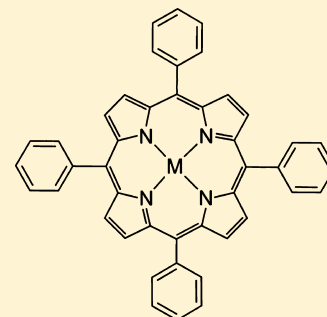


Parent Anions of Iron, Manganese, and Nickel Tetraphenyl Porphyrins: Photoelectron Spectroscopy and Computations

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ABSTRACT: The singly charged, parent anions of three transition metal, tetraphenyl porphyrins, $M(\text{TPP})^-$ [$\text{Fe}(\text{TPP})^-$, $\text{Mn}(\text{TPP})^-$, and $\text{Ni}(\text{TPP})^-$], were studied by negative ion photoelectron spectroscopy. The observed (vertical) transitions from the ground state anions of these porphyrins to the various electronic states of their neutral counterparts were modeled by density functional theory computations. Our experimental and theoretical results were in good agreement.



INTRODUCTION

Metalloporphyrins are large, often highly symmetric macrocyclic molecules, which play important roles in nature. In heme proteins, iron porphyrins are the prosthetic groups responsible for the transport and storage of oxygen in hemoglobin and myoglobin.¹ Synthetic metal porphyrins mimic many of the chemical and physical properties of their biological counterparts. These properties can be tailored by coordination of specific metal centers, typically those of Fe, Mg, Ni, and Co. Metalloporphyrins can also be found as building blocks in some metal–organic frameworks (MOFs). These materials are finding applications in selective gas storage and separation and in catalysis.^{2–13} Metalloporphyrins can be considered to be models for important portions of some MOFs. Identifying the electronic and structural properties of isolated metal porphyrins is important for understanding their ability to bind small molecules and to transfer electrons. This may lead to insight into how to design MOFs for specific applications.

Several gas-phase studies of porphyrins have been conducted by collision-induced dissociation (CID),^{14–16} although resonance Raman¹⁷ and ion cyclotron resonance (ICR) mass spectrometry^{18,19} studies have also been reported. Additionally, photoelectron spectroscopy experiments on both neutrals²⁰ and anions²¹ of porphyrins have been conducted. In particular, multiply negatively charged anions of meso-tetra-(4-sulfonato-phenyl)-porphyrins with Mn and Cu metal centers were studied by Kappes and co-workers using anion photoelectron spectroscopy.²¹ Similarly, phthalocyanines, which are closely related to porphyrins, have also been examined by negative ion photoelectron spectroscopy. Specifically, Wang and co-workers studied multiply negatively charged copper phthalocyanine tetrasulfonate anions and found the excess charges to be localized on the peripheral $-\text{SO}_3^-$ functional groups.^{22,23} Nevertheless, until now, no photoelectron spectra of singly charged, parent negative ions of porphyrins or porphyrin analogues have been measured.

Here, we focus on studying singly charged, transition metal, tetraphenyl porphyrin parent anions, $M(\text{TPP})^-$. Tetraphenyl porphyrins are heterocyclic macromolecules composed of four modified pyrrole subunits linked together around a metal center, M, by four methine ($=\text{CH}-$) bridges, each of these having a phenyl functional group, i.e., $M(\text{TPP})$. The structure of these porphyrins is depicted in Figure 1. Singly charged

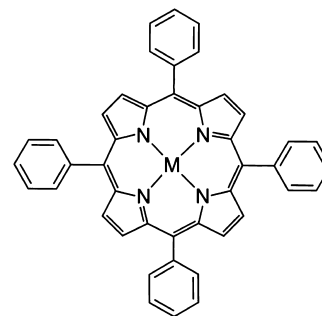


Figure 1. Tetraphenylporphyrine with a metal center, i.e., $M(\text{TPP})$.

negative ions of both $\text{Fe}(\text{TPP})^-$ and $\text{Ni}(\text{TPP})^-$ were first observed by Ridge and co-workers in ICR mass spectrometric experiments, from which they reported electron affinities.^{18,19} Somewhat later, a theoretical study by Liao and Scheiner found that $\text{Fe}(\text{TPP})^-$ accommodates its excess electron among iron's d orbitals, whereas in $\text{Ni}(\text{TPP})^-$ the excess electron was found to reside in the π^* orbital of the porphyrin's heterocyclic moieties.²⁴

In this work, we present a negative ion photoelectron spectroscopic and density functional theoretical (DFT) study of three such systems, i.e., $\text{Fe}(\text{TPP})^-$, $\text{Mn}(\text{TPP})^-$, and $\text{Ni}(\text{TPP})^-$,

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from which we determine the electron affinities of their neutral counterparts. These are compared with results from previous studies.

