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Influence of Symmetry on the Vibrational Spectra of Zn(TPP), Zn(TPC), and Zn(TPiBC)

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To evaluate the effects of sequential pyrrole ring reduction, we have examined the vibrational spectra of tetracoordinate Zn^{II} complexes of *meso*-tetraphenylporphyrin [Zn(TPP)], *meso*-tetraphenylchlorin [Zn(TPC)], and *meso*-tetraphenylisobacteriochlorin [Zn(TPiBC)]. The phenyl substituents of these macrocycles fall into distinct symmetry classes: for Zn(TPP), all four phenyl groups are equivalent; for Zn(TPC), the phenyl groups are of two different types; and for Zn(TPiBC), there are three types of phenyl substituent. This variation leads to marked differences in the resonance Raman spectra of the three complexes, particularly for the phenyl vibrational modes. Thus, a single totally symmetric C_m–phenyl stretch [$\nu(C_m–Ph)$] is observed for Zn(TPP) at 1236 cm^{-1}. In contrast, two $\nu(C_m–Ph)$ modes are observed at 1247 and 1236 cm^{-1} for Zn(TPC). For Zn(TPiBC), three $\nu(C_m–Ph)$ modes are observed at 1269, 1252, and 1235 cm^{-1}. Other phenyl-related vibrational modes undergo similar splittings as the symmetry of the phenyl substituents varies from Zn(TPP) to Zn(TPC) to Zn(TPiBC). The vibrational patterns for these macrocycles are in harmony with ^1H NMR results demonstrating one, two, and three type(s) of *meso*-phenyl substituents for H_2TPP, H_2TPC, and H_2TPiBC, respectively. The vibrational spectra of Zn(TPC) and Zn(TPiBC) are more complex than the spectra of Zn(TPP), owing to their lowered symmetries. Nonetheless, the spectra of Zn(TPiBC) display features distinct from those of Zn(TPC).

Introduction

Functional diversity for heme proteins and enzymes derives from variations in the peripheral substituents of the porphyrin macrocycle, the axial ligand(s), and the protein environment.[2] Alternatively, a variety of biological processes are mediated by hydroporphyrins,[3] which differ far more widely in the macrocycle structure and its substituents and in the identity of the central metal ion. Thus, photosynthesis involves chlorophylls and bacteriochlorophylls (magnesium chlorins and magnesium bacteriochlorins).[5] A saturated porphyrin is also the prosthetic group for some fungal and bacterial catalases[6] and some terminal oxidases[7,8] (iron chlorins), mammalian myeloperoxidase (iron chlorin),[9] assimilatory nitrite reductases and sulfite reductases (iron isobacteriochlorins, also termed sirohemes),[10] and dissimilatory nitrite reductases (iron dioxoporphyrins).[11] Related to these are the highly saturated corrin[12] and corphinoid[13] macrocycles of cobalt vitamin B-12 and nickel factor F-430, respectively.

In efforts to better understand the functional advantages of biological hydroporphyrins, attention has been focused on chemical and spectroscopic properties of model systems.[8,14-16] X-ray crystallography of model hydroporphyrins has provided important structural information.[17,18] Structures have been reported for pyridine-ligated pentacoordinate zinc complexes of *meso*-tetraphenylchlorin[17a] and *meso*-tetraphenylisobacteriochlorin.[17b] These data indicate that the pyrroline ring(s) of Zn(TPC)[19] and Zn(TPiBC) differ considerably from their pyrrole rings. The data also demonstrate that hydroporphryins exhibit an overall S_4 ruffling and slight saucer shape[17] in comparison with the analogous porphyrin.[20]

As part of our ongoing spectral characterization of biological and model hydroporphyrins,[8,14,15,21] this paper presents resonance Raman (RR) and Fourier transform infrared (FTIR) spectra of tetracoordinate Zn(TPP), Zn(TPC), and Zn(TPiBC), whose structures are shown in Figure 1. The goals of this work were to evaluate the effects of sequential pyrrole ring reduction and consequent changes in molecular symmetry. The vibrational pattern for the *meso*-phenyl substituent (C_m-Ph) modes of Zn(TPP), Zn(TPC), and Zn(TPiBC) unambiguously concurs with predictions from symmetry analysis. The increase in spectral complexity observed for Zn(TPC) and Zn(TPiBC) relative to Zn(TPP) is characteristic of their lowered effective symmetry. Spectral differences between Zn(TPC) and Zn(TPiBC) also arise as a consequence of the specific macrocyclic structure.

Experimental Section

Free-base TPP was prepared and purified according to the method of Adler et al.[22] The free-base TPC and TPiBC macrocycles were prepared according to the method of Whitlock et al.[23] Metallation with Zn^{II} followed the method of Whitlock and Oester.[24] The crystalline samples

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(3) Macrocycles derived from porphyrins by partial saturation of one or more pyrrole rings are collectively known as hydroporphyrins,[4] although the substituents on the saturated ring are not necessarily hydrogens. Dihydroporphyrins (chlorins) have one pyrroline ring; tetrahydroporphyrins have two. When the two pyrroline rings are opposite one another, the macrocycle is a bacteriochlorin (BC); if the two pyrrolines are adjacent, the macrocycle is an isobacteriochlorin (iBC).

