Effects of Metal and Ring Reduction on Metallo(octaethylisobacteriochlorins). Resonance Raman Spectra of the Nickel(I), Copper(I), and Zinc(II) Radical Anion Complexes

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Resonance Raman (RR) spectra are reported for a series of metallo(octaethylisobacteriochlorin) (M(OEiBC)) anions, including $Ni^I(OEiBC)^-$, $Cu^I(OEiBC)^-$, $Zn^{II}(OEiBC)^-$, and their respective β,γ,δ-meso-deuteriated isotopomers ($M(OEiBC\text{-}d_3)^-$). In the course of these studies, RR spectra were acquired for both the high-spin (HS) and low-spin (LS) complexes of $Ni^{II}(OEiBC)$. These neutral and anionic complexes constitute a series in which the $d_{x^2-y^2}$ orbital of the metal ion is vacant [$Ni^{II}(OEiBC)$ LS] or singly [$Ni^{II}(OEiBC)$ HS, $Ni^I(OEiBC)^-$, $Cu^{II}(OEiBC)$] or doubly [$Cu^IOEiBC)^-$, $Zn^{II}(OEiBC)$, $Zn^{II}(OEiBC)^-$] occupied. The RR data for the neutral and reduced M(OEiBC) complexes indicate that reduction at the metal significantly perturbs the structures of the macrocycles. The structural changes that occur upon formation of the Ni(I) complex are not as large as those associated with the conversion of the Ni(II) species from LS to HS. The larger structural changes associated with the conversion to the HS form are attributed to the six-coordinate species adopting a more planar ring conformation. Both the RR and absorption data for the Ni(I) complex are consistent with significant metal-d_π–OEiBC back-bonding. The structural changes that occur upon formation of the Cu(I) complex are larger than those that occur upon conversion of Ni(II) LS to either Ni(II) HS or to the Ni(I) complex. The origin of the large structural changes that occur upon reduction to the Cu(I) complex is not clear. It is possible that the tendency of this ion to prefer a tetrahedral configuration drives the macrocycle into a highly nonplanar conformation. Finally, the vibrational data for $Zn^{II}(OEiBC)^-$ suggest that the structural changes associated with reduction to the ring-based radical anion are for the most part small.

Introduction

Cofactor F_{430} of methylreductase is a nickel-containing hydrocorphinoid macrocycle (Figure 1).[1-3] The hydrocorphinoid ring is highly saturated and supports the formation of a Ni(I) species which is thought to be an intermediate in the turnover of the enzyme.[4] Less highly reduced macrocycles also support the formation of Ni(I) complexes (as opposed to ring-based radical anions).[5-7] One-electron reduction of Ni(II) octaethylisobacteriochlorin, $Ni^{II}(OEiBC)$, affords a stable, isolatable Ni(I) complex (Figure 1);[7] consequently, this model complex and other nickel isobacteriochlorins have frequently been used as model systems for cofactor F_{430}.[7-11] More recently, Stolzenberg and co-workers have shown that the OEiBC macrocycle will also
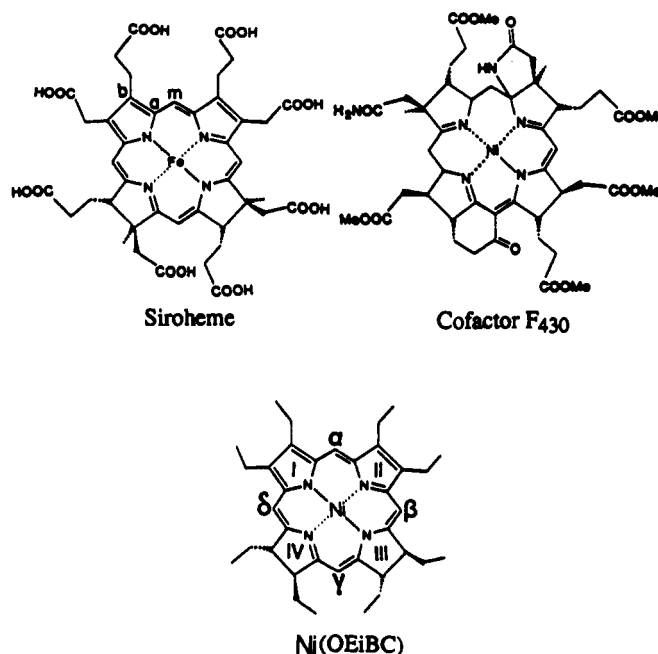

Figure 1. Structures and labeling scheme for cofactor F_{430}, siroheme, and Ni(OEiBC).

support the formation of the Cu(I) complex.[12] $Cu^I(OEiBC)^-$ is considerably less reactive with O_2 and alkyl halides than is $Ni^I(OEiBC)^-$ despite the fact that the two have nearly identical reduction potentials. The Cu(II) and Fe(II)/Fe(III) complexes of OEiBC have also been used as models for the sirohydrochlorin

† University of California.
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(1) Wolf, R. S. *Trends Biochem. Sci.* (*Per. Ed.*) 1985, *10*, 369.
(2) Ellefson, W. L.; Whitman, W. B.; Wolf, R. S. *Proc. Natal. Acad. Sci. U.S.A.* 1982, *79*, 3707.
(3) Pfaltz, A.; Juan, B.; Fassler, A.; Eschenmoser, A.; Jaenchen, R.; Gilles, H. H.; Diekert, G.; Thauer, R. K. *Helv. Chim. Acta* 1982, *65*, 828.
(4) (a) Albracht, S. P. J.; Ankel-Fuchs, D.; Van der Zwaan, J. W.; Fontjin, R. D.; Thauer, R. K. *Biochim. Biophys. Acta* 1986, *870*, 50. (b) Albracht, S. P. J.; Ankel-Fuchs, D.; Böcher, R.; Ellerman, J.; Moll, J.; Van der Zwaan, J. W.; Thauer, R. K. *Biochim. Biophys. Acta* 1988, *955*, 86.
(5) Lexa, D.; Momenteau, M.; Mispelter, J.; Saveant, J.-M. *Inorg. Chem.* 1989, *28*, 30.
(6) (a) Kadish, K. M.; Sazou, D.; Maiya, G. B.; Han, B. C.; Liu, Y. M.; Saoiabi, A.; Ferhat, M.; Guilard, R. *Inorg. Chem.* 1989, *28*, 2542. (b) Kadish, K. M.; Franzen, M. M.; Han, B. C.; Araullo-McAdams, C.; Sazou, D. *J. Am. Chem. Soc.* 1991, *113*, 512.
(7) (a) Stolzenberg, A. M.; Stershic, M. T. *Inorg. Chem.* 1987, *26*, 3082. (b) Stolzenberg, A. M.; Stershic, M. T. *J. Am. Chem. Soc.* 1988, *110*, 5397. (c) Stolzenberg, A. M.; Stershic, M. T. *J. Am. Chem. Soc.* 1988, *110*, 6391.
(8) (a) Furenlid, L. R.; Renner, M. W.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* 1990, *112*, 1634. (b) Furenlid, L. R.; Renner, M. W.; Fajer, J. *J. Am. Chem. Soc.* 1990, *112*, 8987. (c) Renner, M. W.; Furenlid, L. R.; Barkigia, K. M.; Forman, A.; Shim, H.-K.; Simpson, D. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* 1991, *113*, 6891.
(9) (a) Shiemke, A. K.; Scott, R. A.; Shelnutt, J. A. *J. Am. Chem. Soc.* 1988, *110*, 1645. (b) Shiemke, A. K.; Kaplan, W. A.; Hamilton, C. L.; Shelnutt, J. A.; Scott, R. A. *J. Biol. Chem.* 1989, *264*, 7276. (c) Shiemke, A. K.; Scott, R. A.; Shelnutt, J. A. *J. Biol. Chem.* 1989, *264*, 11236.