■ EXPERIMENTAL AND COMPUTATIONAL METHODS

Anion photoelectron spectroscopy is conducted by crossing a beam of mass-selected negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The photodetachment process is governed by the energy-conserving relationship $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Measuring electron kinetic energies and knowing the photon energy provide electron binding (photodetachment transition) energies. Because these transitions are vertical, their relative intensities and band shapes are determined by the extent of Franck–Condon overlap between the anion and its corresponding neutral. The apparatus consists of a laser photoemission/oven anion source, a linear time-of-flight mass spectrometer for mass analysis and mass selection, a magnetic bottle electron energy analyzer, and a Nd:YAG photodetachment laser. The instrumental resolution of the photoelectron spectrometer is ~ 35 meV at an EKE of 1 eV. The third (355 nm) harmonic of a Nd:YAG laser was used to photodetach the mass-selected porphyrin molecular anions. Photoelectron spectra were calibrated against the well-known atomic transitions of Cu^- .

To produce the parent porphyrin anions, $\text{Fe}(\text{TPP})^-$, $\text{Mn}(\text{TPP})^-$, and $\text{Ni}(\text{TPP})^-$, small amounts of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron(III) chloride, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine manganese(III) chloride, and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine nickel(II) powder, respectively, were placed in a small oven (heated to 60, 80, and 25 °C, respectively) attached to the front of a pulsed (10 Hz) gas valve (General Valve Series 9), where helium (at 75, 285, and 75 psia, respectively) was expanded over the samples and into a high-vacuum chamber (10^{-6} Torr). Just outside the orifice of the oven, low-energy electrons were produced by laser/photoemission from a pulsed Nd:YAG laser beam (10 Hz, 532 nm) striking a translating, rotating, copper rod (6.35 mm diameter) (see Figure 2). Negatively charged anions were then pulse-extracted into the spectrometer prior to mass selection and photodetachment.

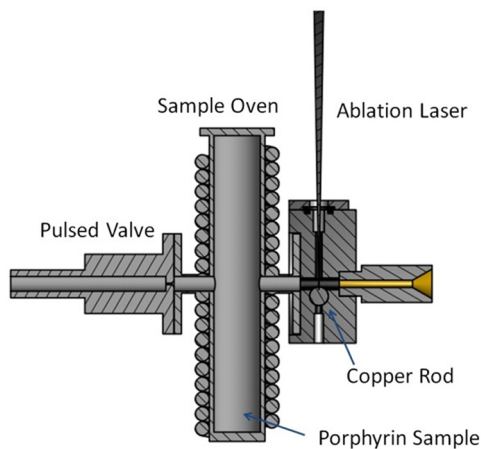


Figure 2. Cross sectional view of the laser photoemission/oven anion source.

Electron detachment spectra from the anion have been calculated using PBE-GGA,²⁵ NRLMOL, and very large Gaussian orbital basis sets.^{26,27} In all cases, the anion geometry has been fully relaxed. For example, for the Fe center we have used 20 single Gaussians, with decay parameters ranging between 0.0452 and 3.87×10^6 , to construct a set of 11 s-type contracted Gaussians, 4 of which have r^2 prefactors, 5 p-type contracted Gaussians, and 4 d-type contracted Gaussians. Similar size basis sets were used for the Ni and Mn calculations. For the nitrogen atoms, we used 13 single Gaussians, with decay parameters ranging from 0.094 to 5.18×10^5 , to construct a set of 8 s-type contracted Gaussians, 3 of which have r^2 prefactors, 3 p-type contracted Gaussians, and 4 d-type contracted Gaussians. For the carbon atoms, we used 12 single Gaussians ranging between 0.077 and 2.22×10^4 with the same contractions as for the N case. For the hydrogen atoms, we used 6 single Gaussians, with decay parameters ranging from 0.0745 to 77.8, to construct a set of 4 s-type contracted Gaussians, 1 of which has an r^2 prefactor, 2 p-type contracted Gaussians, and 1 d-type contracted Gaussians. These basis sets have been well tested on molecular magnets, which contain multiple ligated transition metal centers. The functions satisfy a theorem,²⁷ which says that the shortest range function on each atom should scale as $Z^{10/3}$ to ensure that basis-set superposition error, rigorously for the 1s core electrons, is zero. A discussion of the numerical details and the strategy for massive parallelization has been presented elsewhere.²⁶ Additionally, calculations using this same methodology have been applied to molecules having metal ions^{28–30} and to porphyrin complexes.³¹

