

# Correlation of X-ray Crystallographic Data and Spectroscopic Properties of Divalent Metal Complexes of Octaethylporphyrin<sup>†</sup>

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The infrared and visible spectra of divalent metal complexes of OEP were obtained. The variations in precise absorbances for five metal-sensitive infrared bands at ca. 3050, 1230, 990, 920, and 750  $\text{cm}^{-1}$  are examined as a function of macrocyclic conformation and metal-pyrrolic nitrogen ( $\text{M}-\text{N}_p$ ) bond distances. The exact positions of the bands at ca. 920, 990, 1230, and 3050  $\text{cm}^{-1}$  are dependent on the  $\text{M}-\text{N}_p$  bond distances. Additionally, the bands at 920, 990, and 1230  $\text{cm}^{-1}$  are dependent on the size of the lowest unoccupied  $p_z$  orbital. The 1230- and 3050- $\text{cm}^{-1}$  bands are sensitive to the macrocyclic conformation. In the visible region the variations in  $\lambda_{\text{max}}$  of the  $\alpha$  and  $\beta$  bands are also examined as a function of  $\text{M}-\text{N}_p$  bond distance. These appear to be a function of the  $\text{M}-\text{N}_p$  bond distance and size of the lowest unoccupied  $p_z$  orbital. These findings are discussed in terms of stabilization of the  $a_{2u}$  orbital on the porphyrin ligand. Implications for porphyrin reactivity are considered.

## Introduction

Spectroscopic and spectrometric analyses provide valuable information on the effect of the metal ion on the properties of metalloporphyrins. In electron ionization mass spectrometry, the ratio of doubly charged fragment ions to singly charged fragment ions is markedly dependent on the chelated metal ion.<sup>1,2</sup> Similarly, the abundance of pyrrolic ions formed by the surface-assisted decomposition of metalloporphyrins in chemical ionization mass spectrometry is dependent on the stability of the metalloporphyrin complex.<sup>1</sup> Analyses of metalloporphyrin complexes by Raman spectroscopy indicate that there are several Raman bands which are sensitive to the conformation of the metalloporphyrin.<sup>3</sup> X-ray crystallographic data provide the best method of determining macrocyclic conformation. Crystallographic analyses have been carried out on scores of porphyrin complexes; e.g. structural information is now available for Ni (three forms), Co, Cu, Zn, Mg, Pd, Ag, Cd, and Pt porphyrin complexes.<sup>4-10</sup> The availability of these data allows the researcher an excellent means of evaluating the potential of other techniques for analysis of macrocyclic conformation. A number of investigators have reported the metal dependence of the infrared spectra of

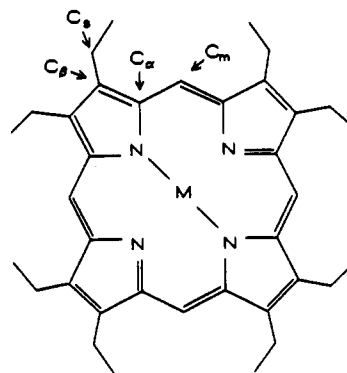


Figure 1. Octaethylporphyrin metalated.

metalloporphyrins.<sup>11</sup> A study by Ogoshi revealed several metal-dependent bands. The greatest metal dependence was observed in the 300–200- $\text{cm}^{-1}$  region.<sup>11a,b</sup> The behavior of these bands was observed to mirror the dependence of the  $\alpha$ ,  $\beta$ , and Soret bands in the electronic spectra. A later study by Kincaid<sup>11c</sup> reveals that there are six metal-sensitive bands in the region between 1700 and 300  $\text{cm}^{-1}$  in the divalent metal complexes of octaethylporphyrin. Additionally, Andersson et al.<sup>12</sup> show that the meso (bridge) C–H stretch at ca. 3050  $\text{cm}^{-1}$  is considerably metal sensitive. Kincaid stipulated that the major sources of the metal dependence may arise from three factors: stabilization of the  $a_{2u}$   $\pi_z$  bonding orbital by metal coordination, occupancy of the  $d_{x^2-y^2}$  orbital and subsequent core expansion, and macrocyclic deformations of the porphyrin ring.

