

Figure 2. Ni 2p spectra of the bis(fulvalene)nickel complexes and the nickelocenium salt, showing the unusual binding energy trend in the series. Intense shake-up satellites are seen in the paramagnetic complexes.

broadening is due to two unresolved lines arising from the mixed valence.

Acknowledgment. We are grateful to Dr. Tihomir Novakov and Dr. Ray Dod for assistance in the use of the AEI spectrometer, Dr. Merle Millard for assistance in the use of the DuPont spectrometer, and Mr. Paul Sharp for the preparation of bis(fulvalene)diiron. This work was supported by the National Science Foundation (Grant CHE 73-05133 AO2) and the Division of Chemical Sciences, Office of Basic Energy

Sciences, U.S. Department of Energy.

Registry No. $(C_5H_5)_2Fe$, 102-54-5; $[(C_5H_5)_2Fe]PF_6$, 11077-24-0; $(C_{10}H_8)_2Fe_2$, 11105-90-1; $(C_5H_5)Co(C_5H_6)$, 33032-03-0; $(C_5H_5)_2Co$, 1277-43-6; $[(C_5H_5)_2Co]PF_6$, 12427-42-8; $(C_{10}H_8)_2Co_2$, 69365-57-7; $[(C_{10}H_8)_2Co_2]PF_6$, 69365-59-9; $[(C_{10}H_8)_2Co_2](PF_6)_2$, 39333-80-7; $(C_5H_5)_2Ni$, 1271-28-9; $[(C_5H_5)_2Ni]PF_6$, 69365-60-2; $(C_{10}H_8)_2Ni_2$, 62518-80-3; $[(C_{10}H_8)_2Ni_2]PF_6$, 62873-73-8; $[(C_{10}H_8)_2Ni_2](PF_6)_2$, 62518-79-0.

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Photoelectron Spectroscopic Study on Metalloctaethylporphyrins

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Received October 25, 1978

The UV photoelectron (PE) spectra of octaethylporphyrin (H_2OEP) and its metallo derivatives containing a variety of divalent cations (Mg, Fe, Co, Ni, Cu, Zn, Pd) are presented. The spectral positions of the first two bands at 6–7 eV which correspond to an electron ejection from the porphyrin π system (A_{1u} and A_{2u} states) show a metal dependence. The first (and the second) ionization potential well correlates to the half-wave potential associated with the OEP ring oxidation obtained by cyclic voltametry. On the basis of this relationship, the ring oxidation potentials for the OEP derivatives with divalent Fe and Co atoms, which have still been beyond experimental observation, are estimated to be 0.4 V vs. SCE. The bands between 7 and 9 eV, which also exhibit a remarkable metal dependence, may be assigned to an electron ejection from the porphyrin π system.

I. Introduction

Studies on the oxidation–reduction properties of metalloporphyrin complexes have long been a keen problem to the biochemist and chemist alike.² Prominent examples of such complexes are iron porphyrins serving as prosthetic groups in peroxidases, catalases, and cytochromes. The redox behavior of metalloporphyrins can be widely modified over a large potential range by changing the central metal ion, the coordinating ligands, and the porphyrin peripheral groups.

Many electrochemical studies have been performed with the aim of elucidating the relationship between the electronic structure and the redox properties of metalloporphyrins. Especially, in relation to the significance of an iron atom, the effect of the central metal ion on the ring redox characteristics has been vigorously studied by cyclic voltametry (CV)^{3,4} in

nonaqueous solvents. The half-wave potentials of the porphyrin ring exhibit substantial variations with the central metal. On the contrary, in photoelectron spectroscopy (PES) which is relevant for obtaining ionization potentials (IP) directly, the IP values for *meso*-tetraphenylporphyrin (TPP)⁵ and its metallo derivatives have been shown to be insensitive to the central metal ion.