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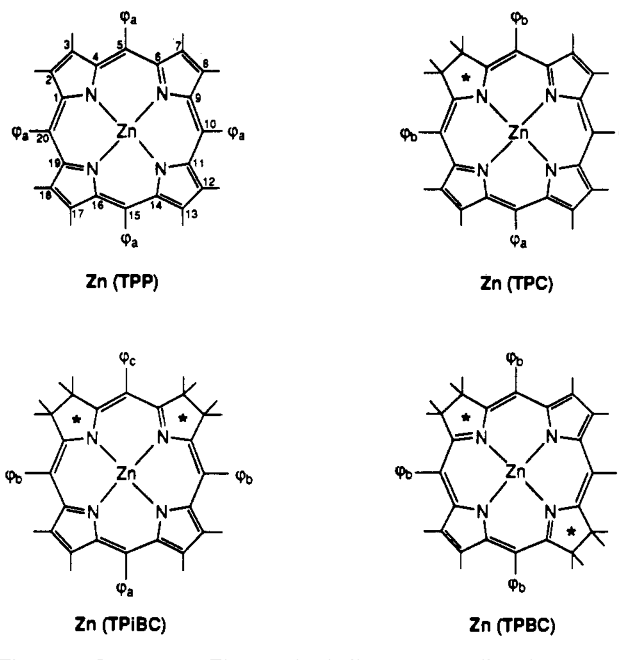

Figure 1. Structures. The asterisk indicates a pyrroline ring.

of Zn(TPP), Zn(TPC), and Zn(TPiBC) were judged to be tetracoordinate because they were shown by ^{1}H NMR spectroscopy to contain <1% water. Cu^{II}(TPC) and Cu^{II}(TPC-d_{20}) complexes were prepared by Chang and co-workers as described previously.[15]

Fourier transform IR spectra (Perkin-Elmer 1800) were obtained from ~1:150 mg KBr pellets. Resonance Raman spectra were obtained from solid-state samples (~1:150 mg KBr matrix) gently hand compressed into the groove of a sample holder that was spun during laser irradiation. Spectra-Physics 2025-11 Kr and 164-05 Ar ion lasers were used as excitation sources. Soret and near-Soret excitation lines (406.7, 413.1, and 457.9 nm) provided RR spectra of high quality. Because the inherent fluorescence of the macrocycles is unquenched by zinc metalation, it was not possible to obtain good quality RR data with visible excitation. Attempts to resolve this difficulty by the use of SERRS[19] spectroscopy were not productive; the samples were highly fluorescent, possibly due to trace levels of free-base macrocycles. The computer-controlled Jarrell-Ash Raman spectrometer and data reduction programs have been described previously.[25] The computer system for the spectrometer has been upgraded to an RMX86-based Intel 310 system, running our own revised Fortran 77 data collection and analysis programs.

Table I. Effects of Symmetry on C_m–Phenyl Modes

compd	max sym	no. of unique groups[a]	sym species of C_m–Ph vibr
Zn(TPP)	D_{4h}	1 all Ph$_a$ equiv	A_{1g} (R) + B_{2g} (R) + E_u (IR)
Zn(TPC)	C_{2v}	2 2 Ph$_a$ opposite 2 Ph$_b$ adjacent	2 A_1 (R, IR) + 2 B_1 (R, IR)
Zn(TPiBC)	C_{2v}	3 1 Ph$_a$ opposite 2 Ph$_b$ adjacent 1 Ph$_c$ between	3 A_1 (R, IR) + B_1 (R, IR)
Zn(TPBC)	D_{2h}	1 all Ph$_b$ equiv	A_g (R) + B_{1g} (R) + B_{2u} (IR) + B_{3u} (IR)

[a] See Figure 1.

Results and Discussion

A. Effects of Symmetry. 1. Molecular Symmetry. The symmetry of a tetrapyrrolic macrocycle can be changed from idealized D_{4h} symmetry in three important ways. First, the solid-state site symmetry of a symmetric complex of TPP or OEP[19] can be lower than D_{4h} (e.g., crystalline Zn(TPP) has C_s site symmetry[26]). Second, the peripheral substituents of a porphyrin may lower the symmetry (e.g., the highest possible symmetry of a protoporphyrin IX complex is C_s). In general, however, these first two ways do not significantly affect the vibrational modes of porphyrin complexes.[27] The third way is the sequential reduction of a porphyrin (idealized D_{4h} symmetry) to a chlorin (idealized C_{2v} symmetry) to an isobacteriochlorin (idealized C_{2v} symmetry, but with a 45° rotation of the C_2 axis). The vibrational effects of these changes in overall symmetry are discussed herein.

