized as either a Cu(I) dianion where reduction has occurred at the metal center or a Cu(II) trianion in which reduction has occurred at the π ring system. Both species will have an identical overall charge of 3− and differ only in the site of the added electron.

The last two reduction waves at potentials greater than −2.4 V (not shown in Scheme I) are irreversible even at the fastest potential sweep rate of 100 V/s. Each wave corresponds to a two-electron transfer. Exhaustive electrolysis at potentials

---

(18) J. H. Fuhrhop, K. M. Kadish and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).

(19) J. H. Fuhrhop, *Struct. Bonding (Berlin)*, **18**, (1974).

(20) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).

(21) L. D. Rollman and R. T. Iwamoto, *J. Am. Chem. Soc.*, **90**, 1455 (1968).

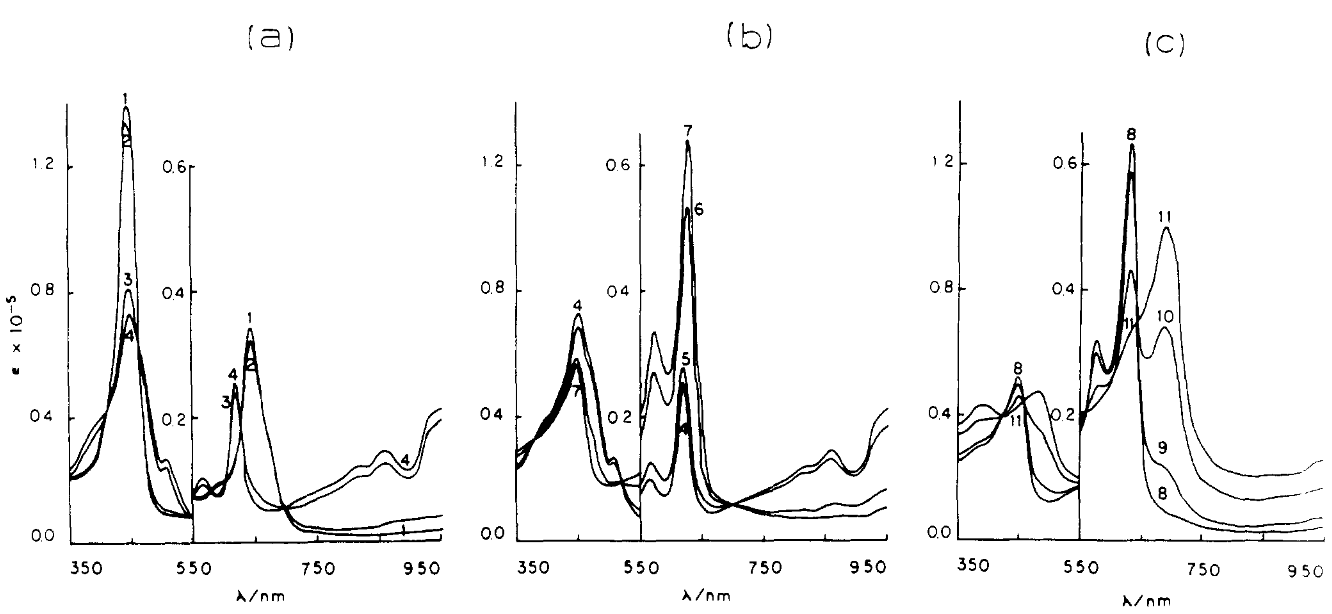


Figure 3. Electronic spectra obtained during reduction of $(CN)_4(TPP)Cu$ at the potentials indicated in Figure 2. The reactions shown are as follows: (a) formation of Cu(II) anion radical; (b) formation of Cu(II) dianion; (c) formation of Cu(I) dianion.

