enough for most purposes. A fuller analysis of the general two-photon kinetics scheme is being prepared for publication and indicates that separate K_1 and K_2 determination is at best very difficult and that the determination of K_1 is in any case not critically sensitive to the K_1/K_2 ratio.

(16) This assumption is supported by the evidence in both ref 11 and ref 12 that the rate of collisional deactivation in the two-photon mechanism is close to the Langevin collision rate.

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Resonance Raman Studies of Macrocyclic Complexes. 1. Structural and Electronic Effects in Synthetic Metal(II) Porphyrin Analogues

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Abstract: Resonance Raman spectra are reported for the Mn(II) ($s = \frac{5}{2}$), Fe(II) ($s = 1$), Co(II) ($s = \frac{1}{2}$), Ni(II) ($s = 0$), Cu(II), and Zn(II) complexes of the dianionic, π-delocalized N_4 macrocyclic ligand 5,7,12,14-tetramethyldibenzo[*b,i*]-[1,4,8,11]tetraazacyclotetradecahexenate (L^{2-}). The resonance Raman spectrum of H_2L is also discussed. All of the A_1 normal modes of the carbon–nitrogen–metal skeleton of $M^{II}L$ are observed among the resonance Raman spectra of the six complexes studied. Vibrational assignments are made for these modes. The assigned vibrations are correlated among the $M^{II}L$ complexes, revealing substantial metal-dependent shifts in ligand vibrational frequencies. The vibrations which exhibit large shifts are associated with the porphyrin-like six-membered chelate rings. These frequency shifts are, in some cases, attributable to electronic (as opposed to structural) effects of the d orbital occupancy of the metal ions. Structural effects upon Raman *intensity* as well as the frequency of ligand modes are observed for $Mn^{II}L$. This complex is distorted due to considerable displacement of the metal ion out of the N_4 coordination plane. Although the peripheral methyl substituents of $M^{II}L$ are not part of the chromophoric π system of the ligand, the Raman scattering due to the methyl group vibrations is nevertheless strongly resonance enhanced. It is suggested that this is a hyperconjugative effect. Selective Raman intensity enhancement of either ligand-centered or metal-associated vibrations is observed when laser excitation is chosen within respectively $\pi \rightarrow \pi^*$ or charge-transfer electronic transitions of $M^{II}L$. The results suggest (a) that metalloporphyrin frequency shifts may be due to electronic as well as structural effects of the metal ion, (b) that vibrations of peripheral alkyl substituents must be considered in assigning resonance Raman spectra of π-delocalized macrocycles, and (c) that selective Raman intensity enhancement may have utility in assigning metal–ligand modes in natural and synthetic macrocyclic complexes. Raman intensity patterns which have important implications in the theory of the resonance Raman effect are observed, and these are discussed in the following paper.

Much of the wide interest in synthetic macrocyclic complexes is a consequence of their relationship to naturally occurring macrocycles, particularly metalloporphyrins.[1] The cyclic Schiff base formed from acetylacetone and *o*-phenylenediamine (H_2L, Figure 1a) shares many common characteristics with porphyrins.[2-6] It forms tetradentate, N_4-coordinated metal complexes in which the ligand deprotonates to form L^{2-}. In these complexes L^{2-} possesses an extensively delocalized (24 electron) π system, and the electronic spectra are dominated by in-plane, $\pi \rightarrow \pi^*$ electronic transitions. The six-membered chelate rings in the L^{2-} complexes are structurally similar to those of metalloporphyrins and undergo analogous structural distortions to accommodate metal ions of various sizes.[3,4,6-8] Complexes of L^{2-} with a wide variety of metal ions have been synthesized.[3,5,9,10] These complexes offer an opportunity to study systematically the effects of metal electronic configuration, size, charge, and chemical parameters upon the structure and properties of the delocalized, macrocyclic ligand framework.

The resonance Raman effect may be observed when the Raman excitation frequency corresponds to an electronic transition of the scattering system.[11] Under this condition, the Raman scattering intensity of vibrations which couple with the electronic transition can be resonance enhanced by several orders of magnitude.[12] Resonance Raman spectroscopy has proven to be a powerful probe for structure and bonding in chromophoric groups,[13] particularly in corrins, hemes (including heme proteins), and metalloporphyrins (including those with various biomimetic characteristics).[14-17] However, the resonance Raman effect has not previously been applied to synthetic macrocyclic complexes. We now report resonance Raman studies of H_2L and a series of $M^{II}L$ complexes, where M is manganese, iron, cobalt, nickel, copper, and zinc.

Several characteristics of L compared to porphyrins have proven to be illuminating in these studies. First, the relatively simple structure of L allows vibrational assignments to be made with confidence. Second, the lowest energy $\pi \rightarrow \pi^*$ electronic transitions of L are in the near ultraviolet rather than in the visible as is the case with porphyrins.[18] Therefore, for $M^{II}L$ complexes having metal-centered electronic transitions in the visible region, resonance Raman effects due to these transitions are separable from those due to the ligand $\pi \rightarrow \pi^*$ spectrum. Thus, the structural and electronic effects of the metal upon the resonance Raman spectra are more easily interpretable for the $M^{II}L$ complexes than for metalloporphyrins or other naturally occurring macrocycles. This report is concerned primarily with these structural and electronic effects. The unusual resonance Raman intensity patterns observed for certain $M^{II}L$ complexes, and the interpretation of these intensity patterns, are the subject of the following report.[19] Our results have important general implications concerning vibrational studies of natural and synthetic metallomacrocycles and also illuminate

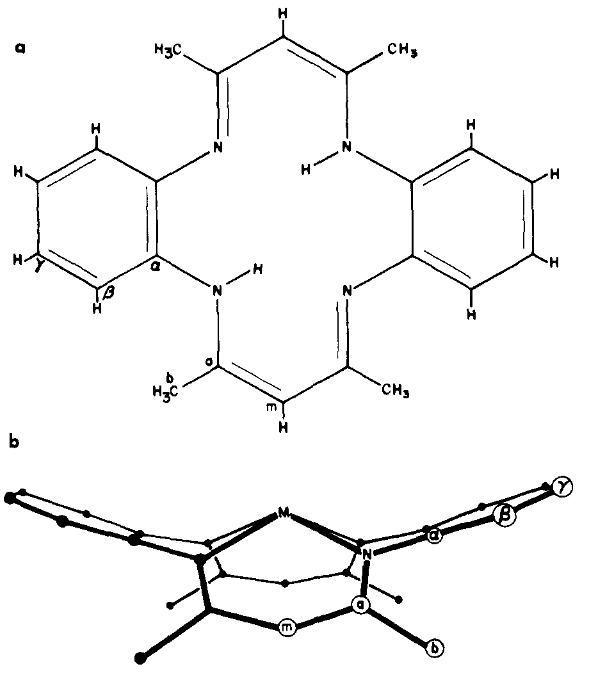

Figure 1. (a) Structure of H_2L, showing bonding, peripheral substitution, and nomenclature of carbon atoms. (b) Perspective structure of a $M^{II}L$ complex, showing typical ligand distortion and a nonplanar metal ion (e.g., Mn^{2+}). The saddle-like (C_{2v}) distortion shown for $M^{II}L$ also is present in H_2L.

certain fundamental points concerning the theory of the resonance Raman effect.