While the latter type of symmetry lowering affords a drastic change in the electronic structure of the macrocycle, it does *not* always result in the observation of the expected spectral features. For example, ^{1}H NMR spectroscopy of H$_2$(TPP), H$_2$(TPC), and H$_2$(TPiBC) complexes revealed splittings of the ortho protons of the phenyl moieties into two types for the chlorin and into three types for the isobacteriochlorin.[28] However, the two types of pyrroline protons in H$_2$(TPiBC) only gave rise to a single ^{1}H NMR resonance.[28,29]

Another example was found in an EPR study of five-coordinate, high-spin Fe(III) tetrapyrrolic complexes. Porphyrins, chlorins, and isobacteriochlorins all gave axial spectra with only two *g* values, in spite of the expectation that the chlorin and isobacteriochlorin complexes would give rhombic spectra with three *g* values.[31] Given this inconsistent behavior, the effect of the porphyrin to hydroporphyrin transformation on vibrational spectra is still an open question and is the focus of this study.

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(19) Abbreviations used are as follows: P, porphyrin; C, chlorin, iBC, isobacteriochlorin; BC, bacteriochlorin; TPP, *meso*-tetraphenylporphyrin; TPC, *meso*-tetraphenylchlorin; TPiBC, *meso*-tetraphenylisobacteriochlorin; TPBC, *meso*-tetraphenylbacteriochlorin; NCA, normal-coordinate analysis; SERRS, surface-enhanced resonance Raman scattering; OEP, octaethylporphyrin.

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Table II. Resonance Raman Frequencies (cm^{-1}) for M(TPP), M(TPC), and Zn(TPiBC) Complexes

porphyrin assignments[a]	(FeTPP)$_2$O[b]	Δd$_{20}$[b,c]	Cu(TPC)[d,e]	Δd$_{20}$[c–e]	Zn(TPP)[d,f]	Zn(TPC)[d]	Zn(TPiBC)[d]
phenyl A							1615
	1599	32	1596	33	1595 (1600)	1596	1593
			1571	35		1576	1578
phenyl C ($\nu(C_m–Ph)$)							1269
	1237	50	1241	60		1247	1252
			1229	48	1236 (1244)	1236	1235
phenyl E							1057?
	1030	166	1030	176	1028 (1038)	1029	1030
			1014	173		1011	1012[g]
phenyl F	995	183	1004	194	1004 (1005)	1004	1004
			968	190		968[h]	965
							?
phenyl G							675
						658	658
	640	23	638	24	637	638	638

[a] Adapated from refs 32–34. [b] Reference 33a. [c] Change for the *meso*-phenyl d$_{20}$-substituted complex. [d] This work, KBr. [e] Reference 15; CH$_2$Cl$_2$ solution. [f] Numbers in parentheses are for CH$_2$Cl$_2$ solution sample.[32] [g] Seen with 413.1-nm excitation. [h] See Figure 3.

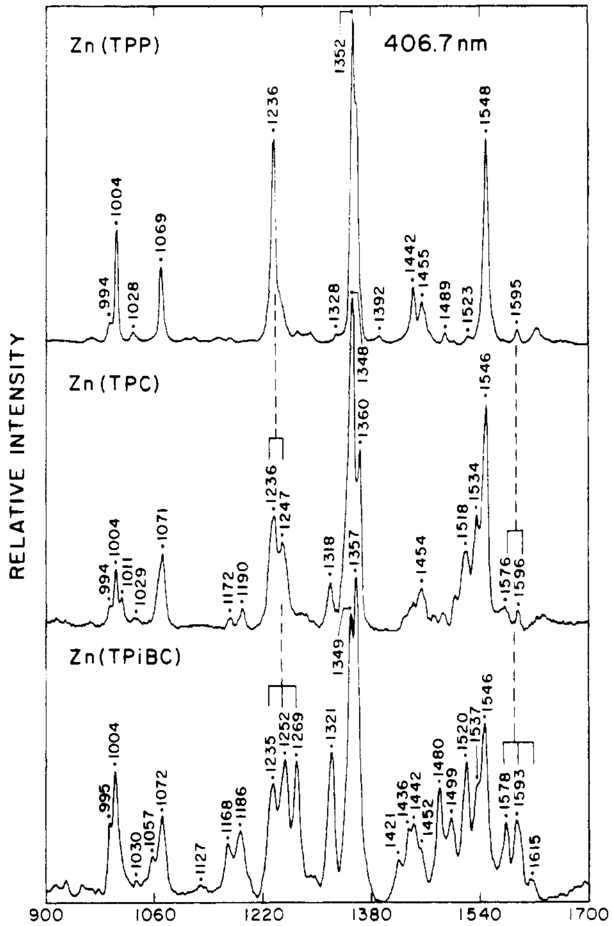

Figure 2. High-frequency resonance Raman spectra. Conditions: laser power, 25 mW at sample, backscattering geometry; solid state samples, ~1:150 mg in KBr.