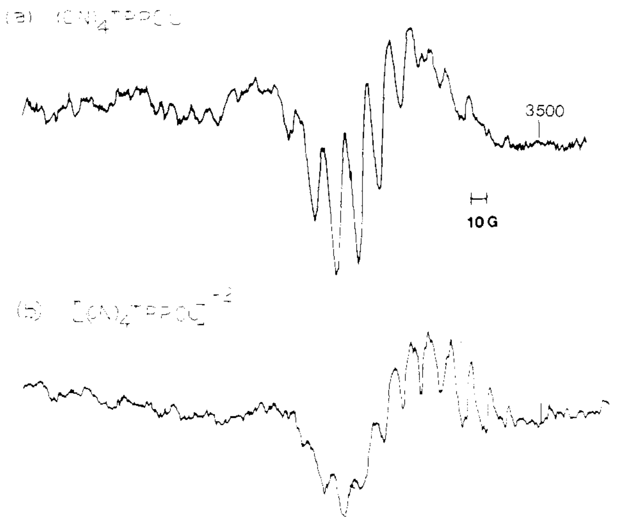


Figure 4. ESR spectra of $(CN)_4(TPP)Cu$ in DMF (0.1 M THAP, T = 298 K): (a) before electrolysis, g = 2.0307; (b) after controlled-potential reduction at −1.5 V vs. SCE, g = 2.0295.

more cathodic than the final reduction step produced a colorless species analogous to that observed upon exhaustive reduction of the free base porphyrin and is probably the porphyrinogen,[6] which results from a six-electron reduction of the porphyrin ring.

Discussion

Numerous theoretical calculations have been carried out for complexes of metalloporphyrins[22-24] and have established the molecular orbital diagrams for diverse complexes with different central metals. Depending on the nature of the central metal, the vacant orbital of lowest energy (LUMO) is either an $e_g(\pi^*)$ orbital of the tetrapyrrole macrocycle or a metal d orbital. These theoretical investigations have yielded predictions as to whether one or more electrons are added to the conjugated π system or to the central metal. For metal-centered reductions, many of these predictions have been confirmed by experiment.[2,3,25]

Copper(II) porphin has been calculated[13] by a variety of quantum-mechanical methods, and in all, the singly occupied $d_{x^2-y^2}$ lies below the porphin $e_g(\pi^*)$ levels. This ordering of energy levels does suggest that the metal ought to be reduced before the ring, contrary to experiment. However, Zerner and Gouterman[13a] pointed out that the extended Hückel method places the $d_{x^2-y^2}$ at a sufficiently high energy that if one considers additional factors (to be discussed below), the predicted site of reduction is the macrocycle and not the metal. For all complexes of copper porphyrins[15,18,26] and phthalocyanines[21] investigated to date, the first reduction always appears to yield an anion radical in solution.

Previous studies of $(CN)_4(TPP)Cu$[15,27] have reported only the first two reductions which, using a number of purely electrochemical criteria as well as comparisons with potentials of other porphyrin complexes, were attributed to reductions of the π system. The ESR results reported here establish unambiguously, for the first time, the existence of a Cu(II) dianion $[(CN_4)(TPP)Cu^{II}]^{2-}$. As might be predicted, the ESR spectrum changes little from that of the neutral complex and is essentially that of a copper(II) porphyrin.

The potential difference between the first two reduction steps of $(CN)_4(TPP)Cu$ is 0.42 V, in agreement with the values of 0.4–0.5 V found initially by Felton and Linschitz[17] for a series of tetraphenylporphyrin complexes and later by Fuhrhop et al.[18] for octaethylporphyrins. The anodic potential shift of the copper tetracyano complex relative to the unsubstituted (TPP)Cu is ~240 mV/cyano group (~1 V in toto) in agreement with values obtained for the free-base porphyrins[27] as well as complexes containing Ni, Zn, and Pd.[15] The Ni, Zn, and Pd complexes do not exhibit a third reversible reduction wave.

The reduction of porphyrins containing metals such as Fe(II), Co(II), or Ag(II) is also facilitated by β substituents, but the potential shifts are smaller than when reduction occurs at the macrocycle.[15,25] Thus, although β-CN substitution does not effect reduction of Cu(II) to Cu(I) before reduction to the

---

(22) M. Gouterman in "The Porphyrins", Vol. III, D. Dolphin, Ed., Academic Press, New York, 1978, p 1.

(23) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(24) S. J. Chantrell, C. A. McAuliffe, R. W. Munn, A. C. Pratt, and R. F. Weaver, *Bioinorg. Chem.*, **7**, 297 (1977).