In this paper we present some details of PE spectroscopic studies of octaethylporphyrin and its metallo derivatives (Figure 1) in the gas phase. OEP derivatives are more suitable than TPP for the investigation of the PE spectra of porphyrins for inquiry into the central metal dependence, since PE spectra of TPP derivatives show a complexity of bands above 7 eV resulting from the phenyl π electrons. We will also point out a relationship between ionization and redox potentials in

Table I. Vertical Ionization Potentials^a from the Photoelectron Spectra of Octaethylporphyrin and Metallooctaethylporphyrins

compd	band no. ^b									
	1	2	3	4	5	6	7	8	9	10
H ₂ OEP	6.39	6.83	7.55 ^c	7.80 ^d	8.13 ^d	8.44 ^d	9.82 ^d			
MgOEP	6.19	6.57	7.42 ^c	7.63 ^d	8.30	8.92	9.33	9.50 ^d	9.68 ^d	9.82 ^d
FeOEP	6.06	6.48	7.29 ^c	7.65 ^d	8.05 ^e	8.21 ^e	9.40 ^f	9.70 ^f		
CoOEP	6.09	6.58	7.48 ^f	7.92 ^f	8.16	8.25	9.92 ^d			
NiOEP	6.38	6.88	7.15	7.80	8.16	8.42 ^d	9.96 ^d	10.24 ^d		
CuOEP	6.31	6.72	7.46	7.78 ^f	8.01 ^f	8.40 ^e	9.74 ^d			
ZnOEP	6.29	6.72	7.71 ^e	8.04 ^f	8.15 ^f	9.74 ^d				
PdOEP	6.37	6.82	7.28	7.42	7.78	8.08	8.30	8.43	9.41 ^f	9.85 ^f

^a Peak maxima in eV (± 0.03 eV). ^b The corresponding peaks among these compounds do not necessarily have the same band number. ^c Shoulder peak. ^d Error limit ± 0.1 eV. ^e Error limit ± 0.04 eV. ^f Error limit ± 0.07 eV.

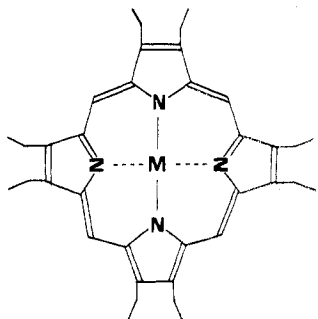


Figure 1. Metallooctaethylporphyrin (MOEP).

relation to the electronic structure of porphyrins and discuss the oxidation of the metal or the ligand of Fe^{II}OEP and Co^{II}OEP complexes.

II. Experimental Section

The preparation of H₂OEP has already been reported,^{6,7} and its metallo derivatives (Mg, Co, Ni, Cu, Zn, Pd) were prepared according to the methods described in the literature.⁸ Fe(OEP)Cl was also prepared by the usual method.⁹ These porphyrin derivatives were characterized by optical absorption spectroscopy.

Photoelectron spectra, with the He I resonance line at 21.21 eV (H₂OEP and Fe-, Co-, Cu-, and ZnOEP) and He II at 40.81 eV (NiOEP and MgOEP) were recorded on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe. The spectra were calibrated by the admission of a Xe-Ar gas mixture into the heated target chamber containing the sample vapor. The sample was heated gradually until the desired temperature was reached. The spectra reported in this paper were all taken in the 280–320 °C range. The instrumental resolution was 20–30 meV for Ar 2P_{1/2,3/2} peaks.

A JEOL 01SG mass spectrometer was used to determine the purity of all compounds studied in the gas phase. The spectra were recorded at 220 °C with an ionizing voltage of 75 V. The parent peak which was essentially the most intense peak demonstrates the existence of the central metal ion for all the compounds except for Fe(OEP)Cl. The parent peak of Fe(OEP)Cl was about 1/600th as intense as the main peak resulting from FeOEP. In fact, Edwards et al.¹⁰ have reported from optical absorption spectra that Fe(OEP)Cl was reduced in a vapor phase to form a divalent iron complex without an axial ligand. This may be also the case for the present study. It is therefore likely that Fe(OEP)Cl in the gas phase also exists as a divalent form under our PES conditions.