Experimental Section

Preparation and Characterization of Complexes. $M^{II}L(NEt_3)$, where M is Mn, Zn. The synthesis and characterization of these compounds have been previously reported.[5] The magnetic moment and EPR spectrum of the manganese(II) complex indicate a high-spin d^5 electronic configuration.[5]

$Ni^{II}L$ and $Ni^{II}L$-d_2. The nickel complex of H_2L was prepared according to the procedure of Goedken et al.[3] The complex is diamagnetic. Anal. ($C_{22}H_{22}N_4Ni$) C, H, N. ^1H NMR (C_6D_6-TMS) δ 1.77 (s, 12 H), 4.67 (s, 2 H), 6.54 (s, 8 H). Mass spectrum, m/e calcd 400, obsd. 400.

The two methine bridge hydrogen atoms of $Ni^{II}L$ (Figure 1a) were exchanged for deuterium using the following procedure. To 50 ml of degassed acetonitrile was added 1 g of $Ni^{II}L$, 1.5 g of DSO_3CF_3, and 7 g of methanol-d_1. The resulting bright green solution was refluxed in a nitrogen atmosphere for 12 h. After this time the solution was cooled and excess triethylamine was added. The violet crystalline solid which formed was removed by filtration, washed with a few mililiters of acetonitrile, and dried under a stream of N_2 gas. The yield was about 0.2 g. ^1H NMR (C_6D_6-TMS) δ 1.77 (s, 12 H) 6.54 (s, 8 H). At high spectral amplitudes a weak signal at δ 4.67 corresponding to the methine proton(s) of the undeuterated material could be observed. On the basis of integration, the percent deuterium in the complex was >90%.

$M^{II}L$ where M is Fe, Co, Cu. The synthesis and properties of these complexes have been briefly reported elsewhere.[4,20,21] For the purposes of this investigation the Fe(II) and Co(II) complexes were synthesized under a dry nitrogen atmosphere in the following manner. A hot acetonitrile solution containing 2.6 mmol of $M^{II}(BF_4)_2$ was added to a hot acetonitrile solution containing an equal molar amount of H_2L. Immediately upon mixing the solutions containing the ligand and the metal ion, 5.2 mmol of dry triethylamine was added. The intensely colored solution was allowed to cool and stand at room temperature for 8 h. The crystalline complex which formed was removed by filtration, washed with acetonitrile, and dried under a stream of nitrogen. The yield of each complex was about 0.75 g. Anal. ($C_{22}H_{22}N_4Fe$) H, N, C. Calcd, 66.35. Found, 65.05. Mass spectrum, m/e calcd 398, obsd 398; μ_{eff}, 3.32 μ_B ($s = 1$, intermediate-spin). Anal. ($C_{22}H_{22}N_4Co$) C, H, N. Mass spectrum, m/e calcd 401, obsd 401; μ_{eff}, 2.95 μ_B ($s = \frac{1}{2}$, low spin).

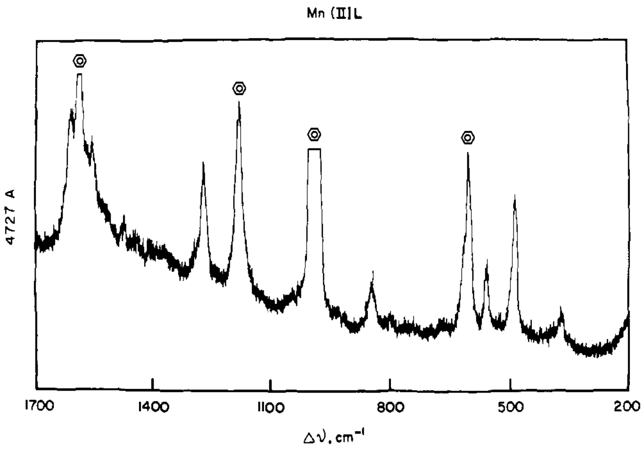

Figure 2. Resonance Raman spectrum of $Mn^{II}L$ using 4727 Å (21 155 cm^{-1}) laser excitation ($\pi \rightarrow \pi^*$ resonance). The benzene solvent peaks are identified by hexagons.

The air stable complex $Cu^{II}L$ was synthesized in acetonitrile in the presence of the tertiary amine from copper(II) acetate monohydrate and the free ligand. On a 2.6 mmol scale the yield of the complex was about 0.7 g. Anal. ($C_{22}H_{22}N_4Cu$) C, H, N. Mass spectrum, calcd 405, obsd 405; μ_{eff}, 1.82 μ_B.

Resonance Raman Spectra. Raman spectra were obtained using a spectrometer based on a SPEX 1401 double monochromator, a Spectra-Physics 166-03 argon ion laser, and a Spectra-Physics 375 tunable dye laser. Samples were contained in 1-mm glass capillaries and illuminated by transverse excitation, except for the $Fe^{II}L$ samples which were photosensitive and therefore were illuminated using the SPEX rotating sample accessory. The sample illuminator stage and the spectrometer fore-optics were of the Nestor design.[23] Spurious Ar^+ plasma emission lines were removed from the argon laser beam using interference filters, and background fluorescence was dispersed from the dye laser beam using a Burke filter (direct-viewing prism). Typical illumination power levels were 50-100 mW. The 90° scattered light from the sample was dispersed by the monochromator and detected by a cooled (−30 °C) Centronix Q4283S-25 photomultiplier tube (S-20 response). The signal from the PMT was amplified dc and displayed on a stripchart recorder.

Solvents used for the $M^{II}L$ complexes in the Raman experiments were acetonitrile, benzene, nitromethane, and tetrahydrofuran. These solvents were purified using established techniques.[24] This variety of solvents was employed to establish whether solvent and sample peaks overlapped. Benzene was settled upon as the solvent which caused least interference with the Raman spectra of the $M^{II}L$ complexes. Concentrations of $M^{II}L$ employed in typical Raman experiments were (2-3) × 10^{-3} M. Air-sensitive complexes ($Mn^{II}L(NEt_3)$, $Fe^{II}L$, and $Co^{II}L$) were handled in a drybox, sealed in the sample capillaries, and kept in liquid nitrogen until immediately prior to recording the Raman spectra.