(25) A. Giraudeau, A. Louati, H. J. Callot, and M. Gross, *Inorg. Chem.*, **20**, 769 (1981).

(26) T. Kakutani, S. Totsuka, and M. Senda, *Bull. Chem. Soc. Jpn.*, **46**, 3652 (1973).

(27) H. J. Callot, A. Giraudeau, and M. Gross, *J. Chem. Soc., Perkin Trans. 2*, 1321 (1975).

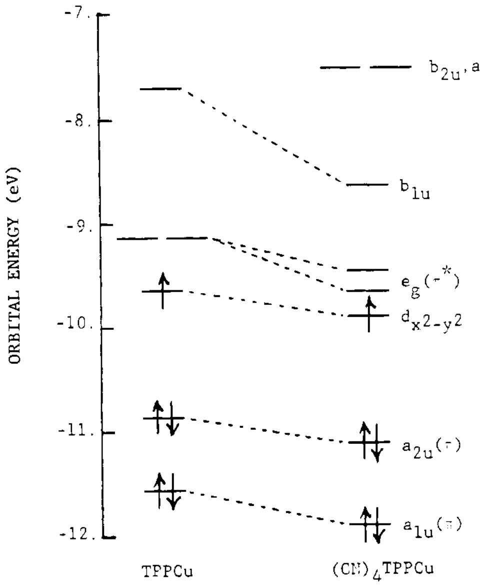


Figure 5. Calculated orbital energies for (TPP)Cu and $(CN)_4$(TPP)Cu. D_{4h} symmetry labels are used for the porphyrin π orbitals although $(CN)_4$(TPP)Cu is formally D_{2h}.

anion radical and dianion, these substituents could shift the Cu(II) $\rightleftarrows$ Cu(I) couple to potentials more positive than those of the last ring reductions (which shift little with substituents). We propose, therefore, that the new (third) reversible wave observed for $(CN)_4$(TPP)Cu is due to generation of a Cu(I) dianion species, not the Cu(II) trianion.

Comparison of the difference between the second and third reduction potentials, $\Delta E_{1/2}{}^{2-3} = E_{1/2}{}^2 - E_{1/2}{}^3$, for the free base and Cu complexes further support the Cu(I) dianion. For $(CN)_4TPPH_2$, $\Delta E_{1/2}{}^{2-3} = 1510$ mV, while for $(CN)_4$(TPP)Cu, $\Delta E_{1/2}{}^{2-3} = 1190$ mV.[25] These values ought to be the same if the Cu(II) trianion were formed.

β substituents remove the degeneracy of the $e_g(\pi^*)$ orbitals. The energy difference between the b_{2g} and b_{3g} components of the $e_g(\pi^*)$ can be estimated from the magnitude of $\Delta E_{1/2}{}^{2-3}$, which gradually increases as more substituents are added to the porphyrin ring. For $(CN)_4TPPH_2$, $\Delta E_{1/2}{}^{2-3}$ is $\sim$500 mV larger than that for $TPPH_2$.

To further explore the effects of β substitution on sites of electron transfer in copper porphyrins, charge iterative extended Hückel (IEH) calculations were performed[28] on neutral, mono-, di-, and trianionic Cu^{II} and Cu^{III} TPP and $(CN)_4$TPP complexes. Relative HOMO and LUMO energies can be correlated with trends in oxidation and reduction potentials and shifts in the optical spectra.[12] These calculations reproduce the anodic shifts of both oxidation and reduction potentials[32] and the red shift of the visible bands[15] for $(CN)_4$(TPP)Cu relative to (TPP)Cu. Although the absolute magnitudes of the calculated potential shifts are smaller than the experimental values, the calculations correctly predict that addition of the β-CN groups will lower the LUMO's ($e_g(\pi^*)$ orbitals) more than the HOMO ($a_{2u}(\pi)$ orbital), as shown in Figure 5. The substituents also lower the singly occupied Cu $d_{x^2-y^2}$ orbital (the shift is smaller than that of the $e_g(\pi^*)$ orbitals) and split the $e_g(\pi^*)$, in agreement with experiment.

