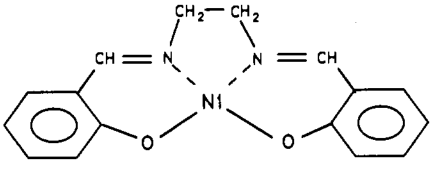

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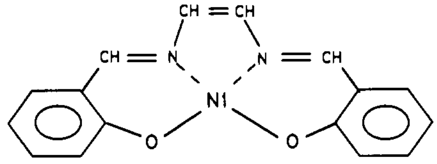
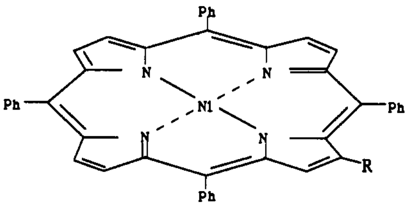


2

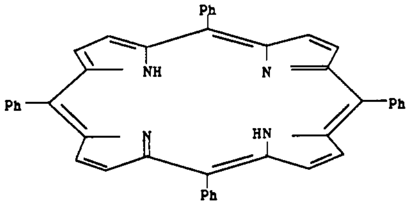
increase from EA(**1**) and EA[$Ni(CO)_3$] suggests significant delocalization of charge from the metal onto the ligand in the conjugated system **2**.

Equilibrium constant measurements give EA = 1.51 ± 0.01 eV for Ni(TPP) (**3**).[13] The reference electrophile in this case is maleic anhydride. The fact that EA(NiTPP) is even greater



3: R=H

5: R=CHO



4

than EA(**2**) suggests significant delocalization of charge into the ligand in the metal porphyrin complex. To further investigate whether charge is delocalized into the porphyrin ring in $Ni(TPP)^-$, the electron affinities of the free base H_2TPP (**4**) and Ni(TPP-CHO) (**5**)[14] were determined by using 1,3-dinitrobenzene (EA = 1.65 eV) as the reference electrophile. H_2TPP has an EA of 1.69 eV, somewhat higher than that of Ni(TPP). This is consistent with extended Huckel MO calculations, which indicate the H_2TPP $e_g(\pi)$ LUMO to be lower in energy than the Ni(TPP) $e_g(\pi)$ LUMO.[15] Ni(TPP-CHO) has an EA of 1.74 eV, a significant increase from that of Ni(TPP). That the electron-withdrawing CHO substituent on a β-pyrrole position on the porphyrin significantly increases the EA also suggests that the Ni(TPP) LUMO is significantly delocalized into the ring.

The question of whether the orbital that accepts an electron to form an anion is substantially delocalized onto the ligand, forming a radical anion, or is primarily a metal orbital, so that a nickel(I) anion is formed, has recently been discussed by Lexa et al.[16] They conclude from spectroscopic evidence and from solvent effects on reduction potentials that the unpaired electron in $Ni(TPP)^-$ resides in an orbital located primarily on the metal [a "Ni(I)" complex]. The metal is coordinated by a solvent molecule, however, and the stability of the anion is solvent sensitive. Thus it may be that the solvent inverts the relative metal and ligand orbital energies. Our results are simply interpreted in terms of an electron delocalized onto the ligand in the gas-phase anion [a Ni(II) radical anion].

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Gas-Phase Synthesis of Metalloporphyrin Ions

Karl K. Irikura and J. L. Beauchamp*

Arthur Amos Noyes Laboratory of Chemical Physics†
California Institute of Technology
Pasadena, California 91125

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Metalloporphyrins are important in biology[1] and in catalysis,[2] with the metal center often playing a key role in electron transfer, oxidation, or more complex chemical transformations. It is often difficult to identify the active species involved in these reactions. For example, the active intermediate in hydrocarbon activation by cytochrome P-450 is too reactive to be isolated.[3] A cationic oxo–iron porphyrin complex is widely supposed to be responsible,[4] but complexes of other metals are more tractable and are usually studied instead.[5] In order to examine the chemistry of well-characterized metalloporphyrin ions, we are investigating methods for the generation of such species, in the gas phase, within a Fourier transform ion cyclotron resonance (FTICR) spectrometer. We report here a straightforward, fairly general procedure that we have used with success to generate a wide variety of both cationic and anionic metalloporphyrin ions.