Visible and ultraviolet spectra were recorded using either a Cary 14 or a Cary 118 spectrophotometer. Raman intensity (depolarization ratio) measurements were based upon integrated peak areas. Magnetic moment measurements at room temperature in the solid state were determined on 10-20 mg of sample using the Faraday method. The diamagnetic correction for H_2L was found to be -215×10^{-6} cgs units. Low resolution mass spectral measurements were supplied by Cornell University, Mass Spectroscopy Service, Ithaca, N.Y. Elemental analyses were performed by Galbraith Labs, Nashville, Tenn., Instranal-Labs, Rennselaer, N.Y., and Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. The spectral properties of the complexes are summarized in Tables I-III.

Results

All of the Raman peaks observed in the resonance-enhanced spectra of H_2L and the $M^{II}L$ complexes are polarized ($I_{\parallel}/I_{\perp} \approx 0.3$) demonstrating that only the Raman scattering due to the symmetric vibrations of these molecules is appreciably resonance enhanced. The frequencies and the vibrational assignments for the $M^{II}L$ complexes are summarized in Table

Table I. Resonance Raman Frequencies (cm^{-1}) and Assignments for $M^{II}L$ Complexes

$Mn^{II}L$	$Fe^{II}L$	$Co^{II}L$	$Ni^{II}L$	$Cu^{II}L$	$Zn^{II}L$	Assignment
1568		1535	1546[a]	1525		C_a-C_m + C_a-N stretch
1548		1520	1520[a]	1500		C_a-C_m + C_a-N stretch
1465	1470	1476	1477[a]	1473		Phenyl (C_α-C_α)
	1445	1438	1437[a]	1436		Phenyl
	1370	1370	1370[a]	1368		Phenyl
1290	1282	1289	1291[a]	1276		6-membered chelate ring
1243		1246	1249[a]	1245		C_a-C_b stretch
		1052	1050	1042		Phenyl
		962		952		Phenyl
846	850	851	850[b]	846		Phenyl (C_α-N)
		798				Combination, 234 + 563
		745	744[c]			Phenyl
621		638	638[c]	628	626	6-membered chelate ring
563[d]	563[d]	563[d]	564[b,d]	565[d]	568[d]	C_a-C_b out-of-plane wag
492	495	496	496[b]	493	496	C_a-C_b in-plane wag
		467				Overtone, 2 × 234
		404	404[c]	404	400	Phenyl
373			391[b]	374	372	C-N-C deformation + M-N stretch
		326	326[b]	323		Phenyl
	265		251[b]	234		C-N-C deformation + M-N stretch
	243	234	200[c]	200		M-N stretch

[a] Resonance enhanced predominantly by ligand-centered ($\pi \rightarrow \pi^*$, 380 nm) electronic transition of $Ni^{II}L$. [b] Resonance enhanced both by ligand-centered ($\pi \rightarrow \pi^*$, 380 nm) and charge-transfer (585 nm) electronic transitions of $Ni^{II}L$. [c] Resonance enhanced predominantly by 585 nm charge-transfer electronic transition of $Ni^{II}L$. [d] Accidentally degenerate (see text).

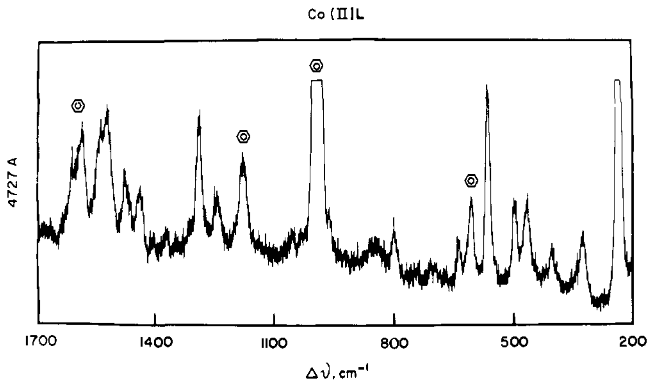

Figure 3. Resonance Raman spectrum of $Co^{II}L$ using 4727 Å (21 155 cm^{-1}) laser excitation ($\pi \rightarrow \pi^*$ plus charge-transfer resonance). The benzene solvent peaks are identified by hexagons.

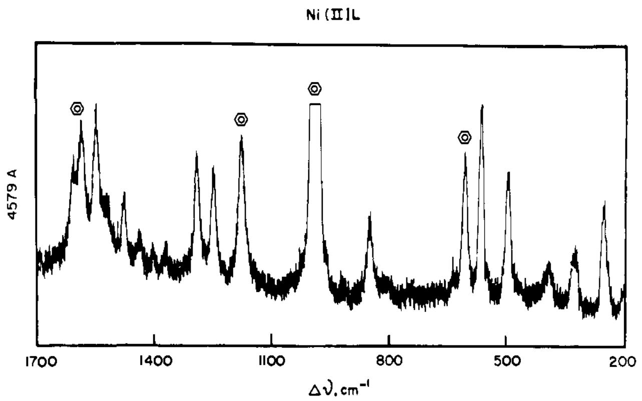

Figure 4. Resonance Raman spectrum of $Ni^{II}L$ using 4579 Å (21 838 cm^{-1}) laser excitation ($\pi \rightarrow \pi^*$ resonance). The benzene solvent peaks are identified by hexagons.

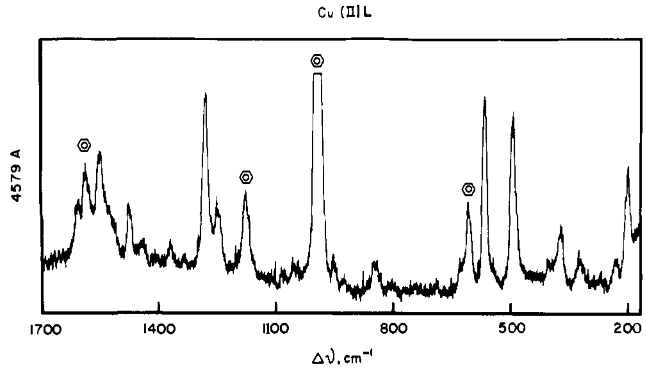

Figure 5. Resonance Raman spectrum of $Cu^{II}L$ using 4579 Å (21 838 cm^{-1}) laser excitation ($\pi \rightarrow \pi^*$ resonance). The benzene solvent peaks are identified by hexagons.