The relative effects of electron-withdrawing β substituents on the LUMO and HOMO orbitals have been previously derived[32] from Hammett σ's and attributed to weak "inductive" interactions with the HOMO and stronger "resonance" interactions with the LUMO's. These effects can also be explained by examining the composition of the molecular orbitals. The a_{2u} orbital, from which oxidation occurs, has negligible electron density at the β-pyrrole positions (the electron density is concentrated on the pyrrole nitrogens and meso carbons). In contrast, the $e_g(\pi^*)$ orbitals, the electron acceptors, include not only the C_β's but also considerable contributions from the nitrogens of the CN substituents as well. Thus β substitution most strongly affects orbitals with electron density at the C_β positions.

All the Cu(II) calculations place $d_{x^2-y^2}$ below the $e_g(\pi^*)$. The gap for (TPP)Cu is $\sim$0.5 eV. Addition of the CN substituents reduces this gap by 0.26 eV. However, although the $d_{x^2-y^2}$ orbital lies lowest, it is not an electron acceptor in the mono- and dianions because of the energy it costs to add an electron to Cu(II). This energy results from d–d repulsion terms[13a] and the fact that one is adding an electron to a strongly antibonding orbital. (The $d_{x^2-y^2}$ is not pure; it contains 58% pyrrole N lone pairs.)

The calculations increase the $d_{x^2-y^2}$ orbital energy by 0.6–0.7 eV upon reduction to Cu(I) even though the IEH method cannot explicitly handle repulsion terms. The $d_{x^2-y^2}$ is raised *above* the $e_g(\pi^*)$ for all Cu(I) species: neutral, mono-, di-, and trianionic porphyrins (which would imply that in all cases we are dealing with Cu(II) species). The $d_{x^2-y^2}$ energy is also very sensitive to the Cu–N distance, due to the strong antibonding character of the orbital. Decreasing this distance by 0.02 Å increases the orbital energy by 0.1 eV.

The same crystal structure parameters were used for both the Cu(I) and the Cu(II) calculations. In actuality, reduction of Cu(II) to Cu(I) would undoubtedly increase the ionic radius of the copper. This would lengthen the Cu–N distance, causing a decrease in the final energy of the product. Thus, two opposing processes probably occur on metal reduction, a large increase in $d_{x^2-y^2}$ orbital energy caused by repulsion effects, offset somewhat by a relaxation of the Cu(I) core.

The strongest evidence in favor of a Cu(I) dianion as the triply reduced species comes from comparison of the experimental $\Delta E_{1/2}$'s for the free base and the Cu complex. The calculations predict $\Delta E_{1/2}$ (mono–dianion) reasonably enough (0.25 eV). However, $\Delta E_{1/2}$(di–trianion) is only 0.32 eV, clearly much too small relative to the 1.51 V observed for the free base. The computed value of 0.65 eV for $\Delta E_{1/2}$(Cu(II) $\rightleftarrows$ Cu(I)) agrees more closely with the observed gap of 1.2 V for $(CN)_4$(TPP)Cu.

The optical spectrum of the triply reduced species can best be rationalized by a Cu(I) dianion. For the Cu(II) trianion, no significant spectral changes relative to the Cu(II) dianion are expected: the $\pi \rightarrow \pi^*$ transitions (which give rise to the Soret and visible bands) should remain at about the same frequencies; the $e_g \rightarrow b_{1u}$ transition (the near-IR band of the Cu(II) anion radical; Figure 3) should be red shifted and therefore not observed. On the other hand, for the Cu(I) dianion, the computations predict a red shift for both the Soret and visible bands (as observed) and that the $e_g \rightarrow b_{1u}$ will occur at wavelengths longer than 950 nm. The second Soret peak in Figure 3c might be $e_g \rightarrow b_{2u}$ since the calculated energy gap is smaller for the Cu(I) than for the Cu(II) species.