(10) (a) Kaplan, W. A.; Scott, R. A.; Suslick, K. S. *J. Am. Chem. Soc.* 1990, *112*, 1283. (b) Kaplan, W. A.; Suslick, K. S.; Scott, R. A. *J. Am. Chem. Soc.* 1991, *113*, 9824.
(11) (a) Shelnutt, J. A. *J. Am. Chem. Soc.* 1987, *109*, 4169. (b) Shelnutt, J. A. *J. Phys. Chem.* 1989, *93*, 6283.
(12) Stolzenberg, A. M.; Schussel, L. J. *Inorg. Chem.* 1991, *30*, 3205.

ring (Figure 1),[13-18] which is the prosthetic group in nitrite and sulfite reductases.[19-21]

In order to gain a more detailed understanding of the effects of reduction on the properties of tetrapyrrolic macrocycles, we and others have been examining the vibrational characteristics of both metal and ring-based anions of these macrocycles.[22-24] Our previous work has been focused on porphyrinic anions.[24a-c] More recently, we have extended these studies to the anions of hydroporphyrin macrocycles.[24d] In this paper, we report the resonance Raman (RR) spectra of a variety of M(OEiBC) anions, including $Ni^I(OEiBC)^-$, $Cu^I(OEiBC)^-$, $Zn^{II}(OEiBC)^-$, and their respective β,γ,δ-meso-deuteriated isotopomers (M(OEiBC-d_3)$^-$). In the course of these studies, we have also examined the RR spectra of both high-spin (HS) and low-spin (LS) complexes of $Ni^{II}(OEiBC)$. The various neutral and anionic complexes constitute a series in which the $d_{x^2-y^2}$ orbital of the metal ion is vacant [$Ni^{II}(OEiBC)$ LS] or singly [$Ni^{II}(OEiBC)$ HS, Ni^I-(OEiBC)$^-$, $Cu^{II}(OEiBC)$] or doubly [$Cu^IOEiBC)^-$, $Zn^{II}(OEiBC)$, $Zn^{II}(OEiBC)^-$] occupied. The occupancy of the $d_{x^2-y^2}$ orbital has a significant impact on the structure of the macrocycle because this orbital is directed toward the four nitrogen atoms of the ring. The vibrational frequencies of the skeletal modes of the macrocycle are particularly sensitive to structural perturbations induced by changes in the occupancy of the $d_{x^2-y^2}$ orbital.[25-32] Collectively, the RR data of the reduced M(OEiBC) complexes reported herein provide new insight into the structural consequences of metal ion and ring reduction.

Experimental Section

trans-OEiBC and *trans*-OEiBC-(β,γ,δ)-d_3 were synthesized and purified as described in refs 14a and 13, respectively. The Ni(II), Cu-

(13) Procyk, A. D.; Bocian, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 3765.
(14) (a) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 364. (b) Stolzenberg, A. M.; Strauss, S. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4763. (c) Strauss, S. H.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 863. (d) Strauss, S. H.; Silver, M. E.; Ibsers, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4108.
(15) (a) Han, S.; Madden, J. F.; Thompson, R. G.; Strauss, S. H.; Siegel, L. M.; Spiro, T. G. *Biochemistry* **1989**, *28*, 5461. (b) Melamed, D.; Sullivan, E. P., Jr.; Prendergast, K.; Strauss, S. H.; Spiro, T. G. *Inorg. Chem.* **1991**, *30*, 1308.
(16) Sullivan, E. P., Jr.; Grantham, J. D.; Thomas, C. S.; Strauss, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 5264.
(17) Ozawa, S.; Fujii, H.; Morishima, I. *J. Am. Chem. Soc.* **1992**, *114*, 1548.
(18) Andersson, L. A.; Mylrajan, M.; Loehr, T. M.; Sullivan, E. P., Jr.; Strauss, S. H. *New J. Chem.* **1992**, in press.
(19) Lancaster, J. R.; Vega, J. M.; Kamin, H.; Orme-Johnson, N. R.; Orme-Johnson, W. A.; Kreuger, R. H.; Siegel, L. M. *J. Biol. Chem.* **1979**, *254*, 1268.
(20) Vega, J. M.; Kamin, H. *J. Biol. Chem.* **1977**, *252*, 896.
(21) Murphy, M. J.; Siegel, L. M.; Tover, S. R.; Kamin, H. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 612.
(22) (a) Ksenofontova, N. M.; Maslov, V. G.; Sidorov, A. N.; Bobovich, Ya. S. *Opt. Spectrosc.* **1976**, *40*, 462. (b) Yamaguchi, H.; Soeta, A.; Toeda, H.; Itoh, K. *J. Electroanal. Chem.* **1983**, *159*, 347. (c) Gurinovich, G. P.; Gurinovich, I. F.; Ivashin, N. V.; Sinyakov, G. N.; Shulga, A. M.; Terekhov, S. N.; Filatov, I. V. *J. Mol. Struct.* **1987**, *172*, 317. (d) Reed, R. A.; Purrello, R.; Prendergaset, K.; Spiro, T. G. *J. Phys. Chem.* **1991**, *95*, 9720.
(23) Teraoka, J.; Hashimoto, S.; Sugimoto, H.; Mori, M.; Kitagawa, T. *J. Am. Chem. Soc.* **1987**, *109*, 180.
(24) (a) Donohoe, R. J.; Atamian, M.; Bocian, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 5593. (b) Atamian, M.; Donohoe, R. J.; Lindsey, J. S.; Bocian, D. F. *J. Phys. Chem.* **1989**, *93*, 2236. (c) Perng, J. H.; Bocian, D. F. *J. Phys. Chem.* **1992**, *96*, 4804. (d) Perng, J. H.; Bocian, D. F. *J. Phys. Chem.* **1992**, *96*, 10234.
(25) Spaulding, L. D.; Chang, C. C.; Yu, N.-T.; Felton, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 2517.
(26) Parthasarati, N.; Hansen, C.; Yamguchi, S.; Spiro, T. G. *J. Am. Chem. Soc.* **1987**, *109*, 3865.
(27) Oertling, W. A.; Salehi, A.; Chung, Y. C.; Leroi, G. E. Chang, C. K.; Babcock, G. T. *J. Phys. Chem.* **1987**, *91*, 5587.
(28) Choi, S.; Spiro, T. G.; Langry, K. C.; Smith, K. M.; Budd, L. D.; LaMar, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 4345.
(29) Spiro, T. G. In *Iron Porphyrins*; Lever, A. P. B., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Vol. 2, pp 89-159.
(30) Warshel, A. *Annu. Rev. Biophys. Bioeng.* **1977**, *6*, 273.
(31) Shelnutt, J. A.; Medforth, C. J.; Berber, M. D.; Barkigia, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077.
(32) Prendergast, K.; Spiro, T. G. *J. Am. Chem. Soc.* **1992**, *114*, 3793.