The primary goal of the present study is to determine more precisely the factors causing the metal dependence of the IR spectra of metalloporphyrins by incorporating X-ray crystallographic data which were not accessible to previous workers. If this is possible, it should be possible to determine whether (1) infrared spectroscopy can be used as a probe of macrocyclic

<sup>†</sup> Dedication: This paper is dedicated to Professor C. W. Rees, F.R.S., with thanks from a grateful student (J.M.E.Q.).

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**Table I.** Metal-Sensitive Infrared Band Assignments

$\nu^a$	band assgnt	$\nu^a$	band assgnt
3050 <sup>b</sup>	C <sub>m</sub> -H str	996 <sup>c</sup>	C <sub>α</sub> -N str, C <sub>α</sub> -C <sub>m</sub> str
1575 <sup>c,d</sup>	C <sub>α</sub> -C <sub>m</sub> str	927 <sup>c</sup>	C <sub>α</sub> -C <sub>m</sub> str, C <sub>β</sub> -Cs str
1501 <sup>c,d</sup>	C <sub>α</sub> -C <sub>m</sub> str	754 <sup>c</sup>	skel out-of-plane bend
1231 <sup>c</sup>	C <sub>α</sub> -C <sub>m</sub> str, C <sub>α</sub> -N str, C <sub>α</sub> -C <sub>m</sub> -H in-plane bend		

<sup>a</sup> The frequency listed is that of metal-free octaethylporphyrin.

<sup>b</sup> Andersson, L. A.; Loehr, T. M.; Stershic, M. T.; Stolzenberg, A. M. *Inorg. Chem.* **1990**, *29*, 2278. <sup>c</sup> Kincaid, J. R.; Urban, M. W.; Watanabe, T.; Nakamoto, K. *J. Phys. Chem.* **1983**, *87*, 3096. <sup>d</sup> These bands were not observed in the current study.

conformation, (2) the factors causing metal dependency in infrared spectra have a similar influence in electronic spectra, and (3) some infrared bands can be used for predicting chemical reactivity.

### Experimental Section

Octaethylporphyrin, OEP, and its Ni(II), Cu(II), Zn(II), Co(II), and Mg(II) complexes were purchased from Aldrich and recrystallized from dichloromethane/methanol (1:1, v/v). The Cd(II), Ag(II), Pt(II), and Pd(II) complexes were prepared using literature methods.<sup>13</sup> The purity of all porphyrin complexes was determined by a combination of thin layer chromatography, nuclear magnetic resonance (General Electric QE 300), where appropriate, and ultraviolet and visible spectroscopy (Shimadzu UV-265 and Cary 2315). Ultraviolet and visible spectra were obtained using dilute solutions of the metalloporphyrin in CH<sub>2</sub>Cl<sub>2</sub>. The three crystal forms of Ni(OEP) were prepared by recrystallization from the appropriate solvent.<sup>4</sup> The nature of each crystal form was ascertained by visual inspection of the crystals.

The samples for infrared study were prepared as CsI pellets. Infrared spectra were obtained using a Perkin-Elmer Model 1800 FT-IR spectrometer. The wavelength is calibrated internally using a He-Ne laser to an accuracy of  $\pm 0.01$  cm<sup>-1</sup>. Each spectrum was run at least three times. The peak positions did not vary by more than  $\pm 0.3$  cm<sup>-1</sup>, even when the spectra were recorded by different workers. We consider the data to be accurate to better than  $\pm 0.5$  cm<sup>-1</sup>. The sample chamber was purged with N<sub>2</sub>(g) from liquid N<sub>2</sub> boil-off for at least 30 min prior to running spectra.