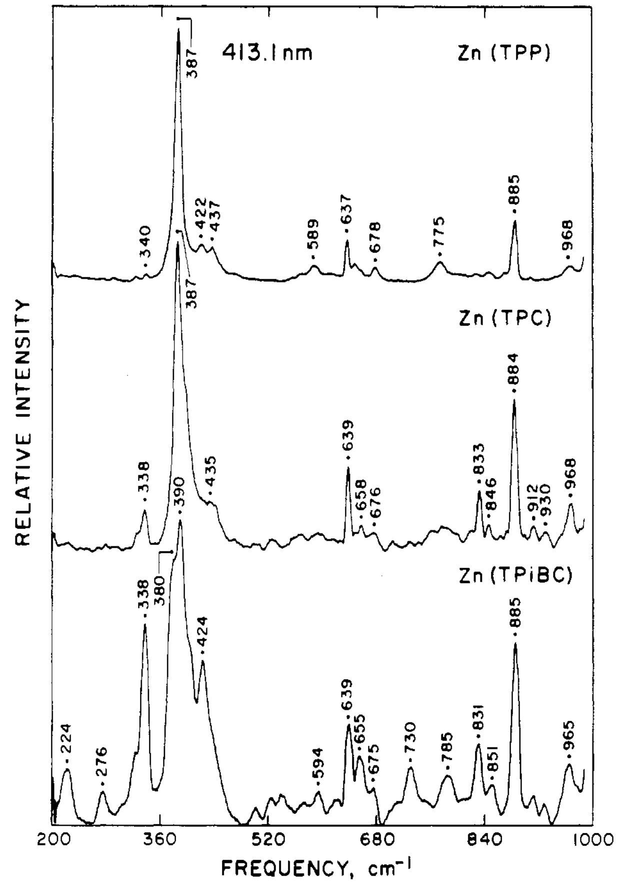

Figure 3. Low-frequency resonance Raman spectra. Conditions: laser power, 24 mW at sample, backscattering geometry; solid-state samples, ~1:150 mg in KBr.

Table I presents an analysis of the effects of symmetry on the phenyl stretching modes of Zn(TPP), Zn(TPC), and Zn(TPiBC). All four phenyl substituents of Zn(TPP) are equivalent, and thus only one totally symmetric $\nu(C_m–Ph)$ mode is expected to be Raman active. For Zn(TPC), the phenyl groups are split into two different types: (a) two that are between two pyrrole rings and (b) two that are between a pyrrole and a pyrroline ring. Consequently, two $\nu(C_m–Ph)$ modes are expected in the vibrational spectra. For Zn(TPiBC), the phenyl moieties are split into three different types: (a) one that is between the two pyrrole rings, (b) two that are between a pyrrole and a pyrroline ring, and (c) one that is between the two pyrroline rings. This analysis predicts that the vibrational spectra of Zn(TPiBC) should display three $\nu(C_m–Ph)$ modes. Although Zn(TPC) and Zn(TPiBC) both have maximal C_{2v} symmetry, the numbers of the C_m–Ph stretching modes of the two hydroporphyrins are predicted to differ. Similar analysis for Zn(TPBC) suggests that only a single C_m–Ph stretching mode should be RR active because all four phenyl groups are equivalent (Table I).

2. Resonance Raman Spectroscopy. High-frequency and low-frequency RR spectra are shown in Figures 2 and 3. RR spectra of Zn(TPC) and Zn(TPiBC) have not previously been reported. Selected RR frequencies and proposed assignments for Zn(TPP), Zn(TPC), and Zn(TPiBC) are listed in Table II. The porphyrin skeletal modes and the *meso*-phenyl substituent modes of M(TPP) complexes were previously assigned.[32-35] The nor-

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mal-coordinate analysis (NCA) of biphenyl[36] was of particular value with regard to assignment of phenyl modes.[33d] Frequencies for Cu(TPC) and Cu(TPC-d_{20}) are also included in Table II in support of the proposed mode assignments. The assignments made herein for M(TPC) and Zn(TPiBC) are consistent with those recently derived from the NCA of Bocian and co-workers.[37]

Phenyl Substituent Modes. The resonance Raman spectrum of Zn(TPP) has a strong band at 1236 cm^{-1} that has been assigned as a ν(C_m–Ph) mode (Table II). However, the RR spectrum of Zn(TPC) has a doublet in this region at 1236 and 1247 cm^{-1}. As shown for Cu–TPC, the phenyl C modes display a sensitivity to isotopic substitution that closely parallels that of the porphyrin ν(C_m–Ph) mode (Table II). We, therefore, assign the 1236/1247-cm^{-1} RR bands of Zn(TPC) complexes as phenyl C (ν(C_m–Ph)) modes. The second ν(C_m–Ph) band is presumably derived from the former B_{2g} mode (Table I) of the porphyrin parent[32-35] (weakly present in the Zn(TPP) spectrum as an ~ 1247-cm^{-1} shoulder). This band has become polarized for the chlorin, and thus strongly enhanced, as a consequence of the decrease in effective molecular symmetry. The presence of two features in the Zn(TPC) RR spectrum is as predicted by symmetry analysis (Table I). In the case of Zn(TPiBC), there are now three such ν(C_m–Ph) bands in this region of the RR spectrum, at 1235, 1252, and 1269 cm^{-1}. This observation is also consistent with the prediction of the symmetry analysis (Table I).

