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Gas-Phase Charge-Transfer Reactions and Electron Affinities of Macrocyclic, Anionic Nickel Complexes: Ni(SALEN), Ni(tetraphenylporphyrin), and Derivatives

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We describe here the gas-phase reactions of radical anions of several Ni complexes of tetradentate ligands. The neutral complexes are 16-electron metal complexes, and the corresponding anions are 17-electron species. We have found that facile electron transfer to an organic electrophile is characteristic of these species and that in some cases it is possible to observe reversible electron-transfer reactions. In these cases the electron affinity (EA) of the complex can be determined from the equilibrium constant of the charge-transfer reaction and the EA of the electrophile. We report several such electron affinities here and believe these to be the first gas-phase electron affinities for such species.

These measurements are made possible by the availability of Fourier transform ion cyclotron resonance techniques.[1] Because of the very long ion trapping time, it is possible to examine reactions of ions with neutral species of very low vapor pressure. Also critical to these measurements is the reliable gas-phase electron affinity scale which was developed by equilibrium constant measurements by Fukuda and McIver[2] and Kebarle et al.[3] and photodetachment studies of SO_2 by Cellota, Bennett, and Hall.[4] We use the numbers given by Kebarle in a recent review.[3]

Ni(SALEN) (**1**) prepared by methods in the literature[5,6] was introduced into the vacuum system of an FT-ICR instrument (FTMS-2000,[7] Extrel, Madison, WI) on a heated probe. An electrophile such as nitrobenzene was introduced through the batch inlet system. The two species at a combined nominal pressure of $\sim 10^{-7}$ Torr were exposed to a 5-ms pulse of a nominal 4-eV electron beam. The radical parent ions of both neutrals were formed by attachment of scattered electrons caught in the trap. The intensities of the ion signals were monitored as a function of delay after the electron beam pulse. When the total ion signal stopped increasing, indicating that all electrons in the trap had been consumed by attachment, one of the ions was ejected. After the ejection, the reversible electron transfer was allowed to come to steady state. The product of the ratio of the steady state ion signals and the ratio of the neutral pressures was taken as the equilibrium constant for charge transfer. Throughout these studies the ratio of neutral pressures was estimated from the electron-impact mass spectrum of the mixture and the relative ionization cross sections of the components.[8] The final equilibrium constants were found to be independent of which ion was ejected and independent of pressure. A typical result for reaction 1 is illustrated in Figure 1. Assuming that $\Delta G = \Delta H$[3] for reaction 1 and taking

$$\mathrm{Ni(SALEN)^- + C_6H_5NO_2 \leftrightarrow C_6H_5NO_2^- + Ni(SALEN)} \tag{1}$$

the electron affinity of $C_6H_5NO_2$ as 1.01 eV gives EA[Ni(SALEN)] = 1.06 ± 0.01 eV. This is strikingly similar to EA[$Ni(CO)_3$] = 1.08 eV.[9]

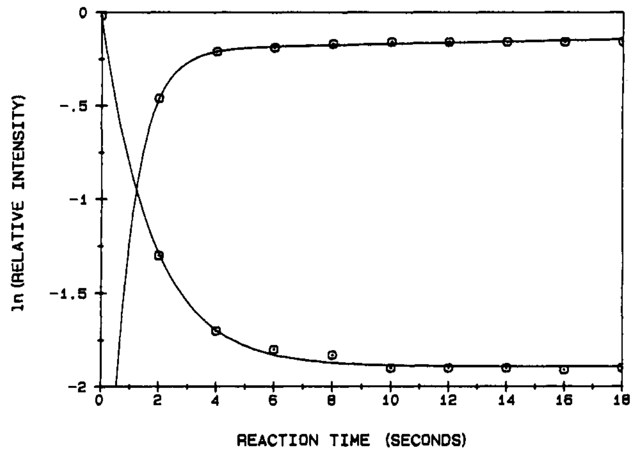

Figure 1. The variation with time of $Ni(SALEN)^-$ and nitrobenzene anion in a mixture of the two neutrals following ejection of $Ni(SALEN)^-$ from the trap. The $Ni(SALEN)^-$ increases and nitrobenzene anion decreases as a result of a reversible electron transfer which eventually comes to equilibrium.

Both $Ni(CO)_3$[10] and $Ni(CO)_3^-$[11] are planar; so are Ni(SALEN) and $Ni(SALEN)^-$. This structural similarity combined with the similarity in EAs suggests that the two anions have similar singly occupied orbitals. This in turn suggests that the added electron in the singly occupied orbital in $Ni(SALEN)^-$ is not substantially delocalized into the ligand.

$Ni(SALEN)^-$ was found not to react with CH_4, CH_3I, C_6H_{12}, CH_3OH, or $(CH_3)_2C{=}O$. The upper limit on the rate constants is about 1.5×10^{-13} cm^3 s^{-1}. This is in contrast to a previous report that $Ni(SALEN)^-$ reacts with CH_4 and $i\text{-}C_4H_{10}$.[12] The earlier work involved reactions in a CH_4 plasma at 1 Torr total pressure. Such a plasma contains a variety of radicals which probably react to produce the ions attributed to CH_4 reaction.

On heating of Ni(SALEN) on the probe, a peak corresponding to the loss of H_2 from Ni(SALEN) appeared in both positive- and negative-ion mass spectra. The relative intensity of the peak increased with temperature, indicating a thermally activated loss of H_2 from the neutral. The peak was attributed to a species with structure **2** as the most thermodynamically favorable H_2 loss product of Ni(SALEN) (**1**). This process provided an opportunity to determine the EA of **2**. Electron transfer between **2** and maleic anhydride and between **2** and 4-bromonitrobenzene is reversible, and from equilibrium constant measurements for these processes, it was found that EA(**2**) = 1.37 ± 0.01 eV. The substantial

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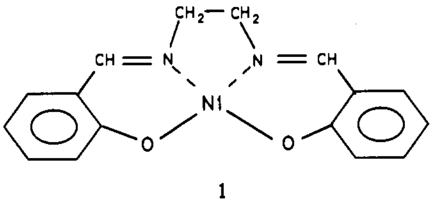

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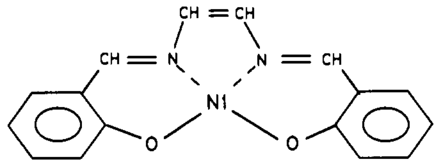
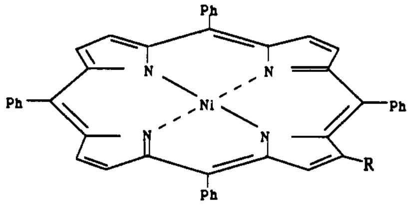


2

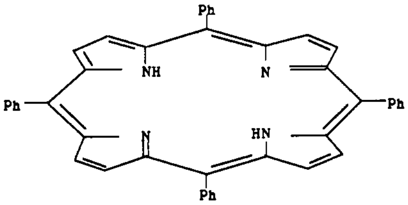
increase from EA(**1**) and EA[Ni(CO)$_3$] suggests significant delocalization of charge from the metal onto the ligand in the conjugated system **2**.

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 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.



3: R-H

5: R-CHO



4

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

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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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