### Results

The metal-sensitive IR bands and their assignments for complexes of OEP are listed in Table I. The assignments listed are those determined by Kincaid et al. using isotopic substitution on the porphyrin ring. Since we wanted to incorporate literature X-ray crystallographic data, we chose to run the samples as solids dispersed in CsI pellets. Five metal-dependent bands were observed. The bands at 1575 and 1501 cm<sup>-1</sup>, reported by Kincaid et al.<sup>11c</sup> were not consistently detected. In most cases we could not distinguish the positions of these peaks from background noise. This is not surprising because the argon matrix sample preparation employed in that study allows observation of weak bands, even when they are close to intense bands.

The exact positions of the metal-dependent bands are listed in Table II together with M-N<sub>p</sub> bond distances for all the metalloporphyrins studied. Where possible, M-N<sub>p</sub> bond distances were obtained from X-ray crystal studies of the metallooctaethylporphyrin; otherwise, the value for a related porphyrin, usually tetraphenylporphyrin, was used. The visible spectral data obtained in this study are listed in Table III.

### Discussion

A number of factors are expected to influence the position of the metal-dependent vibrational bands. The mass of the metal ion will clearly be important if the metal participates directly in

**Table II.** Positions of the Metal-Sensitive Infrared Bands for Divalent Metal Complexes of Octaethylporphyrin

divalent metal ion	d <sup>n</sup>	M-N <sub>p</sub> <sup>a</sup>	IR bands at ca. <sup>b</sup>				
			754	927	996	1231	3050
Ni(a)	d <sup>8</sup>	1.929 <sup>c</sup>	749	924	993	1223	3059
Co	d <sup>7</sup>	1.949 <sup>d</sup>	750	922	991	1228	3064
Ni(b)	d <sup>8</sup>	1.952 <sup>e</sup>	752	923	992	1227	3070
Ni(c)	d <sup>8</sup>	1.958 <sup>f</sup>	751	923	992	1227	3072
Cu	d <sup>9</sup>	2.000 <sup>g</sup>	750	918	985	1224	3057
Pd	d <sup>8</sup>	2.013 <sup>h</sup>	747	923	993	1230	3053
Pt	d <sup>8</sup>	2.012 <sup>i</sup>	748	926	997	1233	3058
Zn	d <sup>10</sup>	2.036 <sup>j</sup>	749	912	980	1219	3045
Mg	d <sup>0</sup>	2.072 <sup>k</sup>	748	911	978	1217	3034
Ag	d <sup>9</sup>	2.092 <sup>l</sup>	746	912	982	1220	n.o. <sup>l</sup>
Cd	d <sup>10</sup>	2.144 <sup>m</sup>	742	905	975	1213	n.o. <sup>l</sup>

<sup>a</sup> In Å. <sup>b</sup> In cm<sup>-1</sup>. Bands quoted at heading are those of metal-free OEP. <sup>c</sup> Meyer, E. F. *Acta Crystallogr.* **1972**, *B28*, 2162. <sup>d</sup> Madura, P.; Scheidt, W. R. *Inorg. Chem.* **1976**, *15*, 3182. <sup>e</sup> Brennan, T. D.; Scheidt, W. R.; Shelnut, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919. <sup>f</sup> Cullen, D. L.; Meyer, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 2095. <sup>g</sup> Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339. <sup>h</sup> Soltzenberg, A. M.; Schussel, L. J.; Summers, J. S.; Foxman, B. M.; Peterson, J. L. *Inorg. Chem.* **1992**, *31*, 1678. <sup>i</sup> Milgrom, L. R.; Sheppard, R. N.; Slawin, A. M. Z.; Williams, D. J.; Polyhedron **1988**, *7*, 57. <sup>j</sup> Scheidt, W. R.; Mondal, J. U.; Adler, A.; Radonovich, L. J.; Hoard, J. L. *Inorg. Chem.* **1986**, *25*, 795. <sup>k</sup> Timkovich, R.; Tulinsky, A. *J. Am. Chem. Soc.* **1969**, *91*, 4430. <sup>l</sup> This band was not observed. <sup>m</sup> Rodesiler, P. F.; Griffith, E. H.; Ellis, P. D.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1980**, 492.