Other modes assigned to phenyl vibrations for M(TPP) also appear to show splittings in the hydroporphyrin spectra (Table II). This pattern, one Zn(TPP) band becoming two Zn(TPC) bands and three Zn(TPiBC) bands, is clearest for phenyl mode A. (The splitting of this feature is also clearly evident in the FTIR spectra, Figure 5.) Some splittings are also present in the RR spectra for phenyl modes E, F, and G (Table II and Figures 2 and 3).

This behavior of the (C_m–Ph) modes of the Zn(TPP), Zn(TPC), and Zn(TPiBC) complexes is consistent with ^{1}H NMR data for H_2(TPP), H_2(TPC), H_2(TPiBC).[28] Harel and Manassen observed one type of phenyl ortho proton resonance for the porphyrin, two types of phenyl ortho proton resonances for the chlorin, and three types of phenyl ortho proton resonances for the iBC.[28] These data were as expected from ring-current analyses of porphyrins and hydroporphyrins,[28-30] given the nonequivalence of phenyl moieties adjacent to pyrrole vs. pyrroline rings. The altered electronic density of the meso carbons adjacent to the pyrroline ring of a chlorin was originally noted by Woodward and Skaric.[38]

Symmetry analysis also suggests that the RR spectrum of M(TPBC) should display only one totally symmetric ν(C_m–Ph) mode. This prediction is borne out by the RR data for Cu^{II}(TPBC) in which only one totally symmetric ν(C_m–Ph) band is observed at 1243 cm^{-1}.[37] Thus, the different molecular symmetries and different phenyl environments of Zn(TPP), Zn(TPC), and Zn(TPiBC) result in a sequential increase in the predicted number of totally symmetric (C_m–Ph) modes. This prediction is very well borne out by the RR spectra of the porphyrin and hydroporphyrins.

B. Effects of Sequential Saturation. The FTIR and RR properties of β-substituted metallochlorins[8,21a,b] were shown to be applicable to meso-substituted chlorins.[15] These diagnostic spectral properties of chlorins (relative to porphyrins) include an increased complexity in the FTIR and RR spectra, and a significant congruence of FTIR and RR frequencies. These features arise as a consequence of the decreased effective molecular symmetry of chlorins.[8,15,21,39-41] Additionally, a cluster of bands in the ~ 1340–1410-cm^{-1} region of the RR spectra (the electron-density marker region of porphyrins[27]) is also typical of chlorins.[8,15,21,39-41]

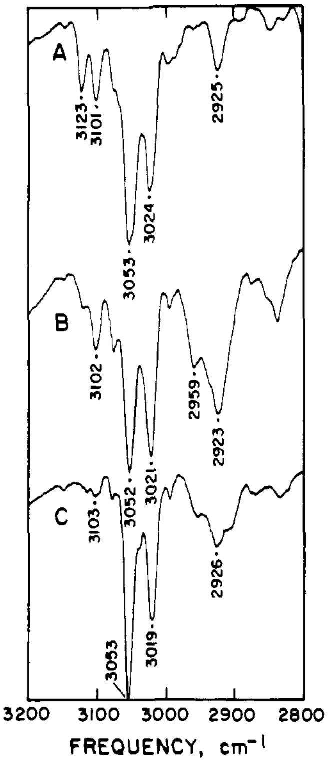

Figure 4. Infrared spectra of the C–H stretching region: (A) Zn(TPP); (B) Zn(TPC); (C) Zn(TPiBC). All samples were recorded as KBr pellets.

1. C–H Stretching Region of the FTIR Spectra. The C–H stretching modes of the three complexes are shown in Figure 4. For Zn(TPP), bands at 3024 and 3053 cm^{-1} correlate with bands of H_2TPP, assigned as ν(C_{Ph}–H) modes.[42-44] The 3021- and 3052-cm^{-1} bands of Zn(TPC) are essentially unshifted from those of Zn(TPP), and correlate with bands assigned for Cu(TPC) as ν(C_{Ph}–H) modes, on the basis of isotopic shifts.[15] The bands of Zn(TPiBC) at 3019 and 3053 cm^{-1} are thus assigned similarly as ν(C_{Ph}–H) modes.