(II), and Zn(II) ions were inserted as described in refs 7c and 14a. Ni^{II}-(OEiBC) HS was formed by adding the complex to a neat piperidine solution. The reduced M(OEiBC) complexes were prepared by placing the samples in degassed DMF (Aldrich, anhydrous grade) solutions into either a 1 mm path length optical cell or an NMR tube (RR studies) containing a 1% sodium amalgam. The solutions were then mechanically shaken until the neutral species were converted to the monoanions (the color changes from purple to red).[7,12] The reduction process was monitored periodically by removing the cell from the shaker and recording the optical spectrum (the rate of the reduction process is extremely slow in the absence of agitation). The monoanions of all complexes undergo further reduction upon extended shaking over the amalgam to afford macrocycle-reduced, secondary reduction products. The secondary reduction products, whose characteristics will be reported elsewhere,[33] have strong absorptions near 300 nm and weaker absorptions in the 400-600-nm regime. In the case of the Zn(II) and to a lesser exten the Cu(II) complex, some secondary reduction product is formed before the neutral complex is completely converted to the monoanion. Consequently, the samples were removed from the shaker when the concentration of monoanion reached a maximum. In order to determine whether the distribution of monoanion and secondary reduction products changed with time, optical spectra were recorded at various time intervals (up to 12 h) after the samples were removed from the shaker. No changes were observed in the product distribution during this time period. Regardless, the optical and RR spectra shown in the figures were recorded immediately after the samples were removed from the shaker. In the case of $Zn^{II}(OEiBC)^-$, optical spectra were also recorded after the RR experiments. These spectra indicated no change in the distribution of monoanion and secondary reduction products. EPR spectra recorded for $Zn^{II}(OEiBC)^-$ further confirmed of the presence of the radical anion species although the exact concentration was not determined. [It should also be noted that the EPR spectra were recorded at 77 K, and it is possible that the product distribution of monoanion and secondary reduction products changes with temperature.] As a final confirmation that the RR spectra obtained for the reduction product of the Zn(II) complex were actually of the monoanion, RR spectra were recorded for samples in which the reduction to secondary products was allowed to proceed to completion. No RR scattering was observed from these species at the excitation wavelengths used to acquire the spectra of the monoanions.

The RR spectra were recorded by using a double monochromator (Spex Industries 1403) equipped with a thermoelectrically cooled photomultiplier tube (Hamamatsu R928) and photon-counting detection system. The excitation wavelengths were provided by the outputs of an Ar ion (Coherent Innova 400-15/3), Kr ion (Coherent Innova 200-K3), or tunable dye (Coherent 590-03) laser. Multiple scans were averaged to obtain the spectra shown in the figures. Each scan was examined for signs of photodecomposition before averaging. However, no photodecomposition was observed under the conditions used to obtain the RR spectra. The incident powers were approximately 25 mW with λ_{ex} = 406.7 and 413.1 nm and 50 mW with λ_{ex} = 528.7 and 551.1 nm. The spectra were collected at 1-cm^{-1} intervals with an integration time of 1 s/point. The spectral slit width was ~3 cm^{-1} at all excitation wavelengths.

Results

A. Absorption Spectra. The absorption spectra of the $Ni^I(OEiBC)^-$, $Cu^I(OEiBC)^-$, and $Zn^{II}(OEiBC)^-$ anions are compared with those of the parent neutral species in Figures 2-4, respectively. The absorption spectra of both $Ni^{II}(OEiBC)$ LS and HS are included in Figure 2. Upon conversion from LS to HS, the B-bands of the Ni(II) complex shift to lower energy whereas the Q bands are not significantly affected. Reduction to the Ni(I) complex shifts both the B and Q bands to higher energy.[7a] In the case of the $Cu^{II}(OEiBC)$, reduction to the Cu(I) species does not significantly perturb the energies of either the B or Q bands.[12] Reduction of $Zn^{II}(OEiBC)$ to the ring-based anion results in a shift to lower energy and splitting of the B bands. The strong Q band is lost, and a number of new features are observed in the visible region. The multiple bands observed in the visible spectra of $Zn^{II}(OEiBC)^-$ are typical of the radical anions of other tetrapyrrolic macrocycles.

B. Resonance Raman Spectra. The high-frequency regions of the B-state- and Q-state-excitation RR spectra of the neutral and

