meso-Aryl Smaragdyrins: Novel Anion and Metal Receptors

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Received January 6, 2000

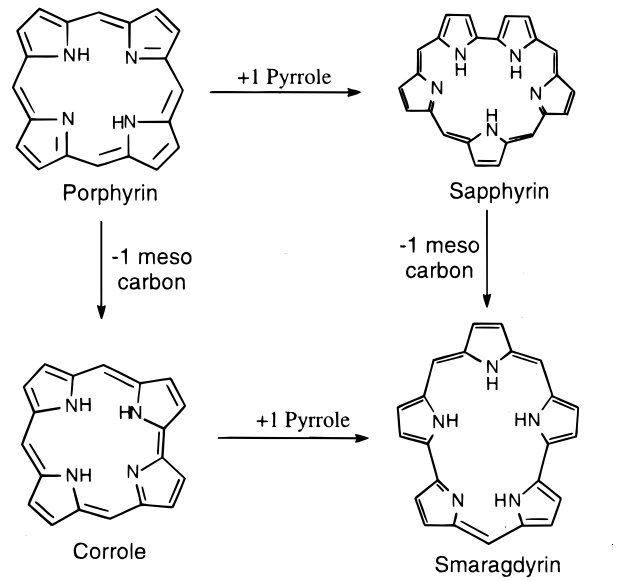
An easy synthesis of core-modified *meso*-aryl smaragdyrins containing oxygen and sulfur in addition to pyrrole nitrogens has been achieved through an α−α coupling involving modified tripyrrane and dipyrromethane. The complexation behavior of these macrocycles toward anions (Cl^-, F^-, AMP^-) and metal cations (Rh(I), Ni(II)) is reported. Specifically, it has been shown that the Rh(I) and Ni(II) ions bind to the smaragdyrin skeleton in its free base form. X-ray structural studies of Rh(I) complex **1** indicate an η^2-type coordination involving only one imino and one amino nitrogen of the dipyrromethane unit. However, all four bipyrrole nitrogens participate in the coordination with the Ni(II) ion. Furthermore, Ni(II) coordination oxidizes the ligand, and the complex is formulated as the π-cation radical of nickel(II) smaragdyrin. The anion complexation is followed in both the solid and solution phases. Solution studies reveal that the binding constants of the ions with the protonated form of smaragdyrin vary as $F^- > AMP^- > Cl^-$. The X-ray structure of the chloride anion complex reveals that the chloride ion is bound above the cavity of the smaragdyrin macrocycle through three N−H···Cl hydrogen bonds. Crystal data with Mo Kα (λ = 0.710 73 Å) are as follows: **1**, $C_{41}H_{27}N_4O_3Rh$, a = 11.836(8) Å, b = 12.495(9) Å, c = 12.670(2) Å, α = 69.09(6)°, β = 78.78(6)°, γ = 77.02(5)°, V = 1692.1(17) Å^3, Z = 2, triclinic, space group P-1, R_1(all data) = 0.0471; **4·HCl**, $C_{41}H_{29}N_4O_1Cl$, a = 11.878(2) Å, b = 17.379(4) Å, c = 16.015(3)Å, β = 109.546-(10)°, V = 3115.47(11) Å^3, Z = 4, monoclinic, space group $P2(1)/c$, R_1(all data) = 0.0850.

Introduction

Porphyrin and corrole rings are ubiquitous in natural systems, performing diverse biological functions.[1−3] Even though both ring systems contain 18π electrons, structurally, corrole is different from porphyrin. Specifically, corrole contains one less methine bridge than porphyrin, resulting in the formation of a direct pyrrole−pyrrole link. Addition of an extra pyrrole ring to a porphyrin skeleton leads to a new 22π sapphyrin ring system[4] (Scheme 1). Sapphyrin is one of the early members of the "*expanded porphyrin family*" [1,2,5] which exhibit diverse chemistry such as receptors for anions[6,7] and a potential ligand for transition-metal binding[8] in addition to certain biomedical applications.[8a,9]

Removal of one meso carbon from a sapphyrin skeleton leads to a new ring system with 22π electrons which has been christened as smaragdyrin[4] or norsapphyrin[10] in the literature. The structural relationship between sapphyrin and smaragdyrin is analogous to that between a porphyrin and a corrole. The chemistry of smaragdyrins is not as well developed as the chemistry of their sapphyrin analogues because of the difficulties encountered in the synthesis as well as its inherent instability. Even though Johnson and co-workers[10] were successful in the synthesis of partially β-substituted smaragdyrin, its instability