A clear-cut difference between the three complexes occurs for the 3123-cm^{-1} band, assigned for M(TPP) as a pyrrole C_β–H stretch.[42-44] The intensity of this feature is significantly decreased for Zn(TPC) and Zn(TPiBC), behavior that parallels the decrease in the number of β-pyrrole protons, from eight for Zn(TPP) to four for Zn(TPiBC). Furthermore, Zn(TPC) now has two protons

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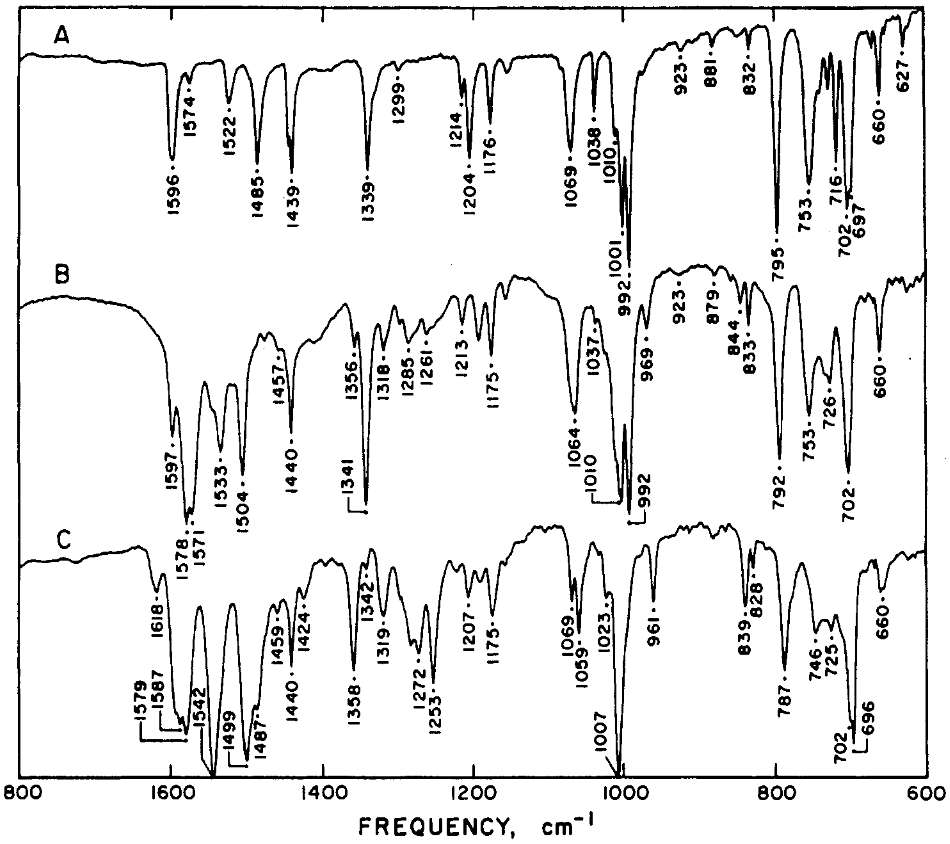

Figure 5. Infrared spectra of the 600–1800-cm^{-1} region: (A) Zn(TPP); (B) Zn(TPC); (C) Zn(TPiBC). All samples were recorded as KBr pellets.

on a pyrroline ring (sp^3 carbons), and Zn(TPiBC) has four pyrroline protons. The ν(C–H) frequency for sp^3 carbons is typically ~2920–2960 cm^{-1},[42] a shift on the order of 180 cm^{-1}. Thus, the new 2959-cm^{-1} band of Zn(TPC) and the bands flanking the 2926-cm^{-1} feature of Zn(TPiBC) may be these pyrroline ν(C$_\beta$–H) modes.

The 2926-cm^{-1} IR band of Zn(TPP) has not previously been assigned. It cannot be a C–H stretching mode or overtone and is thus most likely a combination band arising from, e.g., the strong bands at 1596 and 1336 cm^{-1}. Similar bands are present in the IR spectra of Zn(TPC) and Zn(TPiBC) and could account for their bands at ~2924 cm^{-1}.

2. The 600–1800-cm^{-1} IR spectra of Zn(TPP), Zn(TPC), and Zn(TPiBC) are shown in Figure 5. That of Zn(TPP) was previously reported.[43] The IR spectra of Zn(TPC) and Zn(TPiBC) are both considerably more complex than that of Zn(TPP). A similar increase in complexity was noted for Cu(TPC)[15] and free-base TPC[43] relative to the parent porphyrins as a consequence of the decrease in effective symmetry of the chlorin macrocycles.