**Table III.** Positions of the UV-Visible Bands for Divalent Metalloporphyrins

divalent metal ion	UV-vis bands <sup>a</sup>		
	Soret	β	α
Ni	391	515	551
Co	390	sh	551
Pd	392	512	546
Pt	380	500	535
Cu	398	525	562
Zn	400	531	567
Mg	408	543	580
Ag	412	529	563
Cd	406	540	576

<sup>a</sup> In nm; CH<sub>2</sub>Cl<sub>2</sub> solutions.

the infrared vibration.<sup>14</sup> In those cases where the metal is not directly involved, the effect of the mass of the metal may be minor and the source of the metal dependence should be largely due to changes in the macrocycle owing to chelation to the metal.

The conformation of the macrocycle may influence the behavior of the metal-sensitive bands.<sup>3b,11c</sup> When there is a loss of planarity owing to the nature of the central metal ion,  $\pi$  overlap is decreased with concomitant weakening of the methine bridges. These effects may result in a lowering of the energy of the C<sub>α</sub>-C<sub>m</sub> vibration.<sup>3b,11c</sup> The chelated metal ion can also stabilize the macrocycle's a<sub>2u</sub>  $\pi$  orbital by donating electrons to the metal's empty p<sub>z</sub> orbital.<sup>15-17</sup> This effect should be enhanced for more electronegative metals, as was demonstrated by Gouterman.<sup>15</sup> Such stabilizations would result in an increase in the energies of the C<sub>α</sub>-N and C<sub>α</sub>-C<sub>m</sub> vibrations.<sup>11c</sup> The M-N<sub>p</sub> bond distance is a direct measure of the proximity of the macrocycle's a<sub>2u</sub> orbital to the metal's empty p<sub>z</sub> orbital. Metalloporphyrins with short M-N<sub>p</sub> bonds have the metal's empty p<sub>z</sub> orbital closer to the a<sub>2u</sub> orbital of the macrocycle. These metalloporphyrins should have increased overlap between these orbitals. Additionally, the M-N<sub>p</sub> bond distance and the conformation of the macrocycle are interdependent. Metalloporphyrins with large M-N<sub>p</sub> bonds are more likely to deviate from planarity via doming or tilting of one or more of the pyrrole

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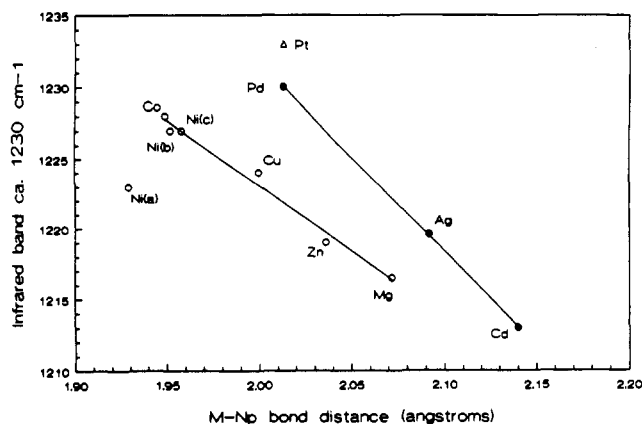


Figure 2. Position of the infrared band at ca. 1230  $\text{cm}^{-1}$  versus  $\text{M}-\text{N}_p$  bond distance for divalent metal complexes of octaethylporphyrin.

rings. Conversely, if the  $\text{M}-\text{N}_p$  bond distance is very small, then the macrocycle may deviate from planarity in a different manner, e.g. by ruffling of the pyrrole rings. For these reasons, it was decided that the influence of the  $\text{M}-\text{N}_p$  bond distance on the infrared spectral behavior merited investigation.

