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Mixed-valence porphyrin π-cation radical derivatives: Electrochemical investigations

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Dedicated to Prof. Piero Zanello.

Abstract

The electrochemistry of [Cu(OEP)] and [Ni(OEP)] are compared with the mixed-valence π-cations $[\mathrm{Cu(OEP)}^{\cdot/2}]_2{}^{+}$ and $[\mathrm{Ni(OEP)}^{\cdot/2}]_2{}^{+}$. These electrochemical studies, carried out with cyclic voltammetry and hydrodynamic voltammetry, show that the mixed valence π-cations have distinct electrochemical properties, although the differences between the $[\mathrm{M(OEP)}]^{+/0}$ and $[\mathrm{M(OEP)}^{\cdot/2}]_2{}^{+/0}$ processes are subtle.

Keywords: Electrochemistry; Metalloporphyrins; Mixed valence; π-Cation radicals

1. Introduction

Electronic interactions between the π systems of two or more porphyrin molecules in close proximity are important in defining the properties of the supramolecular ensemble. Notable examples of such interacting porphyrin π systems are those found in photosynthetic systems [1] and in linearly stacked arrays that are organic conductors [2]. The photosynthetic proteins include the light-harvesting chlorophyll arrays [3] and the photosynthetic reaction center (RC) special pairs [4]. The photoinduced formation of the one-electron oxidized reaction center special pair (the primary donor, often called P^{+}) is the first step in the conversion of light energy to chemical energy. The presence of a strongly interacting pair of bacteriochlorophylls in photosynthetic bacterial reaction centers was originally inferred from spectroscopic measurements. In the green plant photosynthetic apparatus, a similar, although apparently less strongly interacting, pair of chlorophyll *a* molecules is the primary donor for at least one of the photosystem reaction centers (PS II) [5].

X-ray crystal structures of bacterial photosynthetic reaction centers from several organisms [6,7] have now provided detailed information about the ground state geometry of the special pair, P. The special pair has a cofacial arrangement of the two bacteriochlorophyll rings with effective overlap of one pyrrole ring from each macrocycle. The overlap of porphyrin rings has been frequently observed in the solid-state structures of porphyrin compounds [8]. However, most porphyrin compounds exhibit stronger intermolecular interactions than that displayed by the photosynthetic special pairs as judged by the geometric criterion of the degree of inter-ring overlap. The apparent importance of the cofacial bacteriochlorophyll dimer in defining the photophysics and photoinduced electron transfer of the entire RC system, e.g., the excited state P^{*} to oxidized P^{+} transition, has led to the synthesis and characterization of a number of bisporphyrin derivatives.

Abbreviations: Porph, a generalized porphyrin dianion; OEP, the dianion of octaethylporphyrin; $\mathrm{OEP}^{\cdot}$, octaethylporphyrin π-cation radical; $\mathrm{OEP}^{\cdot/2}$, octaethylporphyrin mixed-valence π-cation radical.

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Two different, broad classes of bisporphyrin compounds have been studied as RC models. The first are covalently linked porphyrin dimers and larger assemblies [9] and the second are lanthanide and actinide bisporphyrin or "double-decker" derivatives [10]. These two systems can in principle be used to form oxidized (π-cation radical) species with oxidation states that are formally analogous to P^+. Oxidized double-deckers, in particular, have been studied to develop a further understanding of the electronic structure of P^+. The double-decker compounds have been particularly attractive for study as RC models because of their necessarily cofacial structures and the possibility of varying the porphyrin interplanar spacing by changing the central metal ion. However, the completely overlapped, cofacial geometry of these double-deckers is distinctly different from the slipped conformation of the special pair observed in the reaction center structures. The geometric connection constraint(s) in the covalently linked bisporphyrins also leads to structures different than that displayed by the special pair. Nonetheless, oxidation of covalently linked bisporphyrins does suggest that the geometry between the two porphyrin rings is important in yielding derivatives with physicochemical properties similar to those of photooxidized RC special pairs.