Although Zn(TPC) and Zn(TPiBC) both have approximate C_{2v} symmetry, their IR spectra show many differences. For example, bands at 1253, 1487, and 1618 cm^{-1} in the IR spectrum of Zn(TPiBC) have no counterparts in the spectrum of Zn(TPC) (Figure 5). Furthermore, bands at 746, 787, 961, 1499, 1542, 1579, and 1587 cm^{-1} in the FTIR spectrum of Zn(TPiBC) are shifted by some 5–9 cm^{-1} from similar spectral features of Zn(TPC). Conversely, the FTIR spectra of Zn(TPC) and Zn(TPP) have a strong 992-cm^{-1} band that is absent from the spectrum of Zn(TPiBC). The pair of bands at 1358/1342 cm^{-1} in the Zn(TPiBC) spectrum show a clear reversal in intensity relative to the 1356/1341-cm^{-1} pair of Zn(TPC). Many of these differences are repeated when comparing the resonance Raman spectra of these two hydroporphyrins.

The 795-cm^{-1} IR band of Zn(TPP) is assigned as a pyrrole C$_\beta$–H deformation mode on the basis of previous studies of free-base TPP and M(TPP) complexes.[43] This band shifts to 792 cm^{-1} for Zn(TPC) and to 787 cm^{-1} for Zn(TPiBC). The intensity of this band also decreases with increasing saturation of the macrocycles. This suggests diminishing contributions to the pyrrolic C$_\beta$–H deformation mode as the number of pyrrole hydrogens decreases for the hydroporphyrins.

3. General RR Spectral Patterns. The RR spectra of Zn(TPC) and Zn(TPiBC), shown in Figures 2 and 3, demonstrate an increasing complexity that parallels the increase in saturation of the macrocycles. For example, the Zn(TPP) spectrum has intense bands at 1236, 1352, and 1548 cm^{-1}. In the spectra of Zn(TPC) and Zn(TPiBC), the former 1236-cm^{-1} singlet gives rise to a doublet at 1236/1247 cm^{-1} and a triplet at 1235/1252/1269 cm^{-1}, respectively. The former 1352-cm^{-1} band also gives rise to doublets at 1348/1360 and 1349/1357 cm^{-1}, respectively. Finally, the singlet at 1548 cm^{-1} in Zn(TPP) changes to a triplet at 1518/1534/1546 for Zn(TPC) and a complex multiplet in Zn(TPiBC).

Low-frequency RR spectra of Zn(TPP), Zn(TPC), and Zn(TPiBC) are shown in Figure 3. The ratio of the ~884-cm^{-1} band to the 387-cm^{-1} band for Zn(TPP) is ~1:5; however for Zn(TPC) and Zn(TPiBC), this ratio is ~1:2. The ~884-cm^{-1} band of M(TPP) was assigned as a macrocycle δ_s(ring) mode (ν_7), whereas the ~390-cm^{-1} feature was assigned as a δ(por) mode (ν_8).[33d] In the case of Zn(TPiBC), there is considerable splitting of the ~390-cm^{-1} band and the appearance of new low-frequency modes below 300 cm^{-1}.

The number of RR bands and their patterns of intensity in the ~1340–1410-cm^{-1} region (Figure 2) are of particular interest. This is the location of the electron-density-sensitive ν_4 (C$_\alpha$–N) mode of metalloporphyrins.[27] For metallochlorins, a cluster of C$_\alpha$–N modes in this region is a characteristic feature, with the major band generally being similar in frequency to that of the parent metalloporphyrin.[8,15,21,39–41] This is exemplified by the 1352- and 1348-cm^{-1} bands of Zn(TPP) and Zn(TPC), respectively.

For the Zn(TPiBC) complex, the pattern of intensity in this region is altered, with the dominant RR feature being at 1357 cm^{-1}. (This intensity reversal was also noted in the IR spectra.) The most intense bands in this interval are also anomalously high in frequency for the Fe^{III}(siroheme) of the assimilatory nitrite-reductase from spinach, relative to Fe^{III}(porphyrins)[27] and Fe^{III}(chlorins).[21,39c] Ongoing studies of M(iBC) complexes in our laboratories similarly demonstrate an intense RR band in this region that is atypically high in frequency.[46] In the recent study of Cu^{II}(OEiBC), Bocian and co-workers[47] report an intense 1403-cm^{-1} RR band that is assigned as a C_α–N mode. The frequency of this band of Cu^{II}(OEiBC) is unusually high relative to frequencies typical for Cu^{II}(chlorins).[8,15,21] Han et al.[48] also noted that bands in this region were high in frequency for the extracted siroheme of *Escherichia coli* sulfite reductase. Thus, the high frequency of the dominant band in the ~1340–1410 cm^{-1} RR spectra of iBC's, relative to those of porphyrins or chlorins, appears to be characteristic of the isobacteriochlorin macrocycle.

Conclusions. The data presented herein provide unexpectedly clear-cut examples of the utility of symmetry analysis in the study of complex systems. They also provide the first resonance Raman and Fourier transform infrared spectra for a set of tetrapyrrolic macrocycles that are sequentially reduced from porphyrin to chlorin to isobacteriochlorin.