III. Results and Discussion

Assignment of PE Spectra. The PE spectra of H₂OEP and its metallo derivatives are shown in Figures 2–4. Vertical ionization potentials obtained from peak maxima of these spectra are summarized in Table I. The observed spectra up to 16 eV may be characteristically separated into three distinct regions (I, II, and III), as has been the case for TPP derivatives,⁵ except for intense bands due to the phenyl group. Spectral region I is between 6 and 7 eV, region II between 7 and 9 eV, and region III above 9 eV. The two closely lying peaks in region I are well separated by ca. 0.5 eV which is to be compared with the values for TPP (ca. 0.3 eV). The PE

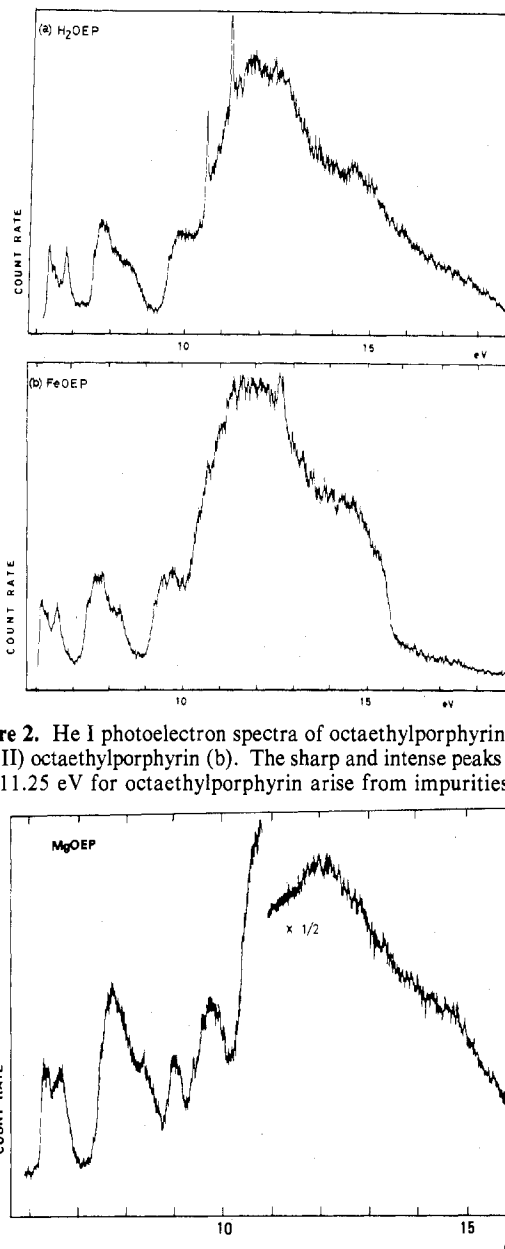


Figure 2. He I photoelectron spectra of octaethylporphyrin (a) and iron(II) octaethylporphyrin (b). The sharp and intense peaks at 10.61 and 11.25 eV for octaethylporphyrin arise from impurities.

Figure 3. He II photoelectron spectra of magnesium octaethylporphyrin.

spectral difference between the second and third band is relatively large (~ 1 eV), as is always the case for OEP and TPP complexes.

(A) PE Spectra in Region I. The shapes of the first two bands in a PE spectrum of H₂OEP closely resemble those¹¹ of pyrrole, which is a basic constituent of a porphyrin ring.