(33) Lahiri, G. K.; Stolzenberg, A. M. *Angew. Chem., Int. Ed. Engl.*, in press.
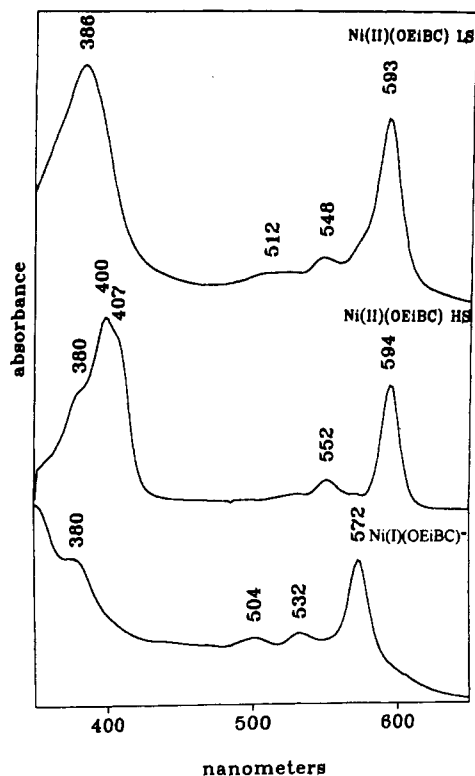
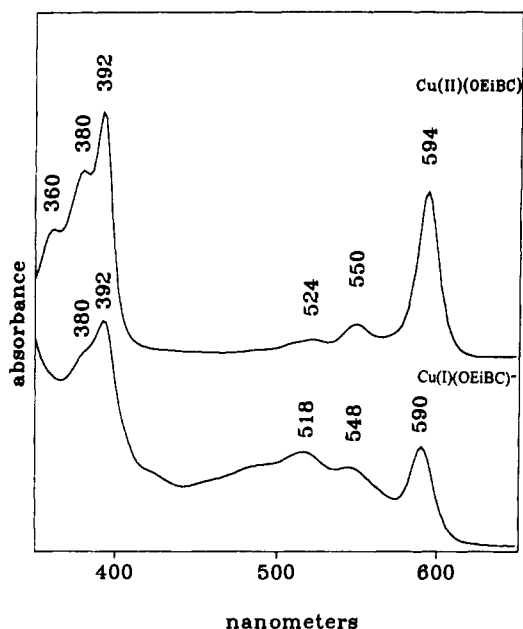**Figure 2.** Room-temperature absorption spectra of Ni^{II}(OEiBC) LS, Ni^{II}(OEiBC) HS, and Ni^{I}(OEiBC)$^-$.

Figure 3. Room-temperature absorption spectra of Cu^{II}(OEiBC) and Cu^{I}(OEiBC)$^-$.

reduced nickel OEiBC complexes are shown in Figures 5 and 6, respectively. The B-state excitation RR spectrum of Ni^{I}(OEiBC)$^-$ is not shown in Figure 5 because high-quality RR spectra could not be obtained with the available excitation wavelengths. The B-state-excitation RR spectra of the copper and zinc OEiBC complexes are shown in Figures 7 and 8, respectively. In the case of these latter two complexes, Q-state-excitation RR spectra could not be obtained due to interference from fluorescence. The RR spectra of the M(OEiBC-d_3) analogs of all the complexes are also shown in Figures 5–8.

The RR frequencies and meso-deuteriation shifts for a number of the prominent high-frequency RR bands of the neutral and reduced M(OEiBC) complexes are summarized in Table I. The
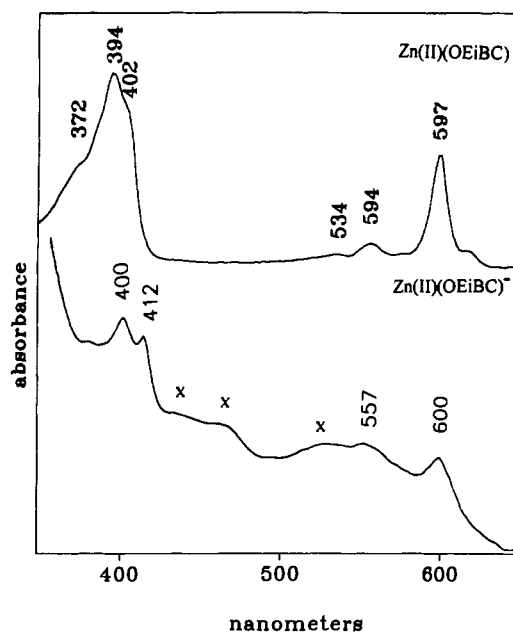

Figure 4. Room-temperature absorption spectra of Zn^{II}(OEiBC) and Zn^{II}(OEiBC)$^-$. The bands marked by the symbol x are due to secondary reduction products.

vibrational assignments shown in the table are based on semiempirical normal coordinate calculations that have previously been reported for Cu^{II}(OEiBC).[13] The assignments for the other neutral and the reduced complexes were made by analogy to those of Cu^{II}(OEiBC) via comparison of the vibrational frequencies and meso-deuteriation shifts.

1. Nickel Complexes. Conversion of Ni^{II}(OEiBC) from LS to HS or reduction of the LS complex to Ni^{I}(OEiBC)$^-$ results in a significant downshift of all the high-frequency skeletal modes of the macrocycle (Figures 5 and 6). Modes that contain substantial C$_a$C$_m$ character in general experience the largest downshifts. For example, the C$_a$C$_m$ stretching vibrations of Ni^{II}-(OEiBC) LS at 1651, 1626, 1526, and 1484 cm^{-1} downshift to 1622, 1594, 1514, and 1464 cm^{-1} upon conversion to Ni^{II}(OEiBC) HS and to 1626, 1604, and 1512 cm^{-1} upon reduction to Ni(I)(OEiBC)$^-$ (the analog of the 1484-cm^{-1} band of the Ni(II) LS complex is not observed for the Ni(I) complex). Conversion to the HS or to the Ni(I) species also downshifts the C$_b$C$_b$ and C$_a$C$_b$ stretching vibrations although to a lesser extent than the C$_a$C$_m$ modes (with the exception of the 1484-cm^{-1} C$_a$C$_b$ band which experiences a large downshift; see Table I). Interestingly, the 1388-cm^{-1} C$_a$C$_b$/C$_a$N mode of Ni^{II}(OEiBC) upshifts slightly to 1392 cm^{-1} upon formation of Ni^{II}(OEiBC) HS and downshifts to 1381 cm^{-1} upon reduction to Ni^{I}(OEiBC)$^-$.