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The Unpredictable Structural Features of Chromium(II) Pyrrolyls: Synthesis and X-ray Structures of Monomeric Square-Planar $(\eta^1\text{-}2,5\text{-Me}_2\text{C}_4\text{H}_2\text{N})_2\text{Cr(py)}_2$, Square-Pyramidal $(\eta^1\text{-C}_4\text{H}_4\text{N})_2\text{Cr(py)}_3$, Dimeric $[(\text{7-azaindolyl})_2\text{Cr(DMF)}]_2$, and Polymeric $[(\eta^1\text{-}2,5\text{-Me}_2\text{C}_4\text{N}_2)_4\text{CrNa}_2(\text{THF})_2(\text{Et}_2\text{O})]_n$. An Aborted Cr–Cr Quadruple Bond Formation?

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Reaction of $\text{CrCl}_2\text{THF}_2$ with 2 equiv of $\text{C}_4\text{H}_4\text{NM}$ or 2,5-$\text{Me}_2\text{C}_4\text{H}_2\text{NM}$ (M = Li, Na) leads to the formation of monomeric $(\eta^1\text{-C}_4\text{H}_4\text{N})_2\text{Cr(L)}_3$ [L = THF (**1**), py (**2**)] and $(\eta^1\text{-}2,5\text{-Me}_2\text{C}_4\text{H}_2\text{N})_2$ Cr(L)_2 [L = THF (**4**), py (**5**)], respectively. The crystal structures of **2** and **5** were solved by X-ray diffraction analyses. In spite of the similarity between the ligands, the two monomeric complexes possess remarkably different structures: **2** has an unusual square-pyramidal geometry, while **5** is square-planar with low- and high-spin electronic configurations of the metal, respectively. Crystal data are as follows (T = 130 K, Mo K$\bar{\alpha}$, λ = 0.71073 Å): **2**, triclinic, space group $P\bar{1}$, a = 9.153 (4) Å, b = 10.659 (2) Å, c = 13.707 (3) Å, α = 86.01 (1)°, β = 82.93 (3)°, γ = 88.65 (2)°, Z = 2. **5**, triclinic, space group $P\bar{1}$, a = 6.986 (2) Å, b = 8.812 (2) Å, c = 9.018 (3) Å, α = 87.09 (2)°, β = 68.95 (2)°, γ = 83.18 (2)°, Z = 1. Dimerization was observed when a donor atom, attached to one of the two α positions of the pyrrolyl ligands, restored the unique geometry of the three-center chelating ligands. The dimeric structure of $[(\text{7-azaindolyl})_2\text{Cr(DMF)}]_2\cdot2\text{DMF}$ (**7**) (DMF = *N*,*N*-dimethylformamide) was demonstrated by X-ray diffraction analysis. Crystal data for **7**: monoclinic, space group $P2_1/a$, a = 9.458 (1) Å, b = 19.085 (2) Å, c = 11.850 (1) Å, β = 109.92 (1)°, Z = 2 Magnetic properties and structural features [Cr–Cr = 2.604 (2) Å] suggest the absence of a Cr–Cr quadruple bond. Reaction of **1** and **4** with 2 equiv of $\text{C}_4\text{H}_4\text{NNa}$ and 2,5-$\text{Me}_2\text{C}_4\text{H}_2\text{NNa}$ leads respectively to the formation of stable polymeric chromates $[(\text{C}_4\text{H}_4\text{N})_4\text{CrNa}_2\text{L}_3]_n$ (**3**) and $[(2,5\text{-Me}_2\text{C}_4\text{H}_2\text{N})_4\text{CrNa}_2\text{L}_3]_n$ (**6**). [L = Et_2O, dioxane, THF]. The polymeric aggregation, demonstrated in the case of **6** by an X-ray structure determination, is achieved via a π interaction of the pyrrolyl ligands with the Na cations from two different $[(\eta^1\text{-pyrrolyl})_4\text{Cr}]^{2-}$ fragments. Crystal data for **6** (T = 130 K, Mo K$\bar{\alpha}$ λ = 0.71073 Å) are as follows: monoclinic, space group $P2_1$, a = 9.045 (1) Å, b = 15.285 (1) Å, c = 13.621 (1) Å, β = 97.42 (1)°, Z = 2.

Introduction

The chemistry of transition-metal complexes containing heterocyclopentadienyl ligands has experienced a steady growth of interest during the last two decades.[1]

The possibility of those ligands being involved in $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ ring slippage processes is especially relevant in view of the role played in homogeneous catalysis. In the case of pyrrolyl ligands, the presence of a donor atom such as nitrogen in the heterocycle enhances this possibility.[2] For pyrrole, in fact, both the π-[3–10] and σ-bonding fashion[11–15] have been widely documented. In this second case the Lewis acidity of the metal determines the extent of nitrogen to metal π-interaction.

In spite of the electronic and steric flexibility of this ligand, the chemistry of pyrrolyl transition-metal compounds is rather limited to date. Following our interest in the chemistry of divalent chromium,[16] we were interested in studying the structural features

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