I. The assignments in Table I are supported in the Discussion section. Typical resonance Raman spectra of $Mn^{II}L(NEt_3)$, $Co^{II}L$, $Ni^{II}L$, and $Cu^{II}L$ using blue (4579 or 4727 Å) laser excitation are shown in Figures 2-5. The spectra of $Fe^{II}L$ and $Zn^{II}L(NEt_3)$ are of poorer quality owing to photolytic instability and luminescence. The spectra of $Ni^{II}L$ using green (5145 Å) and red-orange (5904 Å) laser excitation are shown in Figures 6 and 7.

The resonance Raman intensity patterns as a function of excitation frequency (excitation profiles) are the subject of the following paper and will not be reported in detail here. Briefly, the electronic transition which is principally responsible for resonance enhancement, if green or blue laser excitation is employed, is the intense ($\epsilon \sim 5 \times 10^4$ M^{-1} cm^{-1}) ligand-centered $\pi \rightarrow \pi^*$ electronic transition at approximately 380 nm in $M^{II}L$ (visible and ultraviolet absorption spectra of these complexes are tabulated in Table II). However, some of the complexes (viz., $Co^{II}L$, $Ni^{II}L$, and $Cu^{II}L$) have other prominent, though less intense, electronic transitions in the visible region (see Table II). The effect of excitation within the different absorption envelopes is evident by comparing the $Ni^{II}L$ spectra in Figures 4, 6, and 7. The spectrum in Figure 4 was obtained using 4579 Å excitation, the Ar^+ laser line closest to the $\pi \rightarrow \pi^*$ electronic transition; that in Figure 6 was taken using 5145 Å excitation, which is very nearly at the absorption minimum; and Figure 7 was obtained using 5904 Å excitation, which is near the absorption maximum of $Ni^{II}L$ in the visible region. It is seen that a different set of normal modes of the

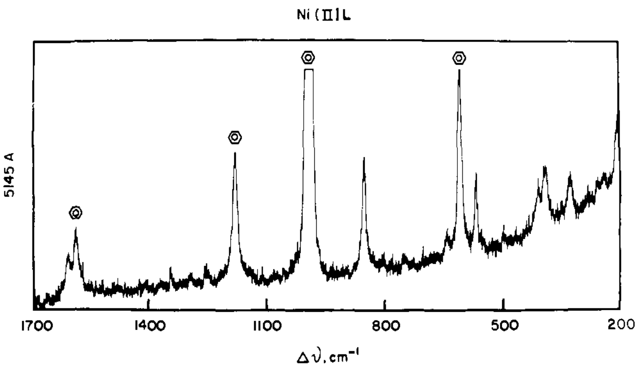

Figure 6. Resonance Raman spectrum of $Ni^{II}L$ using 5145 Å (19 436 cm^{-1}) laser excitation (resonance minimum). The benzene solvent peaks are identified by hexagons.

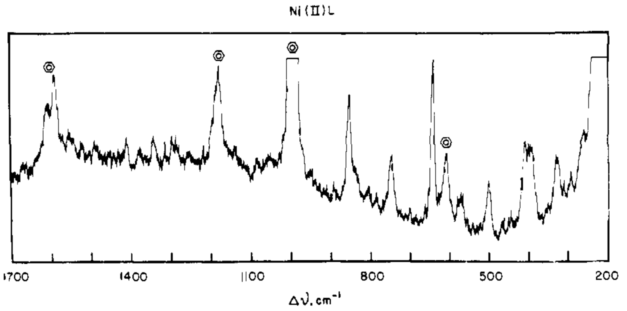

Figure 7. Resonance Raman spectrum of $Ni^{II}L$ using 5904 Å (16 938 cm^{-1}) laser excitation (charge-transfer resonance). The benzene solvent peaks are identified by hexagons.

$Ni^{II}L$ chromophore are resonance enhanced, depending upon the excitation wavelength. The high-frequency ligand vibrations are primarily in resonance with the $\pi \rightarrow \pi^*$ electronic transition and the low-frequency, ligand and metal-associated modes are enhanced predominantly in resonance with the charge-transfer transition in the visible region. This phenomenon of *selective Raman intensity enchancement* is expected for $\pi \rightarrow \pi^*$ and CT resonance enhancement[25] but is not observed in Mn(III) or Cr(III) porphyrins.[25] Effects which are somewhat analogous have, however, been observed in methemoglobin fluoride[26] and hemocyanin.[27] This effect is discussed in detail in the following paper.[19] Not surprisingly, the resonance enhancement of all $Ni^{II}L$ Raman modes is at a minimum near the absorption minimum, ~5145 Å (Figure 6).

In order to elucidate the vibrational assignments in the $M^{II}L$ complexes, we obtained resonance Raman spectra of $Ni^{II}L\text{-}d_2$. In this complex the methine bridge (C_m, Figure 1) protons have been replaced with deuterium. Both proton magnetic resonance and resonance Raman spectra indicated 90% or greater deuteration using the preparative method described (vide supra). The observed deuterium shifts are summarized in Table III. Measured deuterium shifts of greater than 2 cm^{-1} were considered to be significant.

The deuterium shifts observed for $Ni^{II}L$ in the neighborhood of 600 cm^{-1} are noteworthy. Furthermore, the appearance of the spectra in this frequency region as a function of excitation wavelength illustrates an important point, namely that spectra taken at a single excitation wavelength can be very misleading if selective Raman intensity enhancement is a factor. The 525-700 cm^{-1} frequency region is shown in Figure 8 for $Ni^{II}L$, $Ni^{II}L\text{-}d_2$, and an incompletely deuterated mixture which resulted when solutions of $Ni^{II}L\text{-}d_2$ were exposed to atmospheric moisture. It is seen that, while $Ni^{II}L$ with 4727 Å excitation shows only one Raman peak in this region (at 564 cm^{-1}), 5904 Å excitation reveals the fact that there are actually two vibrations, at 638 and 564 cm^{-1}. If only 5904 Å excitation is employed, these peaks appear to shift in $Ni^{II}L\text{-}d_2$ to 658 and 578 cm^{-1}; however, if the deuterated complex is excited at 4727 Å, peaks are seen at 578 and 548 cm^{-1}. If this frequency region is viewed over both excitation conditions (4727 and 5904 Å), two vibrations are evident in $Ni^{II}L$ at 638 and 564 cm^{-1} and three in $Ni^{II}L\text{-}d_2$ at 658, 578, and 548 cm^{-1}.