We have shown that metallooctaethylporphyrinate derivatives can be oxidized to form π-cation radical derivatives in which only one electron is removed per two porphyrin rings rather than the expected one electron per porphyrin ring [11,12]. The species can be prepared by two distinct reactions

$$\mathrm{M(OEP)} + [\mathrm{M(OEP^{\cdot})}]^+ \overset{K_{\mathrm{MV}}}{\rightleftharpoons} [\mathrm{M(OEP^{\cdot/2})}]_2{}^+ \qquad (1)$$

or

$$2\mathrm{M(OEP)} + \mathrm{NR_3SbCl_6} \rightarrow [\mathrm{M(OEP^{\cdot/2})}]_2\mathrm{SbCl_6} + \mathrm{NR_3} \qquad (2)$$

Thus, these new dimeric, supramolecular assemblies of general formula, $[\mathrm{M(OEP^{\cdot/2})}]_2{}^+$, have the same formal oxidation level as the photooxidized special pair of reaction centers. We have suggested "mixed-valence π-cation radical" as a descriptive name for this new class of synthetic porphyrin derivatives. The apparent stability of the mixed-valence π-cation radicals, particularly the absence of significant disproportionation in solution, is striking. Systems of $[\mathrm{M(OEP^{\cdot/2})}]_2{}^+$ that have been studied include derivatives where M = Cu, Ni, Zn, Pd, or VO. A limited set of heterodimeric systems have also been investigated. The mixed valence π-cation radical species have spectral properties that are distinctly different from those of the related neutral or classical π-cation radical metalloporphyrin species; the differences are most pronounced in the near-IR spectral region. These differences allowed the determination of the equilibrium constant for reaction (1); values of K_{MV} are in the range of 10^3–2×10^4 in methylene chloride solution with the Pd derivative having the largest equilibrium constant.

In addition to the solution studies, we have previously reported the detailed solid-state structures of three crystalline $[\mathrm{M(OEP^{\cdot/2})}]_2{}^+$ species.[13] The combination of solid-state and solution studies reported makes evident that these mixed-valence π-cation radicals have many properties that are distinct from those of either neutral or π-cation radical metalloporphyrin species. The relative ease in preparing the mixed-valence π-cation radicals demonstrates the stability resulting from delocalization of the π-radical electron hole over more than one porphyrin ring.

However, despite the fact that metalloporphyrin oxidation and reduction processes for these and similar derivatives have been studied electrochemically for some time, the existence and substantial stability of the mixed valence π-cation radicals was never inferred from electrochemical studies. Surprisingly, it was rather the result of direct synthesis. In this paper, we examine the electrochemistry of the mixed valence π-cation radical derivatives with the view of understanding their electrochemical behavior. We are particularly interested in understanding why the mixed-valence species had not been long seen by electrochemistry.

2. Experimental

2.1. General information

$H_2(OEP)$ was purchased from Midcentury Chemicals, thianthrene, perchloric acid, tris(4-bromophenyl)aminium hexachloroantimonate, and CCl_4 were purchased from Aldrich and all other reagents were obtained from Fisher. Dichloromethane and hexane were distilled from CaH_2 and sodium/benzophenone, respectively. All reactions were performed under an argon atmosphere with oven-dried Schlenkware and cannula techniques. Metal ions were inserted into the free-base $H_2(OEP)$ by standard techniques [14,15]. Crystalline samples of $[\mathrm{Ni(OEP^{\cdot/2})}]_2\mathrm{SbCl_6}$ and $[\mathrm{Cu(OEP^{\cdot/2})}]_2\mathrm{SbCl_6}$ were prepared as described previously [13].

Cyclic voltammetry (CV) was performed in a three-electrode cell with a platinum disk working electrode (1.5 mm in diameter) surrounded by a Pt spiral counterelectrode and an aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. Hydrodynamic voltammetry made use of a platinum electrode with periodical renewal of the diffusion layer, obtained by moving the solid electrode with a time-controlled knocker.[16] Either a BAS 100A electrochemical analyzer or a multipurpose Amel instrument (a Model 566 analog function generator and a Model 522 potentiostat) were used as polarizing units. Controlled potential coulometry was performed in a H-shaped cell with anodic and cathodic compartments separated by a sintered-glass disk. The working electrode was a Pt gauze and a mercury pool was use as counter electrode. The Amel potentiostat was connected to an Amel Model 558 integrator. All potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions the one electron oxidation of ferrocene occurs at $E^{\circ\prime} = 0.34$ V in the temperature range -10 to $+10$ °C and $E^{\circ\prime} = +0.35$ V at RT. The solvent