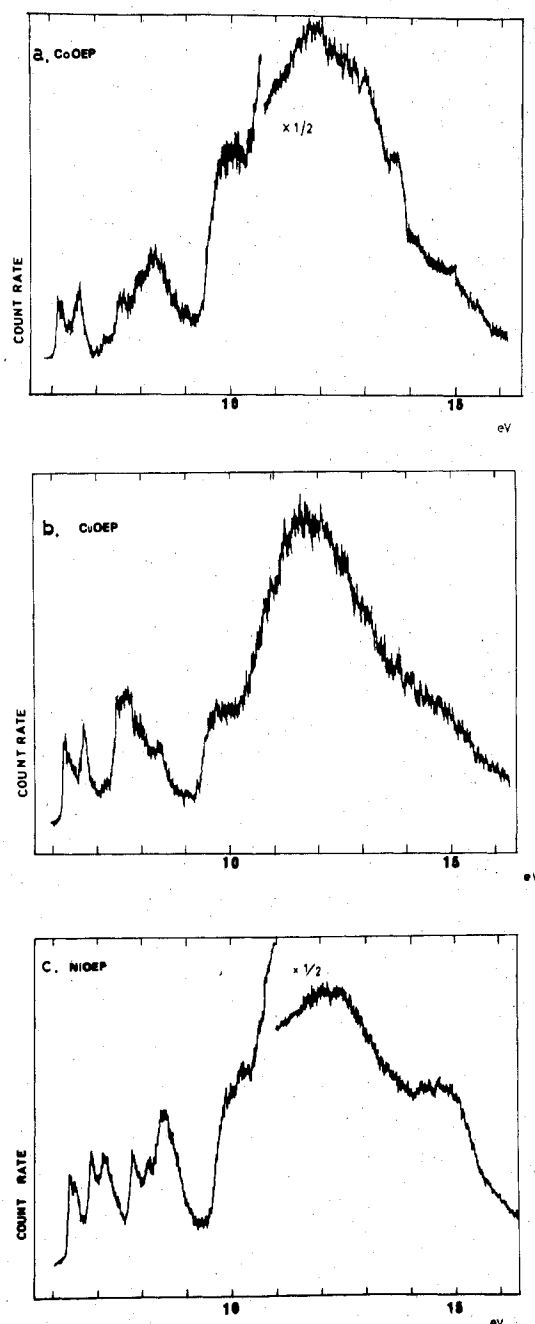


Figure 4. He I photoelectron spectra of cobalt (a) and copper (b) octaethylporphyrin complexes. The He II photoelectron spectrum of nickel octaethylporphyrin is presented in part c.

This suggests that the first two peaks¹² of H₂OEP are associated with electrons of pyrrolic π orbitals. Most theoretical calculations¹⁴⁻¹⁹ have also shown that the highest occupied MO's are closely lying π orbitals of the porphyrin moiety. Recent ab initio SCF-MO studies on porphine¹⁵ and magnesium porphine¹⁶ have reported that, on the basis of Koopmans' theorem, the first two IP values are estimated to be 6.8 (a_u) and 7.2 (b_{1u}) eV for porphine and 6.4 (a_2) and 7.1 (a_1) eV for magnesium porphine. These values are in good agreement with our experimental ones, 6.39 and 6.83 eV for H₂OEP and 6.19 and 6.57 eV for MgOEP (Table I).

With respect to the copper porphine complex, an X α calculation¹⁸ has been performed, from which the g and hyperfine coupling tensors were in good agreement with the experimental results. Unfortunately, however, the predicted value of 9.1 eV for the first IP is much larger than the observed value of 6.31 eV given in Table I. Kashiwagi et al.¹⁹ have

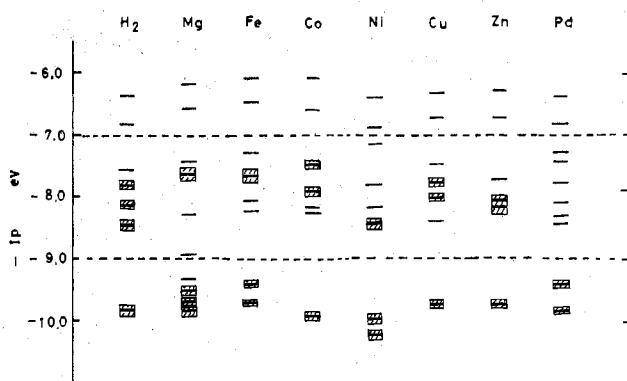


Figure 5. Energy levels for ionized states of metalloctaethylporphyrins and octaethylporphyrin obtained from PE spectra. The shaded portion shows the uncertainty of the observed ionization energies obtained from the broad PE band.