The shift patterns observed for the C$_a$C$_m$ modes of Ni^{II}(OEiBC-d_3) LS upon formation of Ni^{II}(OEiBC-d_3) HS or Ni^{I}(OEiBC-d_3)$^-$ are similar to those of the normal isotopomer. The magnitudes of the meso-deuteriation shifts of the C$_a$C$_m$ modes are also similar for all three complexes with the exception of the 1526-cm^{-1} band. This mode downshifts 13 cm^{-1} in the Ni(II) LS complex and 17 cm^{-1} in the Ni(I) species. The downshift is 25 cm^{-1} in the Ni(II) HS complex. The meso-deuteriation shift patterns are more complicated in the case of the C$_a$C$_b$ and C$_a$C/C$_a$C modes. For example, the 1501-cm^{-1} C$_a$C$_b$ vibration of Ni^{II}(OEiBC) LS upshifts upon deuteriation whereas the analogous modes of Ni^{II}-(OEiBC) HS and Ni^{I}(OEiBC)$^-$ downshift. In addition, the C$_a$C$_b$/C$_a$N modes of Ni^{II}(OEiBC) LS, Ni^{II}(OEiBC) HS, and Ni^{I}(OEiBC)$^-$ that are observed at 1388, 1392, and 1381 cm^{-1}, respectively, occur at 1374, 1370 and 1358 cm^{-1} in the meso-deuteriated complexes. Accordingly, the small upshift in this mode observed upon conversion to the Ni(II) HS complex of the normal isotopomer appears as a small downshift for the meso-deuteriated species. The magnitude of the downshift observed
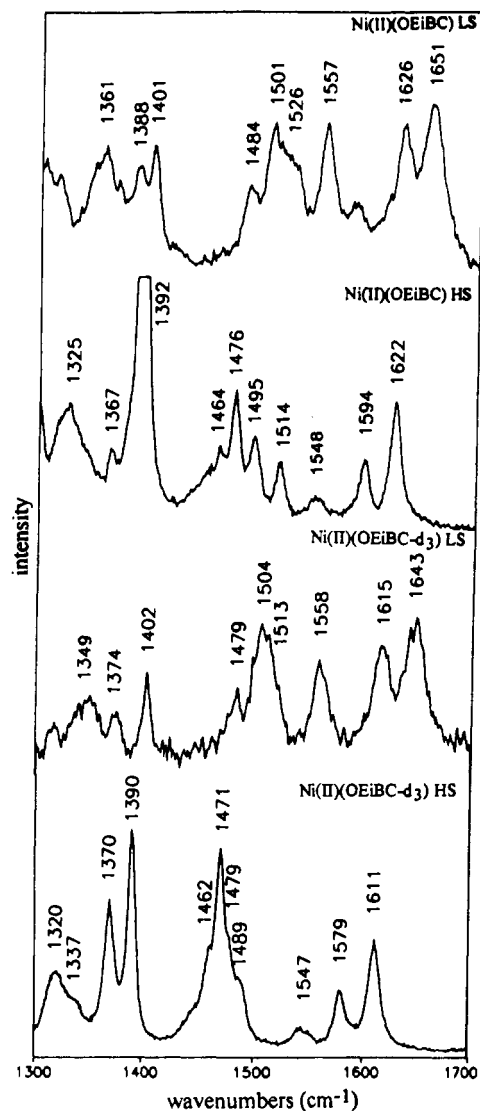
Figure 5. High-frequency regions of the B-state-excitation RR spectra of $Ni^{II}(OEiBC)$ LS, $Ni^{II}(OEiBC)$ HS, and their meso-deuteriated isotopomers. All spectra were acquired at room temperature with λ_{ex} = 406.7 nm.

upon formation of the Ni(I) complex of the meso-deuteriated species is also significantly larger (16 cm^{-1}) than for the normal isotopomer (7 cm^{-1}).

2. Copper Complexes. The vibrational frequencies of the skeletal modes of $Cu^{II}(OEiBC)$ are in general within 5 cm^{-1} of the analogous vibrations of $Ni^{II}(OEiBC)$ LS (cf. Figures 5 and 7). Reduction to the Cu(I) species lowers the frequencies of all of the skeletal modes of the OEiBC macrocycle. These downshifts are substantially larger than those observed upon reduction of the nickel complex. For example, the C_aC_m vibrations of Cu^{II}-(OEiBC) at 1651, 1621, and 1527 cm^{-1} downshift by 44, 40, and 28 cm^{-1} upon reduction whereas the analogous modes of the nickel complex downshift by 25, 22, and 14 cm^{-1}. The reduction-induced downshifts observed for the 1402 and 1390-cm^{-1} C_aC_b and C_aC_b/ C_aN modes of the copper complex are also neary twice as large as those observed for the nickel species. The reduction-induced shifts observed for the C_aC_m modes of $Cu^{II}(OEiBC-d_3)$ follow a pattern similar to those observed for the normal isotopomer. The magnitudes of the meso-deuteriation shifts of the former complex are in general larger than those of the latter. In the case of the C_aC_b and C_aC_b/C_aN vibrations, the meso-deuteriation shifts for the Cu(II) versus Cu(I) complexes are more complicated. There is no obvious pattern to the isotope sensitivity of these modes.

3. Zinc Complexes. Reduction of either $Zn^{II}(OEiBC)$ or Zn^{II}-(OEiBC-d_3) to the ring-based radical anions induces relatively
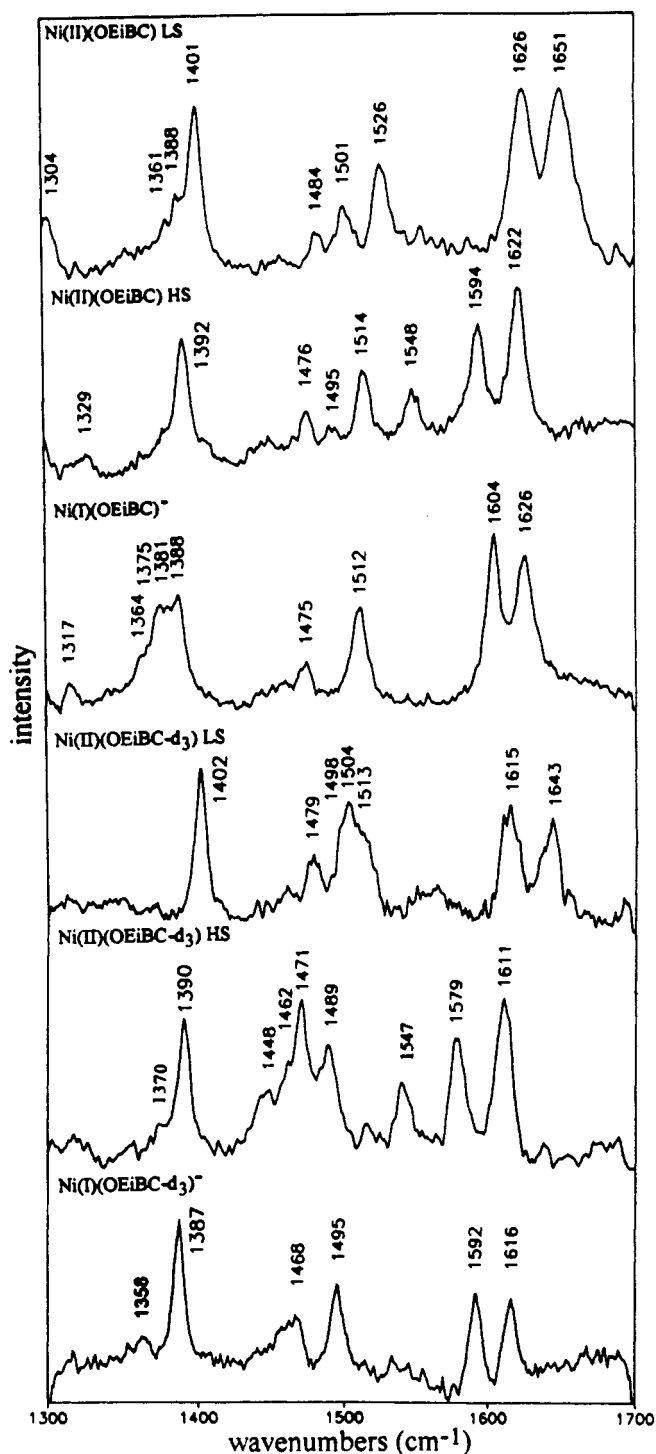