**Band at ca. 1230  $\text{cm}^{-1}$  ( $\text{C}_\alpha-\text{C}_m$  Stretch,  $\text{C}_\alpha-\text{N}$  Stretch,  $\text{C}_\alpha-\text{C}_m-\text{H}$  In-Plane Bend).** The exact position of the 1230- $\text{cm}^{-1}$  band is plotted versus  $\text{M}-\text{N}_p$  bond distance in Figure 2. With the exception of the tetragonal form of NiOEP, the  $\text{M}-\text{N}_p$  bond distance increases for MgOEP and the first-row transition metal complexes of OEP, as the energy of the infrared vibration decreases. Although the second-row transition metal complexes of OEP behave similarly, the precise vibrational energies were higher than those of the first-row transition metal complexes with similar  $\text{M}-\text{N}_p$  bond distances. PtOEP, the only third-row transition metal complex studied, absorbed at higher energy than did PdOEP, although the  $\text{M}-\text{N}_p$  bond distances are similar.

In order to interpret the data for this band, several factors appear to be important. The unusually low vibrational energy of the ruffled NiOEP(a) relative to the planar forms, NiOEP(b) and NiOEP(c), indicates that the conformation of the macrocycle plays a significant role. The  $\text{M}-\text{N}_p$  bond distance is obviously consequential, as demonstrated by the behavior of both the first- and second-row transition metal complexes. As the  $\text{M}-\text{N}_p$  bond distance increases, there is an increasing loss in planarity as discussed earlier; however this is not the only factor. An additional contribution may be due to the decreasing proximity of the metal's  $p_z$  orbital with increasing  $\text{M}-\text{N}_p$  bond distance. The difference in behavior between first- and second-row transition metal complexes might be accounted for by considering the differences in degree of stabilization owing to overlap between the metal ions'  $p_z$  orbital and the  $a_{2u}$  orbital of the porphyrin. Overlap with the larger  $5p_z$  or even larger  $6p_z$  orbital may lead to further stabilization of the macrocycle's  $a_{2u}$  orbital in the second- and third-row transition metal complexes,<sup>16,17</sup> hence the increased energy of this vibration.

**Bands at ca. 920  $\text{cm}^{-1}$  ( $\text{C}_\alpha-\text{C}_m$  Stretch,  $\text{C}_\beta-\text{C}_s$  Stretch) and ca. 990  $\text{cm}^{-1}$  ( $\text{C}_\alpha-\text{N}$  Stretch,  $\text{C}_\alpha-\text{C}_m$  Stretch).** The exact position of the 920- $\text{cm}^{-1}$  band is plotted versus  $\text{M}-\text{N}_p$  bond distances in Figure 3. The plot of the 990- $\text{cm}^{-1}$  band position versus  $\text{M}-\text{N}_p$  shows essentially identical behavior. This implies that the influences of the chelated metal ions on these metal-sensitive bands are similar. In both cases, for MgOEP and the complexes of the first-row transition metals, there is a decrease in the vibrational energy as the  $\text{M}-\text{N}_p$  bond distance increases. In contrast to the vibrational peak at ca. 1230  $\text{cm}^{-1}$ , the vibrational energy for the tetragonal form of NiOEP is greater than that of the triclinic forms. This observation indicates that the influence of the macrocyclic conformation on these two bands is less important than for the 1230- $\text{cm}^{-1}$  band. The vibrational energy for the second- and third-row transition metal complexes increases