carried out ab initio LCAO-SCF-MO calculations on cobalt porphine, predicting that the first and the second IP's are 6.51 and 6.57 eV resulting from A_{1u} and A_{2u} states,²⁰ respectively. These calculated IP's agree well with our experimental values of 6.09 and 6.58 eV in Table I. With the aid of the theoretical results, one can assign the first two peaks to an electron ejection from the porphyrin π systems. The MO calculations, however, may not determine the relative order of these π cationic states because of their very small energy difference (<0.5 eV) as shown in Table I. The ESR and optical spectroscopic studies on porphyrin cation radicals might be more useful to determine the relative order than the theoretical ones. These studies^{21,22} have revealed that $[MgOEP]^+ClO_4^-$ and $[ZnOEP]^+ClO_4^-$ have an A_{1u} state and that each ground state is not interchanged by other ligands such as Br⁻ and Cl⁻ ions. It is therefore likely that in our PE studies these two states of the complexes which have no axial ligands in the gas phase would not be interchanged, and thus the ground state of the cation radical may correspond to the state of the first band in the PE spectrum. Consequently, the first band of both MgOEP and ZnOEP is most probably assigned to an A_{1u} state. Similarly, one can ascribe the first band of the NiOEP and CuOEP complexes to an A_{2u} state. The assignment in the case of FeOEP and CoOEP, however, is hardly possible at this time.

(B) PE Spectra in Region II. In order to facilitate the comparison of PE spectra, we present the energy level diagram of photoionized states of the OEP complexes in Figure 5, constructed from IP values given in Table I. In this figure, one can find that there exist several states in region II which exhibit a remarkable central-metal dependence. This differs from the central-metal independence of the PE spectrum in region II in the case of metallo TPP complexes. This is possibly because very intense peaks from phenyl π electrons may conceal the significant porphyrin π electron peaks.

When the present IP values are referred to the theoretical ones, a striking difference is encountered for the IP values above 7 eV; especially apparent is the gap between the second and the third IP's which is greater by 2 eV than that for the theoretical one. For instance, the calculated values of 9.2 eV¹⁵ for porphine and 9.67 eV¹⁶ for magnesium porphine are quite different from the experimental result of 7.42 eV, given in Table I. Hence, the theoretical calculation for the *ground state* of metalloporphine complexes fails to reproduce experimental results in region II. It is likely that Koopmans' theorem is not applicable for estimation of an IP value larger than 7 eV, except for the first two π cation states. This implies that the reorganization energy for the porphyrin complexes with an excitation energy higher than 9 eV is 1-2 eV. We are thus unable at present to assign the observed bands in detail with the aid of the theoretical studies.

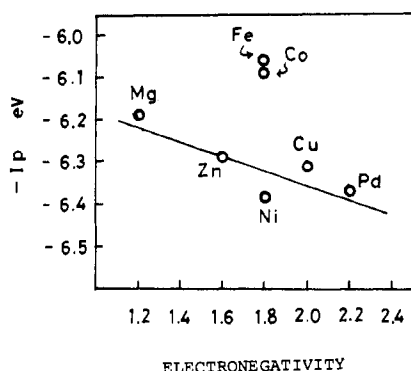


Figure 6. Plots of the first ionization potentials in PES vs. the electronegativity of the divalent metal ion.

As one can see in Figures 2–4, the well-separated third band at 7.15 eV for NiOEP and at 7.48 eV for CoOEP may correspond to the shoulder peak at 7.3–7.5 eV of the fourth broad band for other metallo derivatives. These third bands also appear to be assigned to the porphyrin π electrons, since the corresponding band for H_2OEP also appears at 7.55 eV as a shoulder one.

The PE spectral band due to an electron ejection from a d orbital is hardly detectable for the following reasons: (i) the low ratio of metal to OEP electrons and (ii) the photoionization transition probabilities²³ under our experimental conditions, where the ~ 4 Å wavelength of a photoemitted electron matches the curvature of the delocalized p-type electron wave functions very much better than that of the d electrons. In a recent paper,²⁴ the d-electron bands have been successfully observed for various transition-metal-phthalocyanine complexes by using X-ray-induced photoelectron spectroscopy (XPS), while ultraviolet spectra (UV)²⁵ have shown the much weaker intensities of d-electron bands compared with those of $p\pi$ -electron bands. Therefore, we may expect that our UV PE spectra mainly show the $p\pi$ bands whose intensities are larger than those of d bands. In addition to the above discussion, the spectrum in region II of MgOEP which has no d electrons is not so different from that of the other metallo complexes with d electrons. It is, therefore, likely that the bands in region II which clearly depend on the central metal ion are ascribed to an electron ejection from the ligand porphyrin π system.