Table II. Absorption Spectra of the Complexes[a]

Complex with L^{-2}	Absorption maxima,[b] μm^{-1} (ϵ, M^{-1} cm^{-1})
H_2L[c]	2.50 (Sh), 2.93 (63 000)
Mn(II)[d,e]	2.15 (Sh), 2.38 (Sh), 2.63, 2.78 (Sh)
Fe(II)[e]	2.22 (Sh), 2.58, 2.90 (Sh), 3.19
Co(II)	1.72 (4000), 1.87 (4200), 2.17 (8100), 2.41 (13 400), 2.69 (36 000)
Ni(II)	1.72 (6800), 2.35 (Sh), 2.57 (48 000), 2.98 (8000)
Cu(II)	1.58 (2900), 2.00 (Sh), 2.40 (21 300), 2.61 (58 300), 3.17 (Sh)
Zn(II)[d,f]	2.40 (Sh), 2.66 (42 400)

[a] Unless otherwise noted all spectra were determined in benzene solution. [b] Sh = shoulder. [c] In acetonitrile solution. [d] A 5-coordinate complex having triethylamine as the fifth ligand. [e] Because of the extreme air sensitivity of these compounds reliable values of the molar extinction coefficients could not be determined. The spectra were recorded in toluene solution. [f] The spectral data previously reported for this complex are in error, ref 5.

Table III. Frequency Shifts in C_m-Deuterated $Ni^{II}L$

$\nu(Ni^{II}L)$, cm^{-1}	$\nu(Ni^{II}L\text{-}d_2)$, cm^{-1}	Deuterium shift, cm^{-1}
1546	1537	−9
1520		
1477	1477	0
1437	1437	0
1370	1372	~0 (+2)
1291	1285	−6
1249	1245	−4
850	850	0
744	746	~0 (+2)
638	658	+20
	578	+14[a]
564	548	−16
496	491	−5
404	405	~0 (+1)
391	392	~0 (+1)
326	327	~0 (+1)
251	252	~0 (+1)
200		

[a] Probable shift (see text).

Discussion

Vibrational Assignments. The symmetry of the $M^{II}L$ complexes is C_{2v}, while that of H_2L is C_2. Vibrations associated with axial ligation[5] in $Mn^{II}L$ and $Zn^{II}L$ are not observed. The reduction of symmetry in H_2L (Figure 1) is a consequence of protonation of two opposite nitrogen atoms in the N_4 plane. As a result of this protonation, the $N\text{-}C_a\text{-}C_m\text{-}C_a\text{-}N$ structure in H_2L possesses essentially isolated double bonds. The localized double bonds are evident both in the crystal structure[6] and in the Raman spectra. The latter is dominated by a peak at 1511 cm^{-1}, a frequency typical of the in-phase, double bonded C═C stretch of macrocyclic molecules containing conjugated but nondelocalized double bonds, e.g., vitamin B_{12}.[28] A second strong H_2L peak at 1345 cm^{-1} is assigned to N-H wag, since it vanishes upon N deuteration. Additionally,

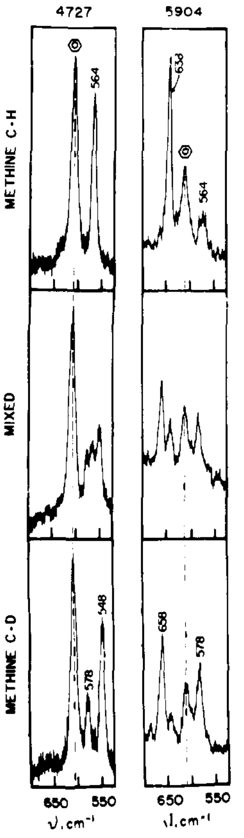

Figure 8. Resonance Raman spectra of $Ni^{II}L$, $Ni^{II}L$-d_2, and a partially deuterated mixture from 525 to 700 cm^{-1}. Both 4727 and 5904 Å laser excitation are shown. The deuterium shifts and Raman intensity changes are evident relative to the 606 cm^{-1} benzene solvent peak. Selective Raman intensity enhancement occurs between 4727 and 5904 Å excitation (see text).

the phenyl ring modes appear in H_2L virtually unchanged from their frequencies in *o*-phenylenediamine (although their intensities are quite sharply altered), indicating that the phenyl moiety is not part of a macrocyclic, electronically delocalized π system in the protonated ligand.

The situation regarding electronic delocalization is quite different in the $M^{II}L$ complexes. The ligand-centered $\pi \rightarrow \pi^*$ electronic transition shifts from 340 nm in H_2L to approximately 380 nm in the $M^{II}L$ complexes (Table II). The $M^{II}L$ crystal structures do not show isolated double bonds in the 6-membered chelate rings.[3,4,6,7] The delocalization of π electron density extends not only over the 6-membered chelate rings but also to some extent over the phenyl rings, as evidenced by the resonance Raman spectra (vide infra). Due to this π delocalization, the resonance Raman spectra of the $M^{II}L$ complexes bear virtually no resemblance to those of H_2L. While some of the normal modes of H_2L can in principle be related to those of $M^{II}L$, this exercise is not pertinent to the points which we wish to consider in the present study, and we will discuss the H_2L spectra no further.

Only vibrations having A_1 symmetry are observed in the resonance Raman spectra of the $M^{II}L$ complexes. There are 37 possible symmetric (A_1) normal modes in the $M^{II}L$ molecule, considering all atoms but discounting possible axial ligation. No vibrations are observed above 1600 cm^{-1} in the $M^{II}L$ resonance Raman spectra, therefore the six predicted symmetric C–H stretches (which occur in the vicinity of 3000 cm^{-1}) have no appreciable intensity. This leaves 31 possible normal modes of A_1 symmetry in the frequency region where Raman peaks occur, 20 of which belong to the carbon–nitrogen–metal skeleton of the macrocycle and 11 of which are C–H deformations. The vibrational frequencies which are actually observed in the $M^{II}L$ complexes are summarized in Table I and are represented as correlation diagrams in Figures 9 and 10 (except for the four $M^{II}L$ modes between 700 and 1200 cm^{-1}).