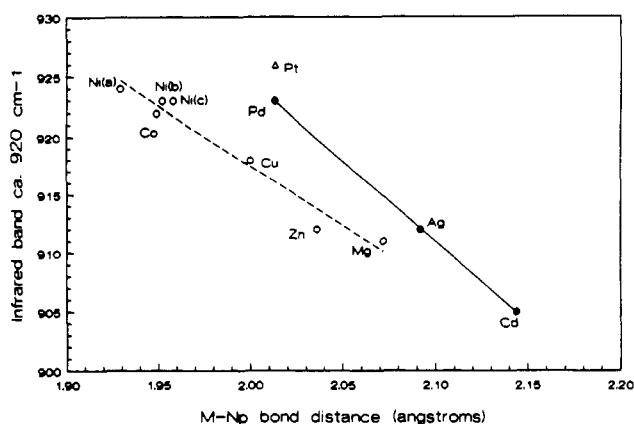


Figure 3. Position of the infrared band at ca. 920  $\text{cm}^{-1}$  versus  $\text{M}-\text{N}_p$  bond distance for divalent metal complexes of octaethylporphyrin.

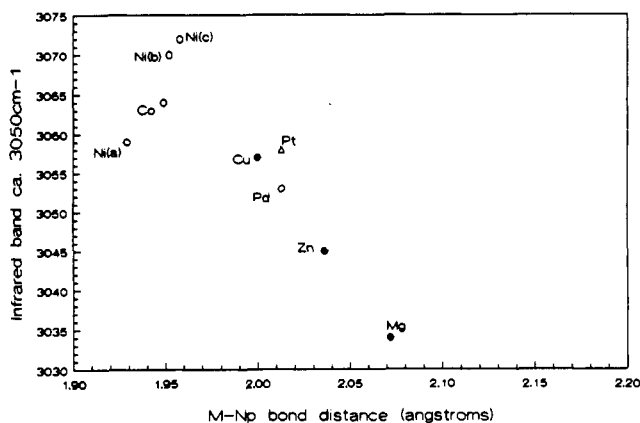


Figure 4. Position of the infrared band at ca. 3050  $\text{cm}^{-1}$  versus  $\text{M}-\text{N}_p$  bond distance for divalent metal complexes of octaethylporphyrin.

compared to that for the first-row transition metal complexes of similar  $\text{M}-\text{N}_p$  bond distances. This is presumably due to overlap with the larger metal's  $p_z$  orbital, as discussed previously.

**Band at ca. 3050  $\text{cm}^{-1}$  ( $\text{C}_m-\text{H}$  Stretch).** This is the most sensitive of the metal-dependent bands which was observed (Figure 4). With the exception of the tetragonal form of NiOEP, there is a general decrease in vibrational energy with increasing  $\text{M}-\text{N}_p$  bond distance. There is no clear-cut distinction between the behaviors of the complexes of metals in the first, second, and third rows of the transition metal series. This is not surprising since the stability of the  $a_{2u}$  orbital should not directly influence the energy of the  $\text{C}_m-\text{H}$  vibration appreciably. The low energy of the  $\text{C}_m-\text{H}$  vibration for the decidedly ruffled NiOEP(a) complex implies that the conformation of the macrocycle influences the strength of the  $\text{C}_m-\text{H}$  bond. This is further supported by the low vibrational stretching frequencies of the ZnOEP and MgOEP complexes. In both of these complexes, the pyrrole rings deviate significantly from planarity.<sup>5,8</sup> Surprisingly, the  $\text{C}_m-\text{H}$  stretch was not observed for AgOEP and CdOEP. It is conceivable that these vibrations are of sufficiently low energy to be obscured by the intense aliphatic  $\text{C}-\text{H}$  stretching vibrations. Isotopic labeling studies are being initiated in order to elucidate the energies of the  $\text{C}_m-\text{H}$  vibration for these two complexes.

**Band at ca. 750  $\text{cm}^{-1}$  (Skeletal Out-of-Plane Bend).** This band shows the least sensitivity to the identity of the complexed metal ion. These are no obvious trends observed.