Redox Properties of Metallo OEP Complexes. According to the cyclic voltametry (CV) of metallo OEP complexes, half-wave potentials ($E_{1/2}$) corresponding to the first IP in the PE spectra indicate the central-metal dependence, varying from 0.46 to 0.95 V vs. SCE.⁴ A similar trend has been observed even for metallo TPP complexes. Moreover, a similar dependence was also observed in photocurrent measurements²⁶ of metallo TPP complexes which afford the first IP with the aid of a theoretical relation. Hence, it is reasonable to conclude that the central metal ion affects substantially the π electronic structure of metalloporphyrin. It is noticeable in Figure 5 that, except for the Fe and Co complexes, the first two states above -7 eV appear to shift to the lower energy region with an increase in electronegativity²⁷ of the central metal, as is more clearly visualized in Figure 6. This shift is attributable to an inductive effect of the central metal on the porphyrin π electronic structure. The reason for deviation from such a linear relation for Fe and Co complexes is at present beyond our knowledge.

The central-metal dependence of both IP's and $E_{1/2}$'s allows us to expect that, when we consider the stable divalent metal ions in the gas phase, plots of ionization potentials of the first (and the second) peak vs. half-wave potentials on the OEP ring oxidation will yield a linear correlation. In Figure 7, one can

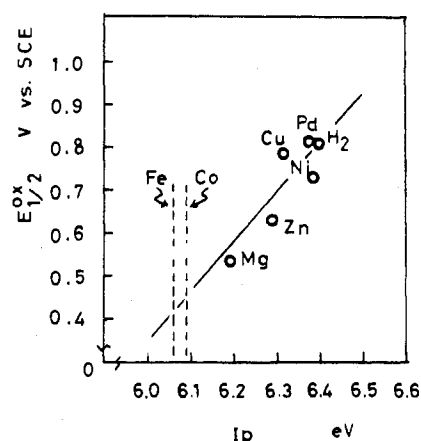


Figure 7. Plots of the first ionization potentials in PES vs. half-wave potentials of the ring oxidation in octaethylporphyrin and its metallo derivatives. The dashed lines show the position of IP values for Fe and Co complexes.

Table II. Redox Potentials of FeOEP and CoOEP Complexes (V vs. SCE)

	metal II \leftrightarrow III	ligand	
		$M^{II}OEP^a$	$M^{III}OEP^b$
Fe	-0.24 ^c	0.4	
Co	-0.34 ^d	0.4	1.00 ^c

^a The potential corresponds to the reaction $M^{II}OEP \leftrightarrow M^{III}OEP^+$. This is a hypothetical "working" value derived from the extrapolation of the linear relation in Figure 6. ^b The potential corresponds to the reaction $M^{III}OEP \leftrightarrow M^{III}OEP^+$. ^c See ref 4. ^d See ref 28.

find such a linear relationship for the six complexes. With respect to Fe and Co complexes, there have been no CV data reported, possibly because the oxidation of the central metal ($M(II) \rightarrow M(III)$) occurs prior to that of the porphyrin ring. It is, then, possible to estimate, by the use of the linear relation in Figure 7, the value of $E_{1/2}$ on the ring oxidation for divalent Co and Fe complexes, yielding the value of ca. 0.4 V vs. SCE. By referring Table II which contains the oxidation potentials associated with central metals and the ring for OEP complexes, one can readily understand that the divalent cobalt complex undergoes the ring oxidation at a lower value of $E_{1/2} = 0.4$ V vs. SCE than that of the trivalent one. This trend is qualitatively explained in terms of changes in the inductive effect of the central metal resulting from the change of the positive charge. Inspection of Table II also reveals that in the CoOEP complex the cobalt ion is more easily oxidized than the porphyrin ring. This is also the case for the Fe complex. However, we note in the present PE studies that the ring oxidation precedes the metal oxidation. This apparent inconsistency is possibly due to the medium effects. The PE measurement is carried out in the gas phase while the CV experiment was done in the solution with an electrolyte²⁹ and a potentially coordinating solvent. In the photocurrent method²⁶ of IP measurement where the nonpolar solvent was used, the ring oxidation preceded the metal oxidation as a consequence of electron ejection from the porphyrin π system. Consequently, the inherent redox properties of iron and cobalt porphyrins may be modified by the polar media of potentially coordinating solvent: solvent coordination to the central metal and/or polar media may reduce the oxidation potential of the metal ion.