Figure 6. High-frequency regions of the Q-state-excitation RR spectra of $Ni^{II}(OEiBC)$ LS, $Ni^{II}(OEiBC)$ HS, $Ni^{I}(OEiBC)^-$, and their meso-deuteriated isotopomers. All spectra were acquired at room temperature. The spectra of $Ni^{II}(OEiBC)$ LS and $Ni^{II}(OEiBC)$ HS were acquired with λ_{ex} = 551.1 nm; the spectra of $Ni^{I}(OEiBC)^-$ were acquired at λ_{ex} = 528.7 nm.

small shifts in all of the high-frequency skeletal modes of the macrocycle (Figure 8). All of the shifts are less than 5 cm^{-1}, and most are in the range of 2–3 cm^{-1}. The meso-deuteriation shifts are also essentially identical for analogous modes of the neutral versus anionic species. Reduction-induced shifts of relatively small magnitudes have also been observed for the related Zn(II) octaethylporphyrin and Zn(II) octaethylchlorin complexes.[24c,d]

Discussion

The absorption spectra of the various M(OEiBC) complexes provide insight into the electronic properties of these species. In
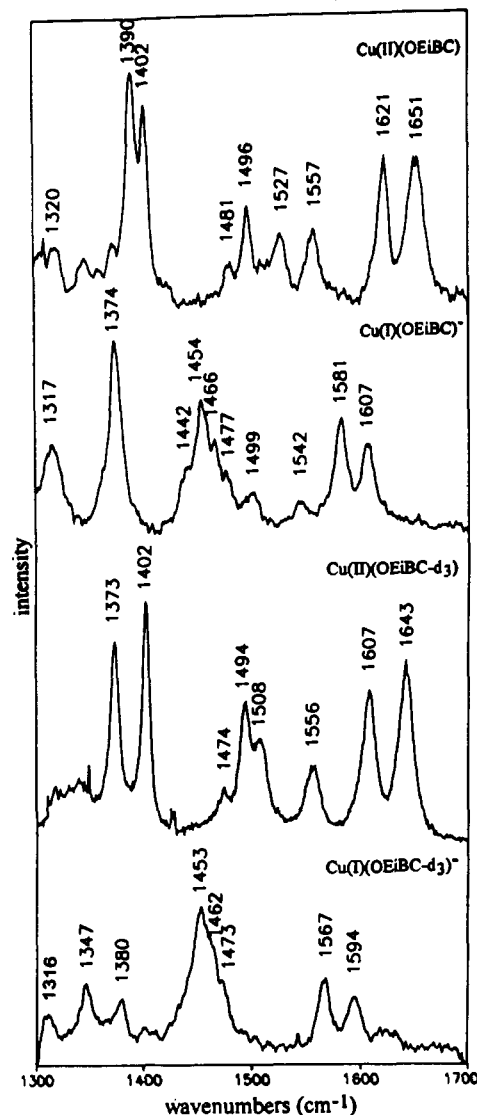
Figure 7. High-frequency regions of the B-state-excitation RR spectra of the Cu^{II}(OEiBC), Cu^{I}(OEiBC)$^-$, and their meso-deuteriated isotopomers. All spectra were acquired at room temperature with λ_{ex} = 406.7 nm.

Figure 8. High-frequency regions of the B-state-excitation RR spectra of Zn^{II}(OEiBC), Zn^{II}(OEiBC)$^-$, and their meso-deuteriated isotopomers. All spectra were acquired at room temperature. The spectra of Zn^{II}-(OEiBC) were acquired with λ_{ex} = 406.7 nm; the spectra of Zn^{II}(OEiBC)$^-$ were acquired with λ_{ex} = 413.1 nm.

the case of the neutral complexes, the B absorption bands systematically shift to the red as the electronegative character of the metal decreases (λ_{max}: Ni(II) < Cu(II) < Zn(II)). In contrast, the Q bands are largely unaffected. The trend observed in the energies of the B-band maxima of the M(OEiBC) complexes is similar to that observed for both the B and Q bands of an analogous series of metalloporphyrins.[34,35] The optical shifts result from perturbations of the a$_{2u}$ orbital (or a$_{2u}$-like orbital for the OEiBCs), which spatially interacts with the p$_z$ orbitals of the metal ion. The a$_{2u}$ orbital of metalloporphyrins is involved in the configurations of both the B and Q excited states whereas the a$_{2u}$-like orbital of M(OEiBC) complexes is only involved in the B excited states.[34,36] This explains why the Q bands of the latter complexes are relatively unperturbed by alteration of the metal ion.

Conversion of Ni^{II}(OEiBC) LS to Ni^{II}(OEiBC) HS red shifts the B-band maximum but does not perturb the Q bands. This can be explained by a destabilization of the a$_{2u}$-like orbital of the macrocycle owing to a diminished interaction with the p$_z$ orbitals of the metal ion.[35] The reduction in the extent of interaction is
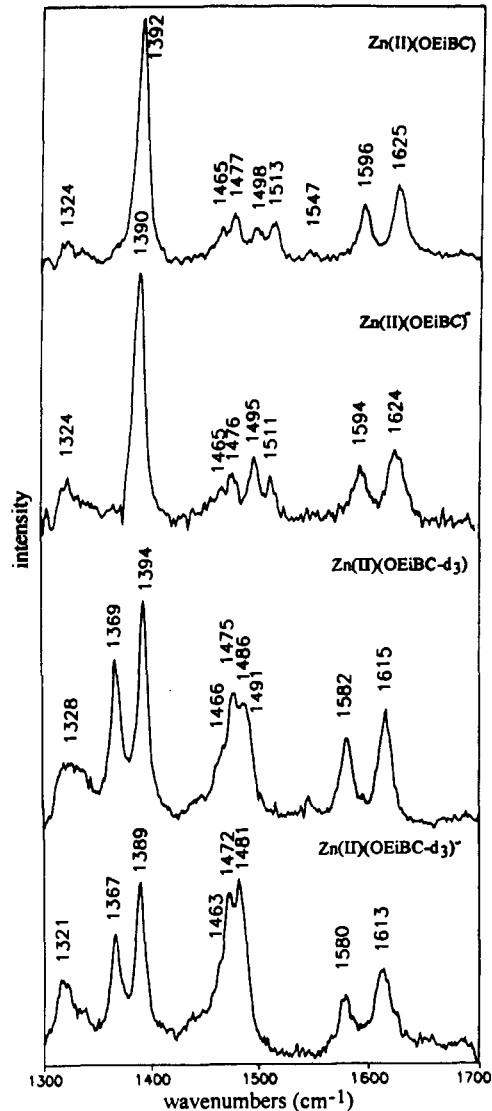
(34) Gouterman, M. *J. Chem. Phys.* **1959**, *30*, 1139.
(35) (a) Shelnutt, J. A.; Ondrias, M. R. *Inorg. Chem.* **1984**, *23*, 1175. (b) Shelnutt, J. A. *J. Phys. Chem.* **1984**, *88*, 4988.
(36) Gouterman, M. In *The porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. III, pp 1–165.