**Comparison of the Behaviors of the Bands at ca. 920, 990, 1230, and 3050  $\text{cm}^{-1}$ .** The differences in the peak positions of the ruffled NiOEP(a) and both planar forms, NiOEP(b) and NiOEP(c), for the 1230- and 3050- $\text{cm}^{-1}$  bands indicate that these bands are significantly affected by the conformation of the porphyrin ring. Furthermore, the  $\text{C}_m-\text{H}$  bond is a major contributor to the vibration in both instances. Conversely, this bond does not make

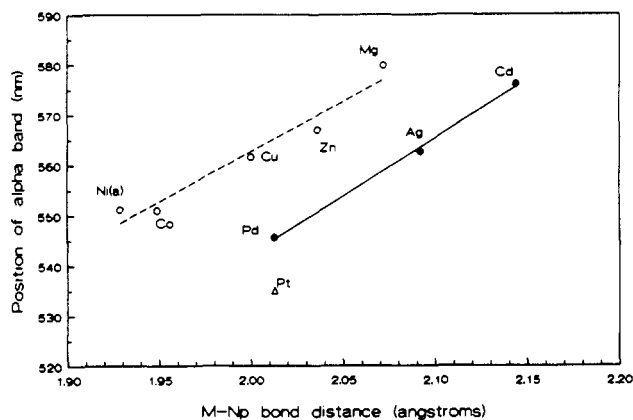
a major contribution to the 920- and 990-cm<sup>-1</sup> bands, which are not strongly influenced by macrocyclic conformation. Therefore, it appears that when the macrocyclic conformation is a factor in determining the energy of a vibration, the C<sub>m</sub>-H bond is a significant component of that vibration. It is not surprising that the C<sub>m</sub>-H bond may be the most sensitive to macrocyclic conformation. When the macrocycle deviates from planarity, much of the strain is borne at the methine bridges. The source of the sensitivity may arise from deviations in the C<sub>m</sub> bonding orbitals from "ideal" sp<sup>2</sup> hybridization. This is supported by studies in which the <sup>13</sup>C<sub>m</sub>-H coupling constants were observed to vary with increasing C<sub>α</sub>-C<sub>m</sub>-C<sub>α</sub> bond angles for the d<sup>8</sup> metalloctaethylporphyrins and tin(IV) octaethylporphyrin.<sup>10</sup>

The 920- and 990-cm<sup>-1</sup> bands do not appear to be sensitive to macrocyclic conformation. The main factor influencing the position of these bands is the stabilization of the ligand's a<sub>2u</sub> orbital via overlap with metal's p<sub>z</sub> orbital.

**Comparison of the Roles of the Chelated Metal Ions in Infrared and Visible Spectra of Divalent Metalloporphyrins.** The α and β bands in the visible spectrum of metalloporphyrins arise from porphyrin-based a<sub>1u</sub>, a<sub>2u</sub> → e<sub>g</sub> transitions. Since there are nodes at the pyrrolic nitrogens in the porphyrin's a<sub>1u</sub> orbital, the nature of the chelated metal ion should have little influence on this orbital. In all the metalloporphyrins studied, the metal's e<sub>g</sub> orbitals are filled; hence the effect of the metal ion on the energy of the ligand's e<sub>g</sub> orbital should be minimal, for complexes where substantial back-bonding does not occur. For such complexes, the major influence on the energy of the α and β transitions would be due to effects on the ligand's a<sub>2u</sub> orbital. If efficient overlap with the metal's p<sub>z</sub> orbital stabilizes the a<sub>2u</sub> orbital, then the positions of the α and β bands might be similarly influenced by the M-N<sub>p</sub> bond distances. The plot of the M-N<sub>p</sub> bond distances versus λ<sub>max</sub> for the α band of the divalent metal complexes of OEP is shown in Figure 5. The plot reveals that the energy of the transition decreases with increasing M-N<sub>p</sub> bond distance, for MgOEP and the OEP complexes of the first-row transition metals. Additionally, the second-row transition metals showed the same trend, but at lower wavelength. The only third-row transition metal studied (PtOEP) showed the transition at significantly lower wavelength than the second- and first-row transition metals of similar M-N<sub>p</sub> bond distance. The fact that similar behavior is observed for the α and β bands as well as the 920- and 990-cm<sup>-1</sup> bands is consistent with both being influenced by a common effect, the stabilization of the a<sub>2u</sub> orbital via orbital overlap with the metal's p<sub>z</sub> orbital.