IV. Summary

We have demonstrated the remarkable central-metal dependence of PE spectra for various metallo OEP derivatives. The bands between 6 and 9 eV are assigned to an electron

ejection from the porphyrin π system, partly with the aid of MO calculations on a ground state of metalloporphyrin complexes. The metal dependence of the first two bands may be interpreted in terms of the inductive effect of metal ion, except for Fe and Co complexes. Then, the first (and the second) IP correlates well with the oxidation potential of porphyrin ring.

Acknowledgment. The authors are grateful to Dr. H. Inokuchi for his support and encouragement of this work. They also thank Dr. T. Inubushi for some of metalloporphyrins and Dr. H. Kashiwagi for making his preprints available to them prior to publication and for helpful discussion. Discussions with Dr. K. Yoshikawa were also helpful. They thank Dr. K. Seki and Dr. K. Kimura for their assistance in the measurement of PE spectra and Dr. T. Ueno and Mr. Y. Hisamoto for the measurement of mass spectra. This work is supported in part by a grant from the Ministry of Education, Japan.

Registry No. H_2OEP , 2683-82-1; $MgOEP$, 20910-35-4; $FeOEP$, 61085-06-1; $CoOEP$, 17632-19-8; $NiOEP$, 24803-99-4; $CuOEP$, 14409-63-3; $ZnOEP$, 17632-18-7; $PdOEP$, 24804-00-0.

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Properties and Reactions of Uranium(IV) Tetrahydroborate by Ion Cyclotron Mass Spectrometry

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Received September 7, 1978

The gas-phase ion chemistry of $U(BH_4)_4$ is studied with the techniques of ion cyclotron resonance spectrometry. An electron impact ionization energy of 9.0 ± 0.5 eV is determined, and appearance energies for several positive fragment ions are reported. These data are analyzed to give $\Delta H_f[U(BH_4)_4] = -7 \pm 14$ kcal/mol as well as several bond dissociation energies for the parent neutral and its fragment ions. $U(BH_4)_4$ attaches thermal electrons to form the molecular anion. Fragment negative ions are observed with higher energy electrons. The reactions of both positive and negative ions in $U(BH_4)_4$ alone and with other gases are reported. The trapped-electron spectrum is obtained and compared with previous optical spectroscopic studies of $U(BH_4)_4$. Irradiation of major positive ions by a low-power CW CO_2 laser produced no evidence of photochemistry.

Introduction

Uranium(IV) tetrahydroborate, $U(BH_4)_4$, is among the most volatile uranium compounds known.¹ To our knowledge, only the monomethyl derivative, $U(BH_4)_3(BH_3CH_3)$, and UF_6 have higher vapor pressures. Because of this, $U(BH_4)_4$ has been suggested as a unique source of atomic uranium.² In addition, the use of this species as a reagent in isotope separation has been proposed.³

Uranium(IV) hydroborate is of intrinsic interest because of the unusual nature of the bonding involved. In the gas phase, the molecular symmetry is tetrahedral. Each boron is attached to the uranium atom by three hydrogen bridges.⁴ In

crystalline form, six BH_4^- groups surround each uranium atom. Two of these retain the three-point attachment seen in the gas phase. The other four, using two-point attachment to each uranium, bridge neighboring uranium atoms in a helical polymeric structure.⁵ The end result is an overall coordination number of 14, compared to 12 in the gas phase. In the similar zirconium(IV) tetrahydroborate, a tetrahedrally symmetric molecule, it has been shown by NMR that the hydrogens, both terminal and bridging, are indistinguishable.⁶

In the present investigation, we have undertaken to characterize the properties and reactions of $U(BH_4)_4$ and its ions both because there is potential technological importance of