

facile for a copper center in a tetragonal binding site, even if a change in coordination number attends reaction. This finding lends support for the mechanism that has been proposed for the blue copper oxidase laccase and that invokes rapid electron transfer from the type 2 copper site under some conditions.⁴⁶

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Correlations between Core Size and Wavelength of the α Band for Nonhyper Metalloporphyrins^{1a}

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A great deal of Raman data on metalloporphyrins^{1b-10} and heme proteins^{1b,11-21} has been reported in recent years. Molecular information is obtained from Raman spectra of these materials by two approaches: (a) Conventional normal-coordinate analyses²²⁻²⁵ give information about porphyrin force constants and molecular structure. (b) Empirical correlations of Raman frequencies with structural or electronic properties give information about comparative differences in these properties.^{2,4,5,11,13,26-30} The former method suffers from a lack of macrocycle normal modes consisting of pure group frequencies. The latter method has been highly successful for the pyrrole-substituted metalloporphyrins, because several Raman lines have been found to be markers of either porphyrin structure or electronic properties.

Empirical correlations between molecular parameters and the wavelength of absorption band maxima, especially the α -band maximum, have also enjoyed considerable success.^{4,31-35} The ultimate goal of this work is to use these empirical correlations to predict chemical activity of metalloporphyrins in proteins and in other environments.

One of the most remarkable empirical structural correlations is that between the frequencies of a group of Raman lines and the center-to-nitrogen (pyrrole) distance or core size.^{2,26} The frequencies of the ν_3 , ν_{19} , and ν_{10} vibrations of pyrrole-substituted metalloporphyrins correlate well with the core size determined from X-ray crystal structures of pyrrole- and meso-substituted metalloporphyrins. The core-size marker lines are not sensitive to the nature of the pyrrole substituents,^{24,25,36} since the correlation is good for a variety of substituent groups. The lines also must be insensitive to the out-of-plane distance of the metal.^{2,3}

Although the core-size lines are excellent structural markers, the correlation must result from electronic effects of the metal

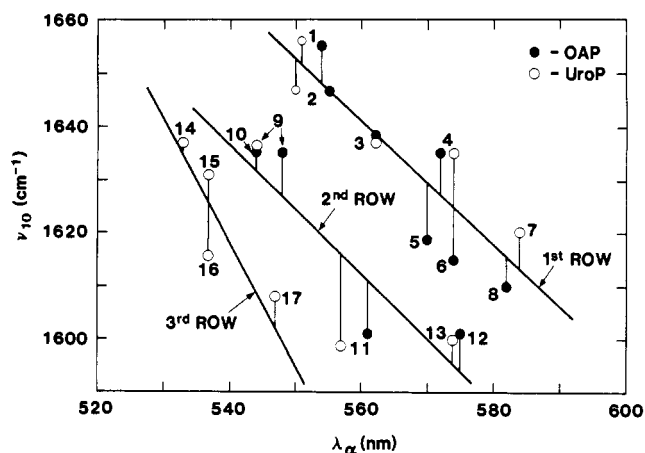


Figure 1. Correlations between frequency of ν_{10} and λ_{α} for first-, second-, and third-row transition metals: 1, Ni(II); 2, Co(II); 3, Cu(II); 4, V^{IV}O; 5, Zn(II); 6, H₂; 7, V^{IV}(OH)₂; 8, Mg(II); 9, Pd(II); 10, Rh^{III}Cl; 11, Ag(II); 12, Sn^{IV}Cl₂; 13, Sn^{IV}(OH)₂; 14, Pt(II); 15, Ir^{III}(CO)(OH); 16, Os^{II}(CO)(py); 17, Ir^{III}(CO)Cl. See Table I. The correlation coefficients are 0.89, 0.86, and 0.87 for periods 4, 5, and 6, respectively. Open circles represent metalloporphyrins in aqueous solution; filled circles are octaalkylporphyrin metal derivatives in organic solvents.

on the porphyrin ring.³⁷ One reason for this conclusion is that the correlation is not the typical one between frequency and

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bond length (Badger's rule). The vibration thought to be the dominant contributor to ν_3 , ν_{19} , and ν_{10} is the $C_\alpha-C_m$ stretch,²² yet a correlation with this bond distance has not been observed. Further, we have found relationships between the frequencies of the core-size marker lines and electronic properties of the metal-porphyrin bond. For example, the frequency of ν_{10} is related to covalency of the metal-porphyrin bond, to stability toward acid demetallation,⁹ and to π charge in the ring.²⁸ Kitagawa et al.⁴ also noted a good correlation between ν_{10} and the frequency of the Q(0-0) electronic transition (α band) for some first-row transition metals and Mg incorporated into octaethylporphyrin (OEP). We have extended the Raman measurements to include metals from periods 5 and 6 and additional metals from period 4. These new Raman results demonstrate that similar relationships hold for metals of the second- and third-row transition series and indicate a possible explanation for the observed relationships.