All possible rotations of phenyl groups in neutral $\text{Fe}(\text{TPP})$ were tested. The structure with all four phenyl groups perpendicular to the plane of the porphyrin was found to be the lowest-energy structure, by 2.93 eV, relative to the structure composed of two in-plane phenyl groups and two phenyl groups perpendicular to the plane of the porphyrin. The structure with all phenyl groups in the plane was found to be 7.16 eV above the lowest porphyrin geometry. The sterically hindered structures are sufficiently high in energy so that they are not expected to be present in the experiment. For the lowest-energy structure, we find the neutral state to have a triplet ground state. The relaxed anion structure with four perpendicular phenyl groups is a doublet. This protocol was utilized for all three porphyrin anion systems studied here for calculating the main features of their photoelectron spectra.

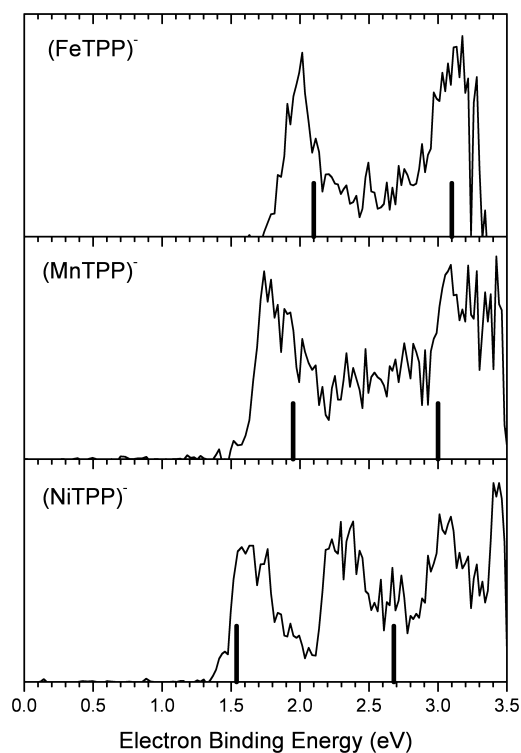
■ RESULTS AND DISCUSSION

The photoelectron spectra of $\text{Fe}(\text{TPP})^-$, $\text{Mn}(\text{TPP})^-$, and $\text{Ni}(\text{TPP})^-$ parent anions are presented in Figure 3. The photoelectron spectrum of the $\text{Fe}(\text{TPP})^-$ anion contains two vibrationally unresolved, electronic transitions (bands), centered at 2.0 and 3.1 eV. Two unresolved electronic bands are also observed in the $\text{Mn}(\text{TPP})^-$ anion spectrum, centered at 1.7 and 3.1 eV. The spectrum of the $\text{Ni}(\text{TPP})^-$ anion contains at least four unresolved bands, centered at 1.6, 2.3, 3.0, and 3.4 eV.

The adiabatic electron affinity, EA, is the difference in energy between the lowest-energy state of the anion and the lowest-energy state of its neutral counterpart. When significant Franck–Condon overlap exists between $\nu'' = 0$ of the anion and $\nu' = 0$ of its corresponding neutral (the origin transition) and when vibrational hot bands are not a significant issue, the EBE of the intensity threshold corresponds to the EA value.