Gas-phase metalloporphyrin ions, $M(P)^+$, have been known since early studies of the mass spectra of metalloporphyrins.[6] The first reports of $M(P)^+$ in a trapped-ion spectrometer are those of Wilkins and co-workers. They identified $M(P)^+$ (P = TPP, FTPP, and TPyP) among the products of fast-atom bombardment or CO_2 laser desorption of films of metalloporphyrins or of porphyrins codeposited with metal salts.[7] We have tested similar procedures in our search for a good source of $M(P)^+$. Pulsed CO_2 laser evaporation of dimethylated bovine hemin[8] deposited on a stainless steel substrate produces a small amount of $Fe(P)^+$, but yields mostly smaller fragment ions. Excimer laser ablation of a pellet of $FeCl_2$ impregnated with porphine provides a weak and rather unstable supply of $Fe(P)^+$.[9] Since these sources do not provide abundant $M(P)^+$ over long periods of time, they are not ideal for chemical studies. Subsequently, we found that many metal ions,

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† Contribution No. 8235.

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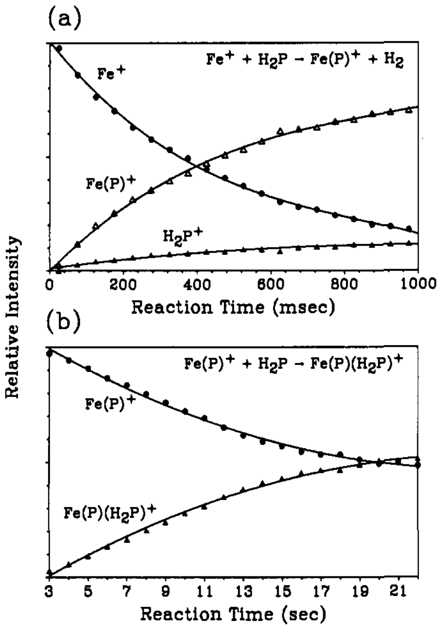

Figure 1. (a) Laser ablated Fe^+ reacts with H_2P by dehydrogenation to produce $Fe(P)^+$ and by charge transfer to produce H_2P^+. (b) $Fe(P)^+$ slowly adds a second porphine molecule to form $Fe(P)(H_2P)^+$.

both bare and ligated, react with porphine vapor to produce metalloporphyrin cations and anions in good yield. Porphine vapor is supplied by a small (1 mm i.d.) heated quartz tube mounted beneath the ion trap. One or two milligrams of porphine lasts for several days.

One example of $M(P)^+$ formation is illustrated in Figure 1. Fe^+ is generated by excimer laser (308 nm) ablation of an iron disk and reacts with porphine[10] to produce $Fe(P)^+$ and hydrogen (Figure 1a). Exothermic charge transfer from Fe^+ (IP = 7.87 eV[11]) to porphine (IP = 6.6 eV[11]) generates H_2P^+ as well. Reaction of Fe^+ with labeled[12] porphine-d_{12} yields only fully deuterated $Fe(P\text{-}d_{12})^+$, reaction 1, indicating an N,N-dehydrogenation process and therefore a metalloporphyrin structure. Although the relevant thermochemistry is not well-established, the exothermicity of reaction 1 can be used to estimate that the Fe^+–P bond strength is greater than about 126 kcal/mol.[13] Condensation

$$Fe^+ + H_2P\text{-}d_{12} \rightarrow Fe(P\text{-}d_{12})^+ + H_2 \qquad (1)$$

with a second H_2P molecule occurs more slowly to yield $Fe(P)(H_2P)^+$ (Figure 1b). In the presence of ligating molecules such as pyridine, complexes $Fe(P)(L)^+$ are also formed. Interestingly, we have not observed any doubly ligated metalloporphyrin ions in the systems studied thus far.