In conclusion, although the calculations describe the behavior of the neutral, monoanionic, and dianionic species reasonably well, they cannot give a definitive answer for the

---

(28) The models calculated were PCu, $[PCu^{II}]^-$, $[PCu^{I}]^-$, $(CN)_4PCu$, (TPP)Cu, $(CN)_4$(TPP)Cu, $[(CN)_4(TPP)Cu^{II}]^-$, $[(CN)_4(TPP)Cu^{II}]^{2-}$, $[(CN)_4(TPP)Cu^{II}]^{3-}$, $[(CN)_4(TPP)Cu^{I}]^-$, $[(CN)_4(TPP)Cu^{I}]^{2-}$, $[(CN)_4(TPP)Cu^{I}]^{3-}$, and $[(CN)_4(TPP)Cu^{I}]^{4-}$. The CN groups were substituted at the 2,8,12,18-β positions in order to optimize the symmetry. Cu–N distances were fixed at either 2.000 Å or 1.981 Å on the basis of crystal structures of (TPrP)Cu[29] and (TPP)Cu.[30] The IEH program[31] and parameters[13a] have been described.

(29) J. Moustakali and A. Tulinski, *J. Am. Chem. Soc.*, **95**, 6811 (1973).

(30) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964).

(31) A. M. Schaffer, M. Gouterman, and E. R. Davidson, *Theor. Chim. Acta*, **30**, 9 (1973).

(32) A. Giraudeau, H. J. Callot, and M. Gross, *Inorg. Chem.*, **18**, 201 (1979).

triply reduced species. There are, however, indications that the Cu(I) dianion gives a better fit to the optical spectrum than the trianion. The strongest evidence in support of the Cu(I) dianion is that $\Delta E_{1/2}{}^{2-3}$ for Cu is less than $\Delta E_{1/2}{}^{2-3}$ for the free base.

Further evidence that a trianion is not produced comes from the fact that similar complexes of Zn and Pd having closed d shells do not exhibit this third reversible wave. In fact, no conclusive evidence for trianions exists in the porphyrin literature. The only species which are known to be reversibly formed with charges of 3– are those in which the charge is delocalized between the metal and the porphyrin ring, as in the case of $[PFe^I]^{3-}$ and $[PCo^I]^{3-}$. Thus, the best alternative is the formation of a Cu(I) dianion. It is interesting to note that the potential for this reaction, Cu(II) $\rightleftarrows$ Cu(I), would be the most negative ever observed for reduction at the metal center of a copper complex, which is usually reduced in the range of +1 V to –0.7 V.

Acknowledgment. The support of the National Science Foundation (K.M.K., Grant No. CHE 79 21536), the Robert A. Welch Foundation (K.M.K., Grant E-680), and the Division of Chemical Sciences, U.S. Department of Energy (L.K.H.), under Contract DE-AC0276 CH 00016 is gratefully acknowledged. The authors wish to thank Dr. J. J. André for aid in the ESR measurements and Dr. Jack Fajer for several helpful discussions.

Registry No. $(CN)_4(TPP)Cu$, 54329-88-3; $(TPP)Cu$, 14172-91-9; $[(CN)_4(TPP)Cu^{II}]^-$, 80471-07-4; $[(CN)_4(TPP)Cu^{II}]^{2-}$, 80471-08-5; $[(CN)_4(TPP)Cu^{I}]^{3-}$, 80471-09-6.

Contribution from the Molecular Theory Laboratory, The Rockefeller University,
Palo Alto, California 94304, the Molecular Research Institute, Palo Alto, California 94304,
and the Extraterrestrial Research Division, NASA-Ames Research Center, Moffett Field, California 94035

Interaction of Metal Ions and Nucleotides: Possible Mechanisms for the Adsorption of Nucleotides on Homoionic Bentonite Clays

