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Visible and infrared spectroelectrochemistry of zinc and manganese porphinones: Metal vs. porphyrin reduction

Florentina Tutunea, Abderrahman Atifi, Michael D. Ryan *

Marquette University, Chemistry Department, PO Box 1881, Milwaukee, WI 53201, USA

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ABSTRACT

The visible and infrared spectroelectrochemistry of zinc and manganese porphinones and porphinediones was carried out in THF solutions. The aim of this work was to use FTIR spectroelectrochemistry and DFT calculation to determine whether the reduction was centered predominantly on the metal or the macrocycle. For zinc(II), the first one-electron reduction must occur on the macrocyclic ring because the metal's d-orbitals are filled (d^{10}). The carbonyl bands on the macrocyclic ring were used to probe the electronic structure because they can be readily observed in the infrared spectra. The results of this study are complementary to previous spectroelectrochemical studies that have been reported for the iron and cobalt complexes of the same macrocycles. As expected for the formation of a π-radical anion species, significant downshifts in the carbonyl bands were observed. DFT calculations showed that the behavior of the porphinedione complexes were most sensitive to the electronic structure of the $M(OEPdione)^-$ species. If a M^I species is formed, the two carbonyl groups will be downshifted by similar energies. For M^{II}-radical anions, one carbonyl will be downshifted significantly, and the second one will be downshifted by a small amount. On the basis of this criterion, it was determined that cobalt(I) and iron(I) complexes were formed, while zinc and manganese formed π-radical anion species. The visible spectroelectrochemistry was also consistent with these electronic structures.

1. Introduction

The active site of several dissimilatory nitrite reductases contains heme d_1 as the prosthetic group. Heme d_1 is an iron porphinedione, one of the many unusual porphyrin prosthetic groups involved in the nitrogen cycle. The structure of heme d_1 was identified by Chang [1]. Work has been carried out in our laboratory investigating the voltammetry, spectroelectrochemistry and reactivity of iron porphinones and porphinediones [2,3].

While visible spectroelectrochemistry can provide valuable information on the electronic structure of the low valent metal complexes, infrared spectroscopy can provide more definitive information. Previous work on cobalt porphyrin complexes has shown that the reduction of $Co^{II}(P)$ (where P = porphyrin) will lead to a $Co^{I}(P)^-$ complex [4]. On the other hand, $Zn^{II}(P)$ complexes are known to reduce to the porphyrin π-radical anion because zinc is a d^{10} complex. Zinc porphyrins (octaethylporphyrin, OEP, and tetraphenylporphyrin, TPP) have been extensively studied by voltammetry [5] and spectroelectrochemistry [5–7]. The resonance Raman spectroscopy of $Zn(P)^-$ has also been reported [7,8]. Unlike the zinc complex, there have been fewer studies carried out on the reduction of $Mn^{II}(P)$ complex. Fuhrhop et al. [9] characterized $Mn(P)^-$ as a manganese(II) radical anion, as did Kelly and Kadish [10] and Boucher and Garber [11]. Additional information confirming the radical anion structure was provided by Guldi et al. [12], who observed a broad absorption band around 770 nm, which is characteristic of porphyrin π-radical anions. On the other hand, DFT calculations by Liao and Huang [13] predicted a Mn(I) structure for manganese porphine.

The aim of this work will be to use infrared spectroelectrochemistry along with DFT calculations in order to correlate the changes in the infrared spectra with the electronic structure of the formal M(I)-porphyrin or M(II) π-radical anion complex. Reduction of zinc porphinones should reveal features in the infrared and visible typical of π-anion radicals, as zinc is a d^{10} complex. The previous work on cobalt porphinones has allowed us to obtain spectra characteristic of a metal reduction [14]. Using the insight gained from these two metals, the spectroelectrochemistry of manganese and iron [15] can be better understood. There still remains considerable controversy as to the electronic structure of the $Fe^{I}(P)^-$ complex. This investigation should help clarify this issue. The carbonyl group, which is present on the macrocycle, can be easily observed with infrared spectroscopy, and is sensitive to the degree of

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* Corresponding author.
E-mail address: Michael.ryan@marquette.edu (M.D. Ryan).

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delocalization of the metal electron density onto the macrocycle. The magnitude of the shift and the behavior of the two carbonyl groups in the porphinediones upon reduction should provide this insight.