due to an increase in the metal–nitrogen bond length arising from population of the d$_{x^2-y^2}$ orbital. The observation that the Q bands are unaffected by the spin-state conversion suggests that either the a$_{1u}$-like and e$_g$*-like orbitals are relatively unperturbed upon conversion to the HS complex or the energies of both of these orbitals are shifted by approximately equal amounts. In contrast, the blue shifts observed for both the B and Q bands upon reduction to Ni^{I}(OEiBC)$^-$ suggests that the e$_g$*-like orbitals are strongly perturbed by the addition of an electron. These orbitals would be expected to be raised in energy if the d$_\pi$ orbitals of the metal are capable of significant back-bonding into the OEiBC ring.[36] If the back-bonding is sufficiently large, the blue shifts of the B bands could outweigh the red shifts expected for these band due to destabilization of the a$_{2u}$-like orbitals (due to the lengthening of the metal–nitrogen bonds that occurs upon addition of an elecron to the d$_{x^2-y^2}$ orbital).

The features observed in the absorption specrum of Cu^{I}-(OEiBC)$^-$ can also be rationalized in terms of the electronic effects discussed above. The Q bands of this complex are at somewhat higher energy than those of Cu^{II}(OEiBC), which suggests that the e$_g$*-like orbitals are perturbed via back-bonding. However, the blue shifts are not nearly as pronounced as those of the nickel system, which suggests that the back-bonding is significantly weaker in the copper complex. In the case of the B bands, the

Table I. Vibrational Frequencies and Deuteriation Shifts (cm⁻¹) for M(OEiBC) Complexes

Ni(II) LS	Δd₃	Ni(II) HS	Δd₃	Ni(I)	Δd₃	Cu(II)	Δd₃	Cu(I)	Δd₃	Zn(II)	Δd₃	Zn(II) anion	Δd₃	assgnt[a]
1651	8	1622	11	1626	10	1651	8	1607	13	1625	10	1624	11	$\nu[C_aC_m(\beta,\delta)]$
1626	11	1594	15	1604	12	1621	14	1581	14	1596	14	1594	14	$\nu[C_aC_m(\beta,\delta)]$
1557	+1	1548	1			1557	1	1542		1547				$\nu[C_bC_b(I,II)]$
1526	13	1514	25	1512	17	1527	19	1499	26	1513	22	1511		$\nu[C_aC_m(\alpha,\beta,\delta)], \nu[C_bC_b(I,II)]$
		1495	16			1512	8	1477	15	1498	12	1495	14	$\nu[C_aC_m(\beta,\delta)]$
1501	+3	1476	5	1475	7	1496	2	1466		1477	2	1476	4	$\nu[C_aC_b(I,II)]$
1484	5	1464	2			1481	7	1454	1	1465	+1	1465	2	$\nu[C_aC_m(\beta,\delta)]$
1401	+1	1392	2	1388	1	1402	0	1374	+6	1392	+2	1390	1	$\nu[C_aC_b(I,II)], [C_aN(I,II)]$
1388	14	1392	22	1381	23	1390	17	1374	27	1392	23	1390	23	$\nu[C_aC_b(I,II)], \nu[C_aN(I,II)]$

a Taken from ref 13.
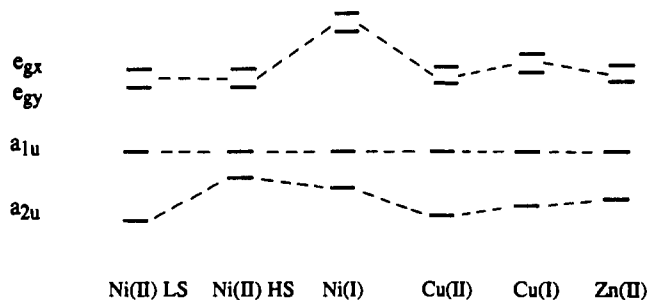
Figure 9. Qualitative molecular orbital diagram for the neutral and reduced M(OEiBC) complexes.

small blue shifts that might be expected from back-bonding could be offset by small red shifts due to destabilization of the a_{2u}-like orbital. The red shifts for the copper complex might be expected to be smaller than those for the nickel system because the relative destabilization that occurs upon adding a second $d_{x^2-y^2}$ electron to a half-filled shell (copper complexes) would be expected to be less than that which occurs upon adding an electron to an empty shell (nickel complexes).

The orbital shifts due to the electronic effects discussed above can be represented in the qualitative molecular orbital diagram shown in Figure 9. The relative energies of the orbitals shown in the diagram are not to scale but are drawn for pictorial clarity. In constructing the diagram, we have assumed that only the a_{2u}- and e_g^*-like orbitals are perturbed by altering the metal amd/or its oxidation state. For the M(OEiBC) complexes, the B and Q excited states arise primarily from configurations involving the $a_{2u} \rightarrow e_g^*$ and $a_{1u} \rightarrow e_g^*$ promotions, respectively.