The frequency shifts which are observed upon deuteration of the C_m carbon atom in $Ni^{II}L$ are presented in Table III. One very important point is evident from consideration of the deuterium shifts, namely that *the* A_1 *(out-of-plane)* C_m*–H wag is not observed in* $Ni^{II}L$. By analogy to assignments previously made for acetylacetonate complexes[29] and metalloporphyrins,[30] the C_m–H wag is expected in the neighborhood of 1300 cm^{-1}. No Raman mode in this or any other frequency region of the $Ni^{II}L$ spectrum exhibits a deuterium shift large enough to be the C_m–H wag. All of the deuterium shifts in Table III, then, are shifts in $M^{II}L$ modes which are induced by mixing or kinematic coupling with the C_m–H wag which is itself invisible. Similar effects have previously been observed upon methine bridge deuteration of synthetic macrocyclic complexes[31] and metalloporphyrins.[14,17]

The absence of resonance-enhanced Raman peaks in any of the $M^{II}L$ complexes due to any of the C–H stretches or to

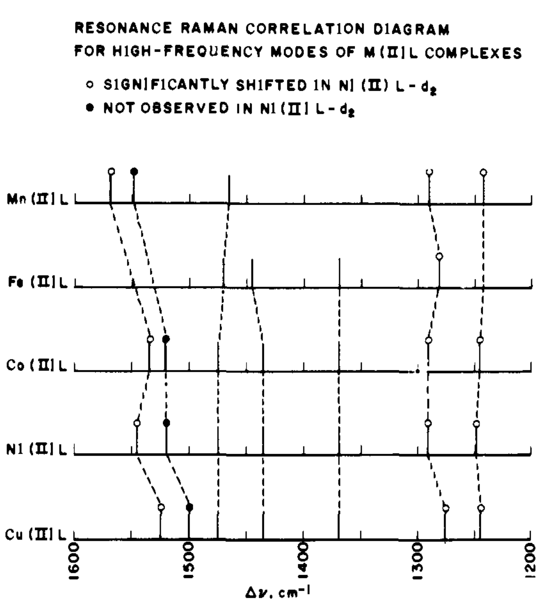

Figure 9. Correlation diagram of the observed resonance Raman frequencies of $M^{II}L$ complexes, from 1200 to 1600 cm^{-1}.

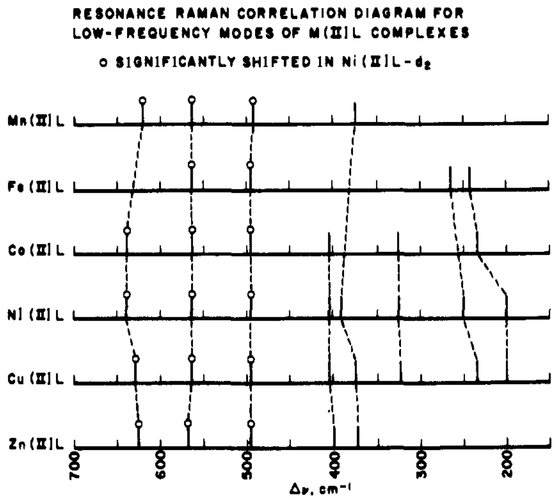

Figure 10. Correlation diagram of the observed resonance Raman frequencies of $M^{II}L$ complexes, from 200 to 700 cm^{-1}.

the C_m–H wag is strong evidence that none of the other C–H modes experience resonance enhancement in these systems. The other C–H vibrations which might be observed (six C_b–H deformations and two C_β–H and two C_γ–H wags) are more remote from the chromophore (the delocalized π system) of the $M^{II}L$ molecule than is the C_m–H bond. That resonance-enhanced Raman modes due to the C_m–H bond are not observed leads us to the conclusion that *all of the observed resonance Raman modes of these complexes are due to the carbon-nitrogen-metal skeleton.* As noted above, 20 A_1 modes are expected for this structure, and Table I lists 19 of these. The remaining mode is evident in the spectrum of $Ni^{II}L$-d_2 (Table III) at 578 cm^{-1}. We suggest that this vibration is accidentally degenerate with another vibration (probably the one at ~564 cm^{-1}) in all of the $M^{II}L$ complexes and that this degeneracy is lifted in $Ni^{II}L$-d_2. Thus it appears that all of the A_1 skeletal modes, and only those modes, are observed in the $M^{II}L$ complexes.

The deuterium shifts in Table III have further utility in assigning the $M^{II}L$ vibrations. Since the deuteration occurs at C_m, it is most unlikely that vibrations of the $Ni^{II}L$ structure other than those of the 6-membered chelate ring will be significantly shifted in $Ni^{II}L$-d_2. Therefore all of the vibrations which show significant deuterium shifts can be associated with the C_a–N, C_a–C_b, or C_a–C_m bonds. There are seven such vibrations observed, including the 578 cm^{-1} mode of $Ni^{II}L$-d_2 which appears to be accidentally degenerate in $Ni^{II}L$. Additionally, we assign the 1520 cm^{-1} vibration of $Ni^{II}L$ to the 6-membered chelate ring, based upon previous assignments for acetylacetonate[29] and diiminate[31] complexes in which two modes above 1500 cm^{-1} are assigned to C–C and C–O or C–N stretch. The deuterium shift of the 1520 cm^{-1} vibration is not known because the corresponding peak evidently has very low intensity in the spectra of $Ni^{II}L$-d_2. Thus eight normal modes of $M^{II}L$ are assigned to vibrations associated with the symmetry species C_a, C_b, and C_m, and eight is precisely the number of A_1 normal modes that these symmetry species are expected to contribute.

The remaining high- (>1200 cm^{-1}) and medium-frequency (700–1200 cm^{-1}) vibrations are assigned to phenyl ring C–C and C_α–N modes. The C_α–N stretch probably corresponds to either the 74X or (more likely) the 85X cm^{-1} vibration, but this is not certain due to the possibly large effect of π delocalization in the macrocyclic structure upon the force constant on this bond.

A resonance Raman correlation diagram for the high-frequency vibrations of $M^{II}L$ complexes is presented in Figure 9 and for the low-frequency vibrations (<700 cm^{-1}) in Figure 10. The four intermediate-frequency vibrations are easily correlated (the frequency shifts among all of the metals are small), and these frequencies are presented only in Table I. It can be seen from these correlations that the seven intermediate- and high-frequency vibrations which have been assigned to the phenyl structure are generally insensitive to the identity of the metal ion. On the other hand, several of the modes assigned to the C_a–C_b–C_m structure show quite substantial metal-induced frequency shifts. This is expected on the basis of the $M^{II}L$ crystal structures,[2,3,6,7,32] in which it is seen that the structural parameters of the phenyl rings vary little among different metal ions, while the structure of the 6-membered chelate ring (particularly the C_a–C_m–C_a bond angle) is quite sensitive to the size of the metal ion. Additionally, the π system of the 6-membered chelate ring is probably more sensitive to electronic effects due to the metal ion than is the π system of the phenyl group. This point has previously been discussed by Goedken in relation to the crystal structures.[6]

However, three vibrations assigned to the C_a–C_b–C_m structure exhibit nearly absolute frequency invariance among all of the $M^{II}L$ complexes. These are the modes at 124X, 56X, and 49X cm^{-1}. These vibrations must be due to a symmetry species which is not affected by either structural or electronic effects of the metal ion, that is, a symmetry species remote from effects due to distortions around either C_m or the nitrogen atoms and also insensitive to effects of the metal ion upon the π system of the 6-membered chelate ring. The only such symmetry species in the diiminate structure is C_b. As a symmetry species which resides on none of the symmetry elements of the molecule, C_b contributes three A_1 normal modes, namely the symmetric C_a–C_b stretch and the two symmetric C_a–C_b wags. We assign the 124X cm^{-1} vibration to the stretch and the 56X and 49X cm^{-1} vibrations to the wags. These assignments are consistent with previous assignments of the analogous vibrations of acetylacetonate complexes.[29]

It is possible on the basis of the deuterium shifts to propose which of the two low-frequency C_b modes is the in-plane and which is the out-of-plane wag. The source of these shifts is the A_1 C_m–H wag, which is required by symmetry to be out of plane. Thus, the vibration which causes the observed deuterium shifts is almost orthogonal to the C_a–C_b in-plane wag, and the deuterium shift of the C_a–C_b in-plane wag should be substantially smaller than that of the C_a–C_b out-of-plane wag. On this basis, we assign the 56X cm^{-1} vibration as the out-of-plane wag and the 49X cm^{-1} vibration as the in-plane wag.