Figure 1 shows the correlations between ν_{10} and λ_α , the wavelength of the α -band maximum. Distinct linear relationships are observed for first-, second-, and third-row transition metals. The metalloporphyrins such as Fe and Ru that have been classified by Gouterman³⁸ as hyper have been omitted in Figure 1, because their absorption spectra are complicated by additional transitions in the visible and near-ultraviolet regions. These transitions can obscure or shift the wavelength of the normal $\pi-\pi^*$ transitions that give rise to the α band. Only the metalloporphyrins with normal (or pseudonormal) and hypso absorption spectra³⁸ have been plotted in Figure 1.

Substantial deviations (not experimental errors) from the straight lines in Figure 1 indicate that the factors determining the values of ν_{10} and λ_α are not all the same; nevertheless, the factors involved must be similar for such relationships to exist. In spite of the deviations, there is no overlap of metals from different rows, so the correlations given in Figure 1 have predictive ability for core size. That is, given λ_α and the row in which the metal occurs, the frequency of ν_{10} can be determined from Figure 1, and it can be used to estimate the core size of the metalloporphyrin.^{2,26}

The correlations that exist between these two spectroscopic parameters can be explained by considering another correlation—that between electronegativity of the metal and λ_α . Gouterman³² originally pointed out a linear relationship between frequency of the α band and electronegativity E_N for metallotetraphenylporphyrins for group 1A, 2A, and 2B metals and Cu. Later, Allison and Becker³⁹ demonstrated a lack of correlation with E_N ; however, they included hyperporphyrins and also used some less precise electronegativities. Figure 2 shows the correlation obtained for over 30 metals, excluding known hyperporphyrins and using more accurate electronegativities.⁴⁰ Considering that electronegativity ignores the

Table I. Spectroscopic and Molecular Parameters for Normal and Hypso Metallooctaalkylporphyrins (and Metallouroporphyrins)

metal	E_N^a	λ_α , nm	ν_{10} , cm^{-1}	ref
Cu(II)	2.0	562 (562)	1638 (1637)	4 28
Ni(II)	1.8	554 (551)	1655 (1656)	4 29
Co(II)	1.7	555 (550)	1647 (1647)	4 29
Zn(II)	1.5	570	1619	4
Mg ^{II} (py) ₂	1.2	582 (580)	1610	2, 42 this work
Pd(II)	2.0	548 (544)	1635 (1636)	4, 42 this work
Pt(II)	2.1	536 (533)	1637 (1637)	42 this work
V ^{IV} O	1.7	572 (574)	1635 (1635)	2, 42 43
V ^{IV} (OH) ₂	1.7	584	1620	43
H ₂	2.1	574	1615	4
Rh ^{III} Cl(DMA) ₂	2.1	544	1635	2, 42
Ag(II)	1.8	561 (557)	1601 (1599)	2, 42 this work
Sn ^{IV} Cl ₂	1.8	575	1601	2, 44
Sn ^{IV} (OH) ₂	1.8	574 (574)	1600 (1600)	44 this work
Ir ^{III} (CO)(OH)	2.1	537	1631	this work
Ir ^{III} (CO)Cl	2.1	547	1608	45, this work
Os ^{III} (CO)(OH)	2.0	537	1616	this work
Li ^I	0.95	590		39
Na ₂	0.9	592		46
K ₂	0.8	595		46
Ca(II)	1.0	581		39
Sr(II)	1.0	590		39
Ba(II)	0.9	605		39
Cd(II)	1.5	585		39
Hg(II)	1.8	577		39
Si ^{IV} Cl ₂	1.8	571		44
Ge ^{IV} Cl ₂	1.8	571		44
Pb ^{IV} (OMe) ₂	1.8	570		44
Ga ^{III} Cl	1.5	572		46
In ^{III} Cl	1.5	578		46
Nb ^V O ₃	1.7	569		47
Ta ^V F ₃	1.7	565		47
Ti ^{IV} O	1.6	572		47
Zr ^{IV} (OAc) ₂	1.5	565		47
Hf ^{IV} (OAc) ₂	1.4	564		47
Sc ^{III} (OAc)	1.3	571		47
Y ^{III} (OH)	1.2	572		48
Lu ^{III} (OH)	1.2	571		48
Ti ^{III} (OH)	1.9	581		49
Al ^{III} X	1.5	569		50

^a Electronegativities are taken from Gordy and Thomas;⁴⁰ electronegativities of Zhang^{52,53} and Sanderson^{54,55} were also used (see caption of Figure 2).

details of the metal geometry and bonding to the porphyrin ligand, the correlation is reasonably good ($r = 0.8$).