2. Experimental

2.1. Chemicals

Octaethylporphyrin (H_2OEP) was purchased from Sigma–Aldrich Chemical Co. Tetrabutylammonium perchlorate (TBAP) was purchased from Alfa Aesar and dried at 90 °C in a vacuum oven overnight. Bis(triphenylphosphine)iminium chloride (PNPCl) was obtained from Sigma–Aldrich Chemical Co. Anhydrous tetrahydrofuran (THF) was refluxed in the presence of sodium and benzophenone under nitrogen until the solution was blue. The solution was deoxygenated at least three times by freeze–pump–thaw cycles before being used in the glove-box. All other solvents were spectrophotometric grade and used without further purification. Octaethylporphinone ($H_2OEPone$) and octaethylporphinedione ($H_2OEPdione$) were synthesized by literature methods [16–18]. The ZnOEPone was prepared by a two-step reaction via OsO4 oxidation of ZnOEP and acid catalyzed pinacolic rearrangement using the literature method published by Chang et al. [16,18,19]. This reaction gave a mixture of unreacted H_2OEP, ZnOEPone and 2,6-OEPdione. After removing the solvent, the mixture of zinc complexes was purified using an alumina column and elution was initiated with chloroform. A small violet band containing free base 2,6 porphinedione, H_2(2,6-OEPdione), which did not react with zinc acetate, eluted first. The second band containing ZnOEP (pink) from unoxidized starting material was eluted with chloroform containing 0.5% methanol. The third band (blue) was eluted with chloroform containing 5% methanol, which contained ZnOEPone. The manganese porphinone complexes were synthesized using manganese acetate tetrahydrate, sodium acetate, and sodium chloride in acetic acid. The mixture was heated at reflux for 24 h. The resulting solution was cooled at room temperature, reduced to a volume of less than 5 mL, and washed 3 times with 100 mL of water, 5%$NaHCO_3$ solution (2 × 100 mL), then once more 3 times with 100 mL of water. The crude manganese complex was purified using an alumina column. Elution started with chloroform to remove the unreacted material and continued with chloroform containing 1% methanol.

To obtain zinc and manganese porphinediones, the H_2(2,4-OEPdione) compound was allowed to react with the corresponding metal acetates in $CHCl_3$/MeOH (20/10 mL) at reflux for 1 h, in case of zinc, or 24 h for manganese. The completion of the reaction was monitored using thin layer chromatographic techniques. Silica gel TLC plates were immersed in a solvent mixture of hexane:dichloromethane (1:1 ratio). The resulting solution was cooled at room temperature and washed 3 times with 300 mL of water. After removing the solvent, the crude metal complex was purified on silica gel column. Elution was initiated with chloroform.

2.2. Equipment

The UV–visible spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with an OLIS data acquisition system. An optically transparent thin layer electrode (OTTLE) cell was used for visible spectroelectrochemistry. The cell assembly was based on the design of Lin and Kadish [20]. A silver wire was used as a reference electrode. The electrode potentials that corresponded to each spectra were obtained using an E-corder (eDAQ Pty Ltd., Australia), which was controlled by the software program, Chart (eDAQ). Each time that the diode array slit opened, the E-corder was triggered to acquire the potential from the potentiostat. The potentials recorded in this work were the average potentials during the spectral acquisition time. The infrared spectra were obtained with a Thermo Nicolet-FTIR spectrophotometer (Model 670 Nexus) with a MCT detector. Infrared spectra of solid materials were collect as KBr pellets. The FTIR OTTLE cell has been described previously [15].

2.3. Procedures

All samples for spectroelectrochemical analysis were prepared and the cells filled in the glove box under argon. The supporting electrolyte was 0.10 M TBAP. FTIR spectra were obtained using 32 scans, and 2 cm^{-1} resolution unless noted differently. The UV–visible spectra were obtained from cyclic scans of the potential, while FTIR spectra were obtained at constant potential. All potentials are reported vs. SCE (V vs. SCE = V vs. Ag/$AgClO_4$ + 0.36 V). In some cases, small amounts of residual starting material could be observed in the final spectrum due to the fact that the working electrode did not cover the entire beam. In these cases, the residual amounts were digitally subtracted in order to obtain the final spectrum of the oxidized/reduced species. For all the spectroelectrochemical experiments (visible and infrared), the potential was returned to the initial potential after the experiment was completed in order to verify that the starting spectrum could be recovered. This indicated that an irreversible chemical reaction had not occurred. This condition was fulfilled for all reported spectra.

2.4. Computation

Electronic structure and vibrational spectral calculations were carried out using the m06 or the bp86 DFT functionals and the TZVP basis set for all elements except for the transitional metal using the Gaussian 09 suite of programs [21]. The TZVP basis set was also used for zinc. The Wachters' basis set was used for manganese, iron and cobalt [22]. All calculations converged using the tight optimization criteria. The high-spin $Mn(P)^-$ complexes were all solved using the anti-ferromagnetic coupling procedure available at the Gaussian website. Two fragments were used in the calculation: Mn^{II} (high spin, sextet) and the macrocycle (−3 charge, doublet), antiferromagnetically coupled. A plot of observed and calculated ν_{CO} wavenumbers of M(II) and M(III) porphinones (where M is the metal) for the m06 functional is shown in Fig. S1 of the Supporting information. All the calculated wavenumbers were about 6% higher than the experimental values. As a result, a scale factor of 0.94 was used for the ν_{CO} values. The porphyrin vibrations, as calculated by the m06 functional, were closer to the experimental values and a scale factor of 0.97 was more appropriate. Complementary calculations were performed using the bp86 functional. The carbonyl vibrational energy was always underestimated by this functional, but not in a fashion that could be corrected by a scale factor. The observed ν_{CO} values were 13 ± 6 cm^{-1} lower than the experimental values. No scale factor was used for this functional, but comparisons between the experimental data and the bp86 predicted values should be interpreted in light of this tendency. The redox potentials for the metalloporphinones were calculated using the method of Holland et al. [23].

3. Results and discussion

3.1. Voltammetry of zinc porphinones

Zinc(II) porphyrins and porphinones were reduced by one electron to the π-radical anion at about −1.6 V vs. SCE in THF. The results are summarized in Table 1. Further reductions occur at