The very low frequency (<500 cm^{-1}) vibrations of $M^{II}L$ may have substantial contributions from M–N stretch. Any vibration with such a contribution is expected to be strongly metal dependent in frequency. Three of the very low frequency vibrations (Figure 10) show such a dependence, and two do not. We assign the former to modes intimately associated with the M–N bonds and the latter to low-frequency phenyl ring modes. The lowest frequency vibration in $Fe^{II}L$ (243 cm^{-1}), $Co^{II}L$ (234 cm^{-1}), $Ni^{II}L$ (200 cm^{-1}), and $Cu^{II}L$ (200 cm^{-1}) is also the most metal dependent in frequency. We assign this vibration as predominantly the M–N symmetric stretch. This assignment is consistent with the previously assigned manganese–N stretch (270–300 cm^{-1}) in Mn(III) tetraphenylporphyrin halides.[15]

In the nickel and cobalt complexes, this M–N stretching vibration experiences extremely strong enhancement of Raman scattering in resonance with electronic transitions at longer wavelength than the major $\pi \rightarrow \pi^*$ peak. These are the 460 nm shoulder (ϵ = 8100 M^{-1} cm^{-1}) in $Co^{II}L$ and the 580 nm peak (ϵ = 6800 M^{-1} cm^{-1}) in $Ni^{II}L$. In metalloporphyrins it has been predicted that charge-transfer resonance should lead to strong enhancement of the M–N stretching mode, but this has not been observed.[25] We assign the resonant electronic states in the $Co^{II}L$ and $Ni^{II}L$ cases as predominantly charge-transfer transitions, although in $Co^{II}L$ some $\pi \rightarrow \pi^*$ character must be present.[19] These assignments are discussed in more detail in the following report.[19]

Structural and Electronic Effects upon Vibrational Frequencies. Crystal structure studies of H_2L and $M^{II}L$ complexes have been carried out by Goedken[3,4,6,32] and more recently by Day.[8] Additionally, the structure of the Ni(II) complex of a ligand similar to L^{2-} (minus two opposite methyl groups) has been reported.[7] On the basis of these structures the following conclusions relevant to the present study may be drawn. (a) The ligand in both $M^{II}L$ and H_2L adopts the saddle-like conformation shown in Figure 1. This is due to steric interferences between the protons on C_b and C_β. (b) The metal-nitrogen distances in the $M^{II}L$ complexes parallel those in the metalloporphyrins,[33] although the metalloporphyrin distances are generally longer. The difference between the M–N ($M^{II}L$) and M–N (metalloporphyrin) distances diminishes with increasing displacement of M from the N_4 plane of $M^{II}L$. (c) The saddle-like (C_{2v}) distortion of the ligand increases with increasing displacement of the metal ion out of the N_4 plane in the $M^{II}L$ complexes. This distortion is a minimum for $Ni^{II}L$ and a maximum for $Mn^{II}L$ ($M-N_4$ plane distances ~0 and 0.73 Å, respectively).[7,32] (d) The $C_a-C_m-C_a$ angle expands to accommodate metal ions which exhibit longer M–N distances (122° for $Ni^{II}L$, 131° for $Mn^{II}L$).[7,32] This expansion of the $C_a-C_m-C_a$ angle is accompanied by increased displacement of the metal ion from the N_4 plane, hence by increased C_{2v} distortion of the entire ligand as pointed out in (c) above. Thus out-of-plane displacement of the metal ion in the $M^{II}L$ complexes is accompanied by structural distortions of the ligand, especially at the methine bridge carbon atom, analogous to those observed in metalloporphyrins.[33]

The most pronounced metal-dependent frequency shifts in the $M^{II}L$ complexes occur in the vibrations of the 6-membered chelate ring and in the vibrations associated with the M–N bond. The latter shifts are probably due primarily to differing M–N force constants resulting from the electronic nature of the various metal ions. The shifts in the higher frequency (ligand) vibrations may be due either to direct electronic effects of the metal ion upon the ligand π system or to metal-induced distortions of the ligand structure. The nature and magnitude of the metal-induced shifts in ligand vibrational frequencies is the question which we now wish to address.

The possible magnitude of nonstructural, electronic effects of the *metal* ion upon the *ligand* vibrational frequencies can be ascertained by comparing the spectra of $Fe^{II}L$, $Co^{II}L$, and $Cu^{II}L$. The M–N bond distances in these three complexes are estimated to be the same within 0.01 Å, therefore the *conformation of the ligand should be approximately the same in each case.* The data in Table I and Figures 9 and 10, however, reflect substantial frequency shifts in purely ligand vibrations among these three complexes. Since the complexes are approximately isostructural, these shifts must be due to electronic effects of the metal ions. In particular, the two highest frequency vibrations (which are assigned to C_a-N and C_a-C_m stretch) shift to lower frequency by 10 to 20 cm^{-1} from $Co^{II}L$ to $Cu^{II}L$. Indeed, the ligand vibrations of $Cu^{II}L$ are generally at lower frequency than those of either $Fe^{II}L$ or $Co^{II}L$. This may be due to the electron in the strongly antibonding $d_{x^2-y^2}$ orbital of copper(II), which is absent in both low-spin cobalt(II) and intermediate-spin ($s = 1$) iron(II). The relationship between the metal electronic configurations and ligand vibrational frequency shifts is not simple, as there is no clearly consistent relationship between the $Fe^{II}L$ and $Co^{II}L$ vibrational frequencies. However, it appears that frequency shifts in the 6-membered chelate ring of up to 20 cm^{-1} can be caused by electronic effects of the metal ion alone.