Since the porphine vapor in our vacuum system condenses before reaching the pressure gauge, we do not know the porphine pressure in our cell and are unable to measure the rate of reaction 1 directly. It is, however, at least 10% as fast as proton transfer reactions that generate H_3P^+. Since gas-phase proton transfer reactions are generally efficient, we estimate that reaction 1 occurs at least once in every 10 collisions.

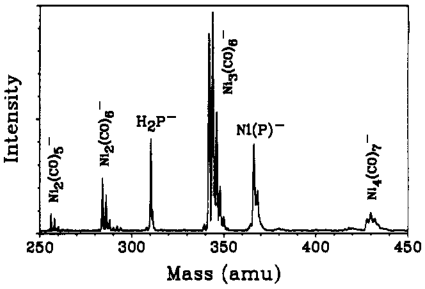

Figure 2. Dissociative electron attachment to $Ni(CO)_4$ generates $Ni(CO)_3^-$, and subsequent clustering produces $Ni_n(CO)_m^-$. These clusters in turn react with H_2P to yield $Ni(P)^-$. Electron transfer to H_2P produces H_2P^-.

Table I. Metal–Porphine Ions Generated

ion	source
$Fe(P)^+$	$Fe^+ + H_2P$ $Fe(CO)_5 + H_2P + e^-$ $FeCl_2/H_2P$ + laser
$Fe(P)(CH_3CN)^+$	$Fe^+ + H_2P + CH_3CN$
$Fe(P)(pyr)^+$	$Fe^+ + H_2P$ + pyridine
$Fe(P)(H_2P)^+$	$Fe^+ + H_2P$
$Fe(P)(acetone)^+$	$Fe^+ + H_2P$ + acetone
$Fe(P)OH^+$ (minor)	$Fe(P)^+$ + *t*-BuOOH
$Ni(P)^+$, $Ni(P)^-$	$Ni(CO)_4 + H_2P + e^-$
$Co(P)^+$, $Co(H_2P)^+$, $Co(P)^-$	$Co(CO)_3(NO) + H_2P + e^-$
$Mn(P)^+$	$Mn^+ + H_2P$
$Mn(P)(pyr)^+$	$Mn^+ + H_2P$ + pyridine
$Cr(P)^+$, $Cr(P)^-$	$Cr(CO)_6 + H_2P + e^-$

Metalloporphyrin anions require a different approach, since we usually obtain no atomic anions from laser ablation of metals. Dissociative electron attachment to metal compounds often yields reactive ligated anions. For example, electron attachment to $Ni(CO)_4$ yields only $Ni(CO)_3^-$, which reacts with the neutral vapor to produce metal cluster ions. The cluster ions are reactive with

$$Ni(CO)_4 + e^- \rightarrow Ni(CO)_3^- + CO \qquad (2)$$

$$Ni(CO)_3^- + nNi(CO)_4 \rightarrow \rightarrow Ni_{n+1}(CO)_m^- + (4n + 3 - m)CO \qquad (3)$$

$$Ni_{n+1}(CO)_m^- + H_2P \rightarrow Ni(P)^- + [Ni_n, mCO, H_2] \qquad (4)$$

porphine, yielding $Ni(P)^-$. This is illustrated in Figure 2. Also evident in Figure 2 is the porphine radical anion, H_2P^-, formed by electron transfer to H_2P. Many metal–porphine and metalloporphyrin ions can be generated by using these methods. Table I contains a list of the results obtained so far. Note that the gas-phase chemistry makes it unnecessary to synthesize a separate complex for each metal.

We have made attempts to oxidize $Fe(P)^+$ to produce $Fe(P)O^+$ as a gas-phase model for the reactive centers of enzymes such as cytochrome P-450 and peroxidase. Unfortunately, we have so far been unable to get closer than $Fe(P)OH^+$, formed as a minor product in the slow reaction between $Fe(P)^+$ and *tert*-butyl hydroperoxide.[14] Since the chemistry of the $Fe(P)O^+$ moiety is strongly influenced by its environment,[15,3] isolation in the gas phase would permit its intrinsic reactivity to be studied. We are continuing our efforts in this direction, as well as investigating other chemistry of both $Fe(P)^+$ and axially ligated $Fe(P)(L)^+$.

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