PETER LIEBMANN, GILDA LOEW,* STANLEY BURT, JAMES LAWLESS, and R. D. MACELROY

Received April 21, 1981

In this study we have used a recently formulated INDO-type semiempirical molecular orbital method to characterize the binding of 5′-AMP, 5′-IMP, 5′-GMP, 2′-AMP, and 3′-AMP to hydrated Zn^{2+} and Mg^{2+}, a process presumed to occur when they are adsorbed in the interlamellar space of ion-exchanged homoionic bentonite cays. The energetics of complex formation and modes of cation–nucleotide binding obtained appear to account for the three types of specificities observed: the preference (1) of Zn^{2+}-exchanged clays for 5′-AMP > 5′-IMP ≥ 5′-GMP, (2) of Zn^{2+}-exchanged clays for 5′-AMP > 2′-AMP > 3′-AMP, and (3) of 5′-AMP for Zn^{2+} rather than Mg^{2+}-exchanged clays. In addition, Zn^{2+} has been shown to bind to the clay more strongly than Mg^{2+}, in keeping with the observed ability of Zn^{2+} to displace Mg^{2+} from bentonite clay. Also, the preference of Mg^{2+} for phosphate-site binding and of Zn^{2+} for N_7–phosphate bridge binding has been clearly demonstrated for 5′-nucleotides. These results strongly implicate direct cation–nucleotide complex formation in the adsorption of nucleotides on homoionic clays and imply that such complexes could then be involved in subsequent polymerizations.

Background

It has been proposed that the origin of life proceeded by the formation of important biomonomers from simpler molecules such as methane, ammonia, and water, postulated as part of the primitive earth's atmosphere. A good deal of work has been done demonstrating the plausibility of such prebiotic organic syntheses. Much less is known about how the biomonomers were concentrated from dilute aqueous solutions and condensed to biopolymers. One suggestion is that clays or other minerals may have provided a surface onto which small molecules could be concentrated and subsequently polymerized.[1-7] However, most clays do not readily adsorb such important biomonomers as amino acids and nucleotides at the nearly neutral pH which is thought to have existed in the primitive ocean.

Recently it has been demonstrated in experiments at NASA-Ames[8] that metal ions as exchangeable cations in the clays alter this behavior markedly. When naturally occurring Wyoming bentonite clay was converted to a homoionic clay by repeated washing with metal halide solution, the Na^+, Li^+, and K^+ clays, in common with the naturally occurring one, did not adsorb 5′-AMP from dilute solution under prebiotic conditions. However, a variety of other metal dications, when exchanged in the clay, did adsorb nucleotides in the order Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Mg^{2+}. Some of these cations, particularly Zn^{2+}, which produced the most effective nucleotide adsorbing clay, are fundamental to contemporary nucleotide biochemistry. In addition, recent experiments have shown that Zn^{2+} is an efficient and stereospecific catalyst in template-directed polymerization of an activated nucleic acid derivative.[9] These works suggest that metal complexes may also have played an important role in organic chemical evolution on the primitive earth.

Subsequent experiments as NASA-Ames have characterized nucleotide adsorption on homoionic bentonite clays in more detail. Specifically, the pH dependence of adsorption of 5′-AMP on Zn^{2+} bentonite has been determined, and a maximum at about pH 7.4 is observed. Under these conditions, the nucleotide is in dibasic form. Langmuir isotherms were obtained at pH 7.4 for the adsorption of a variety of nucleotides: 5′-AMP, 5′-IMP, 5′-GMP, 5′-ADP, 5′-CMP, 5′-UMP, 2′-

---

* To whom all correspondence should be addressed at The Rockefeller University.

(1) Bernal, J. D. "The Physical Basis of Life"; Routledge and Kegan Paul: London, 1951.
(2) Lahav, N.; Chang, S. *J. Mol. Evol.* **1976**, *8*, 357.
(3) Theng, B. K. G. "The Chemistry of Clay-Organic Reactions"; Wiley: New York, 1974; pp 274-281.
(4) Paecht-Horowitz, M.; Berger, J.; Katchalsky, A. *Nature* (*London*) **1970**, *228*, 636.
(5) Paecht-Horowitz, M. *Isr. J. Chem.* **1973**, *11*, 369.
(6) Otroschenko, V. A.; Vasilyeva, N. V. *Origins Life* **1977**, *8*, 25.
(7) Ponnamperuma, C. *Abstr. Int. Clay Conf.* **1969**.
(8) Lawless, J.; Edleson, E. H. "Life Sciences and Space Research"; Pergamon Press: New York, 1980; Vol. VIII, pp 83-88.
(9) Lohrmann, R.; Bridson, P. K.; Orgel, L. E. *Science* (*Washington, D.C.*) **1980**, *208*, 1464.

0020-1669/82/1321-1586$01.25/0