It is not surprising that the largest frequency shifts among the $M^{II}L$ complexes are observed in the highly distorted $Mn^{II}L$ system. The source of these shifts is, however, not clear. They may result primarily from the structural distortions, or they may be due to effects of the high-spin d^5 manganese(II) electronic configuration, which has no close analogue among the other $M^{II}L$ complexes. Unfortunately the high-frequency Raman scattering of $Zn^{II}L$, which would reveal the vibrational shifts in another distorted structure,[8] is obscured by sample luminescence. It should be noted, however, that the C_a-N and C_a-C_m stretching vibrations (as well as the 1290 cm^{-1} vibration) occur at higher frequency in $Mn^{II}L$ than in any of the other complexes studied. We consider it unlikely that the distortion which is observed in the 6-membered chelate ring of $Mn^{II}L$ ($C_a-C_m-C_a$ angle ~131° [32]) could, as a structural effect alone, result in uniformly higher frequencies for all of the high-frequency chelate ring vibrations. We therefore suggest that electronic effects of the manganese(II) ion play a major role in determining the ligand vibrational frequencies of $Mn^{II}L$.

The striking simplicity of the $Mn^{II}L$ spectrum compared to those of $Co^{II}L$, $Ni^{II}L$, and $Cu^{II}L$ is evident in Figures 2–5. It is clear that many of the $M^{II}L$ vibrations experience sharply decreased or negligible resonance enhancement in $Mn^{II}L$. Table I and Figure 10 show that, while all of the 6-membered chelate ring modes persist, *all but two of the assigned phenyl ring modes disappear* in $Mn^{II}L$. We interpret this as support for the previous suggestion[6] that macrocyclic-wide π delocalization can be interrupted by restricted π overlap at the nitrogen atoms in a highly distorted $M^{II}L$ complex. The most distorted complex in the present study is $Mn^{II}L$, and as a consequence its phenyl rings appear to participate to a lesser extent in the $\pi \rightarrow \pi^*$ electronic transition which is the source of the resonance Raman intensity. Accordingly, resonance enhancement of the phenyl ring modes of $Mn^{II}L$ is either greatly diminished or nonexistent. Thus the most unambiguous structural effect upon any of the $M^{II}L$ spectra is an effect upon Raman *intensities* rather than upon vibrational frequencies.

Conclusions

We have studied the resonance Raman spectra of a series of bivalent metal complexes of L^{2-} and have been able thereby to arrive at reasonable assignments for the vibrational modes of the carbon–nitrogen–metal skeleton of these $M^{II}L$ complexes. The identity of the metal has a pronounced effect both upon the vibrational frequencies and the resonance Raman intensities in the various $M^{II}L$ spectra. The effect of the metal ion upon the Raman *intensities* of the ligand vibrations (when $\pi \rightarrow \pi^*$ excitation is employed) appears to be primarily due to metal-induced structural distortions of the ligand. It also appears that purely electronic effects of the metal ion upon the ligand π system can result in *frequency* shifts of up to 20 cm^{-1} in ligand vibrations. The maximum observed ligand frequency shifts, 40–50 cm^{-1} between $Mn^{II}L$ and $Cu^{II}L$, are undoubtedly due in part to the large differences in ligand conformation between these two complexes. However, we conclude that electronic effects of the metal ions also have a major influence upon these large frequency shifts.

Relationship to Vibrational Studies of Natural Macrocycles. The present study has three important implications regarding investigations of the resonance Raman spectra of natural macrocyclic systems. They are the following.

First, the electronic effects of the metal ions upon the ligand vibrational frequencies in the $M^{II}L$ complexes are comparable in magnitude to the frequency shifts which appear to be due to structural effects in heme proteins.[13,30,34] However, these heme structural distortions are generally accompanied by a change in electronic configuration (spin state) of the iron atom.[33,35] The present study suggests that such a change in electronic configuration of the metal atom in a macrocyclic complex can alone be responsible for substantial Raman frequency shifts, even if no structural distortion occurs. Therefore structural interpretations of vibrational frequency shifts must be approached with caution, whenever the structural change is accompanied by a change in metal ion electronic configuration.

The second point concerns vibrational assignments of resonance-enhanced Raman modes in natural macrocycles. The possibility of resonance enhancement of vibrations due to unsaturated peripheral substituents such as the vinyl groups in protoheme has been recognized.[34] However, it has generally been assumed that the most strongly resonance-enhanced peaks in the Raman spectra of porphyrins and corrins are due to vibrational modes which are intimately associated with the π electronic system of the macrocycles.[30,34] In one instance, the possibility of significant resonance enhancement of Raman scattering due to vibrations of alkyl substituents on the periphery of a metalloporphyrin has been suggested (on the basis of excitation profile data),[25] but this possibility is often disregarded.[14,17,34] In the $M^{II}L$ complexes of present study, the C_a-C_b single bond cannot participate in the π delocalization of the $M^{II}L$ macrocycle (see Figure 1), except via a hyperconjugative mechanism.[36] However, the Raman peaks assigned to the three C_a–C_b vibrational modes are consistently among the most intense in all the $M^{II}L$ spectra. This is the first such observation based upon vibrational assignments independent of the resonance Raman effect. The apparently anomalous enhancement of these C_a–C_b modes may be a result of hyperconjugation involving the C_b methyl group and the π chromophore of the macrocycle. The possibility of hyperconjugation is supported by the short (1.46–1.52 Å) C_a–C_b bond distances in $M^{II}L$ complexes.[6-8] The C_b methyl group can be considered analogous to the alkyl substituents on the pyrrole rings of, for example, octamethylporphyrin, octaethylporphyrin, or mesoporphyrin IX.[18] We suggest that similar enhancement of Raman scattering due to vibrations of peripheral substituents can occur in porphyrins and corrins and that this possibility must be considered in assigning the vibrational spectra of these natural macrocycles.

The third point concerns selective Raman intensity enhancement and the utility of this phenomenon in assigning metal-associated vibrations. In $Co^{II}L$ and $Ni^{II}L$ the low-frequency (234 and 200 cm^{-1}, respectively) Raman modes assigned to M–N stretch experience extremely strong intensity enhancement in resonance with charge-transfer electronic transitions.[19] Similar charge-transfer transitions are undoubtedly present in metalloporphyrins but are in many cases obscured by the ligand-centered $\pi \rightarrow \pi^*$ transitions. The present study suggests that, by careful examination of the intensity dependence of the low-frequency Raman peaks upon the laser excitation wavelength, the M–N stretching vibrations of natural macrocycles might be identifiable via the selective Raman intensity enhancement effect.

The present study has not addressed the effects of metal oxidation state, axial ligation, ligand structure, or ligand π radical formation upon the resonance Raman spectra of synthetic macrocyclic complexes. Studies of these effects are currently in progress.

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