The RR data provide insights into the structural properties of the M(OEiBC) complexes that can be correlated with the electronic properties reflected in the absorption spectra. In the case of the neutral complexes, the skeletal-mode frequencies of Ni^{II}(OEiBC) are similar to those of Cu^{II}(OEiBC) whereas the frequencies of Zn^{II}(OEiBC) are substantially lower. On the basis of core expansion arguments alone, it would be expected that the skeletal-mode frequencies would systematically decrease along the series Ni(II) > Cu(II) > Zn(II).[15,25-32] The similarity in vibrational frequencies of the Ni(II) and Cu(II) complexes suggests that the OEiBC macrocycle of the former species is more distorted from planarity than is the ring of the latter. In this regard, ruffled Ni(II) octaethylporphyrins exhibit skeletal-mode frequencies that are significantly lower than those of the planar form.[15,37]

The conversion of Ni^{II}(OEiBC) LS to either Ni^{II}(OEiBC) HS or Ni^{I}(OEiBC)⁻ in general lowers the frequencies of the skeletal modes because the larger ions expand the core of the macrocycle.[8,11,15,38] The downshifts are somewhat larger for the HS species than for the anion. This is most likely due to the fact that six-coordinate Ni^{II}(OEiBC) HS probably adopts a more planar

structure than does four-coordinate Ni^{I}(OEiBC)⁻. In the case of large ions, such as Ni(II) HS, the extreme core expansion that must occur to accommodate the ion in a more planar ring results in a core size much further from the ideal size than does a distortion form planarity. Consequently, the π bond orders of the ring skeleton are lower in the former species resulting in lower vibrational frequencies.[29] [In the case of smaller ions, such as Ni(II) LS, the core sizes of planar species are much closer to the ideal size than those of nonplanar rings; consequently, the π bond orders (and vibrational frequencies) of the ring skeleton of the former macrocycles are higher than those of the latter (vide supra).[25,37]]

The RR data for Ni^{I}(OEiBC)⁻ versus Ni^{II}(OEiBC) HS qualitatively supports the presence of back-bonding in the former species but not in the latter. Back-bonding typically lowers the vibrational frequencies of modes that contain substantial contributions from C_aN stretching motions.[29] In this regard, the 1388-cm⁻¹ C_aC_b/C_aN mode of Ni^{II}(OEiBC) LS downshifts in Ni^{I}(OEiBC)⁻ but not in Ni^{II}(OEiBC) HS. The anomalous behavior of the 1388-cm⁻¹ mode of the latter complex could be due to the fact that it is relatively insensitive to the core size but sensitive to the extent of back-bonding. Unfortunately, the shifts of the other C_aN modes of the nickel complexes are not clear and it is difficult to determine whether the shift pattern observed for the 1388-cm⁻¹ band occurs for other C_aN vibrations.

The reduction-induced frequency shifts observed for the copper complex are extremely large. The origin of these unusually large shifts is not clear. One possibility is that the macrocycles of Cu^{II}(OEiBC) and Cu^{I}(OEiBC)⁻ are equally distorted from planarity and the core of the latter complex is expanded by the larger Cu(I) ion. Alternatively, the ring may adopt a more planar structure with a greatly expanded core. A third possibility is that the macrocycle of Cu^{I}(OEiBC)⁻ is extremely distorted from planarity. This could occur because the Cu(I) ion prefers a tetrahedral coordination geometry.[39] An extremely large structural distortion of the macrocycle might be expected to lead to changes in the forms of the vibrational eigenvectors of the ring. The observation that the meso-deuteriation shifts of Cu^{I}(OEiBC)⁻ are different from those of Cu^{II}(OEiBC) is qualitatively consistent with this picture. However, it should also be noted that the meso-deuteriation shifts of the skeletal modes of the former complex are generally larger than those of the analogous vibrations of the latter. This may be due only to the fact that the frequencies of the skeletal modes of Cu^{I}(OEiBC)⁻ are generally lower than those of Cu^{II}(OEiBC), which enhances mixing of the stretching modes with the C_mH deformations at lower frequency. Finally, it should be noted that if the macrocycle of Cu^{I}(OEiBC)⁻ is significantly more distorted from planarity than is the ring of Cu^{II}(OEiBC), it might also be expected that the optical spectra of the two species would be significantly different.[40] The fact that they are not could be due to a series of compensating effects. Regardless, this

(37) (a) Brennan, T. D.; Scheidt, W. R.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919. (b) Alden, R. G.; Crawford, B. A.; Doolen, R.; Ondrias, M. R.; Shelnutt, J. A. *J. Am. Chem.* **1989**, *111*, 2072.
(38) Shelnutt, J. A.; Alston, K.; Ho, J.-H.; Yu, N.-T.; Yamamoto, T.; Rifkind, J. M. *Biochemistry* **1986**, *25*, 620.

(39) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience: New York, 1972; pp 905–909.
(40) Barkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1988**, *110*, 7567.

issue cannot be resolved in the absence of X-ray crystallographic data for the Cu(I) complex.

Reduction of $Zn^{II}(OEiBC)$ to the ring-based anion radical induces relatively small shifts in the frequencies of the skeletal modes, which suggests that most of the structural changes in the ring are minor. The observation that the meso-deuteriation shifts of $Zn^{II}(OEiBC)$ and $Zn^{II}(OEiBC)^-$ are similar is also consistent with this conclusion. It is possible that the small frequency shifts are due to partitioning of the unpaired electron density among a number of atoms in the macrocycle. However, EPR and ENDOR studies on $H_2(OEiBC)^-$ indicate that a large amount of unpaired electron density in this anion resides on the α-methine carbon whereas the remainder is distributed among many atoms in the ring.[41] In this case, skeletal modes that contain large amounts of $C_aC_m(\alpha)$ streching character would be expected to exhibit large frequency shifts upon reduction of the macrocycle. Unfortunately, these modes are not clearly observed in the RR spectra.

Conclusions

The vibrational data for the neutral and reduced M(OEiBC) complexes indicate that reduction at the metal significantly perturbs the structures of the macrocycles. The structural changes

that occur upon formation of the Ni(I) complex are not as large as those associated with the conversion of the Ni(II) species from LS to HS. The larger structural changes associated with the conversion to the HS form are probably attributable to the six-coordinate species adopting a more planar ring conformation. Both the RR and absorption data for the Ni(I) complex are consistent with significant metal-d_π–OEiBC back-bonding. The structural changes that occur upon formation of the Cu(I) complex are larger than those that occur conversion of Ni(II) LS to either Ni(II) HS or to the Ni(I) complex. The origin of the large structural changes that occur upon reduction to the Cu(I) complex are not clear. It is possible that the tendency of this ion to prefer a tetrahedral configuration drives the macrocycle into a highly nonplanar conformation. Finally, the vibrational data for $Zn^{II}(OEiBC)^-$ suggest that the structural changes associated with the reduction to the ring-based anion are for the most part small. Collectively, these vibrational data, in conjunction with the absorption spectra of the complexes, provide a more detailed picture of the effects of metal and ring reduction in the M(OEiBC) system.

(41) Renner, M. W.; Fujita, E.; Fujita, I.; Procyk, A. D.; Bocian, D. F.; Fajer, J. *J. Phys. Chem.* **1992**, *96*, 9597.