**Implications on Porphyrin Reactivity.** There appears to be some correlation between the Falk stability classification and the position of the band at ca. 1230 cm<sup>-1</sup>.<sup>18</sup> Class I metalloporphyrins which are the hardest to demetallate appear between 1230 and 1233 cm<sup>-1</sup>. Class II metalloporphyrins appear between 1220 and 1228 cm<sup>-1</sup>. Only one class III metalloporphyrin was studied, and it absorbs at 1219 cm<sup>-1</sup>. Class IV metalloporphyrins appear between 1213 and 1217 cm<sup>-1</sup>. The 1230-cm<sup>-1</sup> band is the only one which is significantly sensitive to both macrocyclic conformation and a<sub>2u</sub>-p<sub>z</sub> overlap. This implies that, for metalloporphyrin complexes of divalent metal ions, both these factors are important in determining the stability toward demetallation. The better the overlap and the more planar the porphyrin ring, the more stable the metalloporphyrin toward demetallation.

The meso hydrogen is sensitive toward electrophilic substitution.<sup>19</sup> The rate of deuteration of the meso position via electrophilic attack has been observed to vary with different metals



**Figure 5.** Position of the α band versus M-N<sub>p</sub> bond distance for divalent metal complexes of octaethylporphyrin.

in the order Mg > Zn > Ni > Cu > Co. This is the inverse of the order followed for the position of the infrared vibration at ca. 1230 cm<sup>-1</sup>, implying the metalloporphyrins which are nonplanar and have poor a<sub>2u</sub>-p<sub>z</sub> overlap are more susceptible to electrophilic attack at the meso position than planar porphyrins with good a<sub>2u</sub>-p<sub>z</sub> overlap.

**Future Work.** In addition to the deuterium-labeling experiments to clarify the behavior of the 3050-cm<sup>-1</sup> bands mentioned previously, this study will be expanded to include an investigation of trivalent and tetravalent metal complexes of OEP. The potential effect of the stabilization of the e<sub>g</sub> orbital of the ligand by delocalization into empty e<sub>g</sub> orbitals of the metal ion will also be determined by investigating the air-sensitive divalent porphyrin complexes of chromium and vanadium. Work is in progress to determine whether data observed for OEP are applicable to other porphyrins.

## Conclusion

The precise absorbances for five metal-dependent bands of eleven divalent metal complexes of OEP were ascertained. For the 920- and 990-cm<sup>-1</sup> bands, the dominating factor appears to be the stabilization of the a<sub>2u</sub> orbital of the macrocycle by overlap with the empty p<sub>z</sub> orbital of the metal; conformation of the macrocycle does not seem to be a crucial factor. For the 3050-cm<sup>-1</sup> band, conformation is an important consideration and stabilization of the a<sub>2u</sub> orbital does not appear to be as significant. For the 1230-cm<sup>-1</sup> band, both macrocyclic conformation and a<sub>2u</sub> orbital stabilization are important. There also appears to be a correlation between the position of the 1230-cm<sup>-1</sup> band and the chemical reactivity of the divalent metal complexes of OEP. This implies that both macrocyclic conformation and a<sub>2u</sub> orbital stabilization are important in determining the relative reactivity of metalloporphyrin complexes. The precise positions of the α and β bands in the visible spectra appear to be significantly influenced by both M-N<sub>p</sub> bond distance and the size of the lowest unoccupied p<sub>z</sub> orbital. This indicates that the positions of the α and β bands are substantially dependent on the degree of a<sub>2u</sub> orbital stabilization.

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