The electronegativity of a metal is commonly used as a measure of its covalent bonding ability. Indeed, an inverse relationship exists between the difference in electronegativity of two atoms and the degree of covalency of the bond between them. Since the pyrrole nitrogens ($E_N = 3.0$) are the met-

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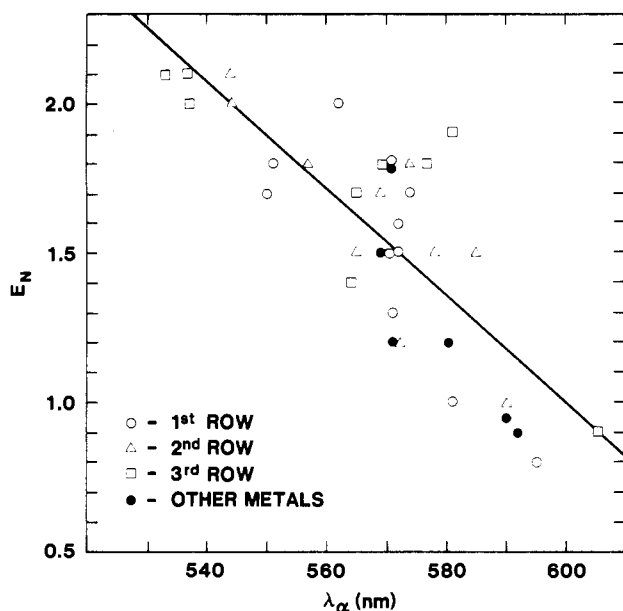


Figure 2. Correlation between electronegativity and λ_α for metalloporphyrins with normal and hypso absorption spectra. See Table I. The correlation coefficient is 0.80. Electronegativities of Zhang^{52,53} and Sanderson^{54,55} gave correlation coefficients between 0.76 and 0.83. Zhang gives electronegativities for different oxidation states of metals obtained from ionization potentials. Either (1) an ionic bonding term must be added, (2) +4 and +5 oxidation states must be omitted, or (3) +2 oxidation-state values must be used. Otherwise, the correlation coefficient is only 0.59, and the high-oxidation-state metalloporphyrins show a systematic error.

al-bonding atoms in metalloporphyrins and the range of E_N for the metals is 0.8–2.2 (see Table I), any increase in metal electronegativity would result in a smaller difference in E_N values and, therefore, increase covalency of the metal–porphyrin bond. The immediate consequences of increased E_N upon the electronic distribution within the porphyrin ring would be increased σ donation to the metal and enhanced π back-donation to the ring.

The relationship between λ_α and E_N in Figure 2 therefore suggests that λ_α is a direct measure of the covalency of the metal–porphyrin bond. Moreover, the degree of covalency might be expected to influence porphyrin geometry in a predictable manner. An indication of this is found in the monotonic dependence of calculated values of σ - and π -ring charge densities, which reflect the degree of covalency for a group of first-row metals and the frequencies of the Raman core-size-sensitive modes.⁹

The correlations in Figure 1 between porphyrin core size and covalency as measured by λ_α can now be explained as follows: (a) Within a row, the more electronegative metals form a tighter, more covalent bond resulting in a smaller core size and, therefore, higher ν_{10} frequency. (b) In the next row down, the valence orbitals have larger spatial extent, and, hence, a larger core size gives the same degree of interaction with the metal orbitals and covalency of the metal–porphyrin bond. This accounts for the shift along the λ_α axis toward higher covalency (lower λ_α) for equal core size when comparing upper row metals with lower row metals.

The correlations presented suggest a direct relationship between porphyrin geometry (as modulated by covalency of the metal–porphyrin bond) and the energetics of the porphyrin π system, indicating that, over the range of metals investigated, the degree of metal–porphyrin covalency affects the $a_{2u}(\pi)$ and $e_g(\pi^*)$ orbital energies in a concerted fashion.^{9,29} It should be noted however that a unique relationship between porphyrin electronic transitions and geometry does not exist. For metal substitution and in some cases of axial ligation (e.g., for VO

and V(OH)₂ porphyrins (see Figure 1) and for Cu porphyrins⁵¹) λ_α is *inversely proportional* to ν_{10} . In contrast, λ_α is *proportional* to ν_{10} for other cases of axial ligation²⁸ and for formation of complexes with π acceptors.^{28–30,41} Therefore, the response of both λ_α and ν_{10} to changes in a metalloporphyrin's interaction with its surroundings carries more information than the shift in either of these spectroscopic parameters alone.

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Resonance Raman Spectra of the Carbon-Bridged Iron Porphyrin Dimer (μ -Carbido)bis[(5,10,15,20-tetraphenylporphinato)iron]

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The characterization of model (porphinato)iron complexes containing metal ions with valence states greater than Fe(III) is of current interest,^{2–6} in large part because highly oxidized porphyrin complexes serve as intermediates in a number of heme protein reactions.^{7–9} One type of model complex that has attracted attention^{2,3,10} is the series of neutral and oxidized single-atom bridged dimers of the form ((TPP)Fe)₂X (TPP = tetraphenylporphyrin; X = O, N,^{11,12} C¹³). The Fe ions of ((TPP)Fe)₂O are known to be high-spin Fe(III).¹⁴ On the other hand ((TPP)Fe)₂N and ((TPP)Fe)₂C contain low-spin Fe ions.^{13,15} Recent Mössbauer studies¹⁰ indicate that the

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