Table 1. Experimentally Observed and Theoretically Calculated Transitions of Metal–Tetraphenyl Porphyrins and Their Anions (All EA and VDE Units in eV)

porphyrin	EA		VDE		vertical transition to first excited neutral state	
	experiment	experiment	theory		experiment	theory
Fe(TPP)	1.8	2.0	2.1 ($S = 1/2$ to $S = 1$)		3.1	3.1 ($S = 1/2$ to $S = 0$)
Mn(TPP)	1.6	1.7	1.95 ($S = 1$ to $S = 3/2$)		3.1	3.0 ($S = 1$ to $S = 1/2$)
Ni(TPP)	1.5	1.6	1.54 ($S = 1/2$ to $S = 0$)		2.3	2.68 ($S = 1/2$ to $S = 1$)

**Figure 3.** Anion photoelectron spectra of $\text{Fe}(\text{TPP})^-$, $\text{Mn}(\text{TPP})^-$, and $\text{Ni}(\text{TPP})^-$ measured with 355 nm photons. The calculated transitions are shown as stick spectra.

Because the structures of these anions and their neutral counterparts are similar, we expect the origin transitions to be present under the observed spectral bands. Although the presence of vibrational hot bands is more difficult to assess *a priori*, the strong helium expansions and the low porphyrin densities that were used in these experiments make it likely that the porphyrin anions were relatively cool. Thus, we interpret the EBE values of the observed intensity thresholds in these anion spectra to be the EA values of their neutral counterparts. The EA values for $\text{Fe}(\text{TPP})$, $\text{Mn}(\text{TPP})$, and $\text{Ni}(\text{TPP})$ were thus determined to be 1.8, 1.6, and 1.5 eV, respectively. We designate an uncertainty of ± 0.1 eV in each case.

Computationally, the vertical detachment transition energies (no geometry relaxation) are determined by calculating the vertical energy difference between the anion's ground state and the various electronic states of their neutral counterpart, each of these at the structure of the anion. For $\text{Fe}(\text{TPP})^-$, we identified a bound doublet anion with vertical transitions to its neutral triplet and singlet states at 2.1 and 3.1 eV, respectively. A bound triplet anion was found for $\text{Mn}(\text{TPP})^-$ with vertical transitions to its neutral quartet and doublet states occurring at 1.95 and 3.0 eV, respectively. $\text{Ni}(\text{TPP})^-$ exists as a bound doublet anion with vertical transitions to its neutral singlet and triplet states at 1.54 and 2.68 eV, respectively. In most cases, our calculated

transition energies are consistent with our experimentally determined values. However, there is a small discrepancy between experiment and theory in the case of the second calculated photoelectron transition for $\text{Ni}(\text{TPP})^-$. It is well-known that the application of DFT is often more challenging for nickel than for other transition metals,³² where Hubbard-U approximations are often needed to obtain a qualitatively correct valence, within PBE-GGA, for the Ni ion.³³ Nevertheless, this suggests that the relatively large molecular systems discussed here, especially the Ni system, should provide good tests for the recently proposed self-interaction-corrected density functional methods.^{34,35} These have recently been applied to systems containing isolated and open metal centers, similar to those discussed here.³⁵

Our experimental and computational results are summarized in Table 1. The transition energy from the anion's ground state to the ground state of its corresponding neutral is generally termed the vertical detachment energy, VDE, this being the EBE of the intensity maximum for that band. Similarly, the next higher-energy transition is from the anion's ground state to the first excited state of the anion's neutral counterpart. These six values are listed in Table 1. Likewise, the first two calculated transition energies for all three porphyrin systems studied here are also presented there. Our experimentally reported electron affinities for $\text{Fe}(\text{TPP})$, $\text{Mn}(\text{TPP})$, and $\text{Ni}(\text{TPP})$ are 1.8, 1.6, and 1.5 eV, respectively. Those for $\text{Fe}(\text{TPP})$ and $\text{Ni}(\text{TPP})$ are in excellent agreement with the experimental EA values obtained previously by Ridge and co-workers^{18,19} (1.87 and 1.51 eV, respectively) as well as with the calculated values for the same two systems determined by Liao and Scheiner²⁴ (1.82 and 1.51 eV, respectively). In the cases of $\text{Fe}(\text{TPP})$ and $\text{Ni}(\text{TPP})$, the excellent agreement between our photoelectron-determined EA values, the ICR-determined EA values of Ridge and co-workers, and the calculated EA values of Liao and Scheiner validates our assumption of insignificant vibrational excitation (hot bands) in their anions.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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