Scheme 1. Structural Relationship between Various Macrocycles



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10.1021/ic000031v CCC: $19.00
Published on Web 07/21/2000

toward acid and light prevented them from pursuing further studies. Only in 1997, Sessler and co-workers[11] found that the stability of the smaragdyrin skeleton can be increased by substituting all the β positions by alkyl substituents. They were successful in synthesizing a stable isomer of β-substituted smaragdyrin.[12] Very recently, a preliminary communication[13] from this laboratory has shown that it is possible to synthesize stable *meso*-aryl smaragdyrins by an oxidative coupling reaction of modified tripyrrane and dipyrromethane. In this paper, we report the details of the synthesis, structure, and receptor ability of smaragdyrins toward anions and metal cations. Specifically, it has been shown that the *meso*-aryl smaragdyrins are quite stable unlike their β-substituted analogues and can form stable metal and anion complexes. It has been shown that the Rh(I) ion binds to only two bipyrrolic nitrogens of smaragdyrin in an η^2 fashion while the Ni(II) ion binds to four bipyrrolic nitrogens in an η^4 fashion. The furan oxygen remains uncoordinated. In contrast, the Cl^- anion binds to the protonated form of smaragdyrin, where the Cl^- ion is situated above the plane of the macrocycle and is held by three strong N−H···Cl hydrogen bonds. To the best of our knowledge, this work represents the first report on the complexation behavior of the *meso*-aryl smaragdyrin skeleton.

Results and Discussion

Synthesis. Initial attempts by Grigg and Johnson[10] and Woodward and co-workers[4] on the synthesis of β-substituted smaragdyrins were only partially successful due to the instability of the precursors as well as the final macrocycles toward light and acid. Attempts to synthesize metal complexes resulted in decomposition of the macrocycle. Only recently Sessler and co-workers[1] were successful in the synthesis of an isomer of smaragdyrin by substituting alkyl groups on β-pyrrole carbons. In all the above cases a 3+2 MacDonald[14] type condensation reaction between diformylbifuran and the pyrrolyl dipyrromethane derivative were used to synthesize the macrocycle. We realized that the key step in the synthesis of smaragdyrin is the introduction of two direct pyrrole−pyrrole links. This can be achieved in two ways: (a) by using precursors containing pyrrole−pyrrole links or (b) through the formation of pyrrole−pyrrole links in the final step of condensation. The difficulty of synthesizing precursors with direct pyrrole−pyrrole links lies in the inherent instability of the respective material.[10] This problem can be solved by introducing the pyrrole−pyrrole link in the final step of condensation. Recent work on the *meso*-aryl-core-modified sapphyrins and rubyrins from this laboratory have shown that it is possible to introduce direct pyrrole−pyrrole links through an oxidative coupling reaction between core-modified tripyrranes.[15] We were successful in using this methodology for the synthesis of smaragdyrin by a reaction of modified tripyrrane **8** and dipyrromethane **10** using 0.1 equiv of TFA followed by oxidation with chloranil (Scheme 2). Two products were isolated. The major product was **4**, and the minor product was contracted porphyrin **6**. The yields of **4** and **6** were found to be dependent on the nature of the heteroatom in tripyrrane and the amount of acid catalyst. For example, in 0.1 equiv of TFA, **4** and **6** were isolated in 51% and 3% yields, respectively, while in 1 equiv of TFA, the yields were 25% and 5%, respectively. On the other hand, reaction of 16-thiatripyrrane **9** gave only 4% of **5** and <1% of **7**. This may be due to the increased steric bulk in the core of the macrocycle. The lower yield of **4** at higher acid concentrations is attributed to the acidolysis[16] of the precursors under the reaction conditions. The possible mechanism for the formation of smaragdyrin is shown in Scheme 3. The protonation on the α and β positions of tripyrrane and dipyrromethane leads to intermediates **I** and **II** and **III** and **IV**, respectively.[17] The active intermediates **II** and **IV** were chosen for an $\alpha-\alpha$ coupling[18] reaction between the tripyrrane and dipyrromethane through an intramolecular electrophilic attack to generate intermediate **V**, which on further rearrangement followed by oxidation leads to the formation of smaragdyrin.

Both **4** and **6** were found to be stable in free base form in the solid and solution phases without any noticeable decomposition unlike their β-substituted counterparts.[1,4,10] The corresponding monohydrochloride salt was obtained by shaking a dichloromethane solution of free base in a 10% solution of HCl. This was also found to be quite stable. The rhodium complexes were

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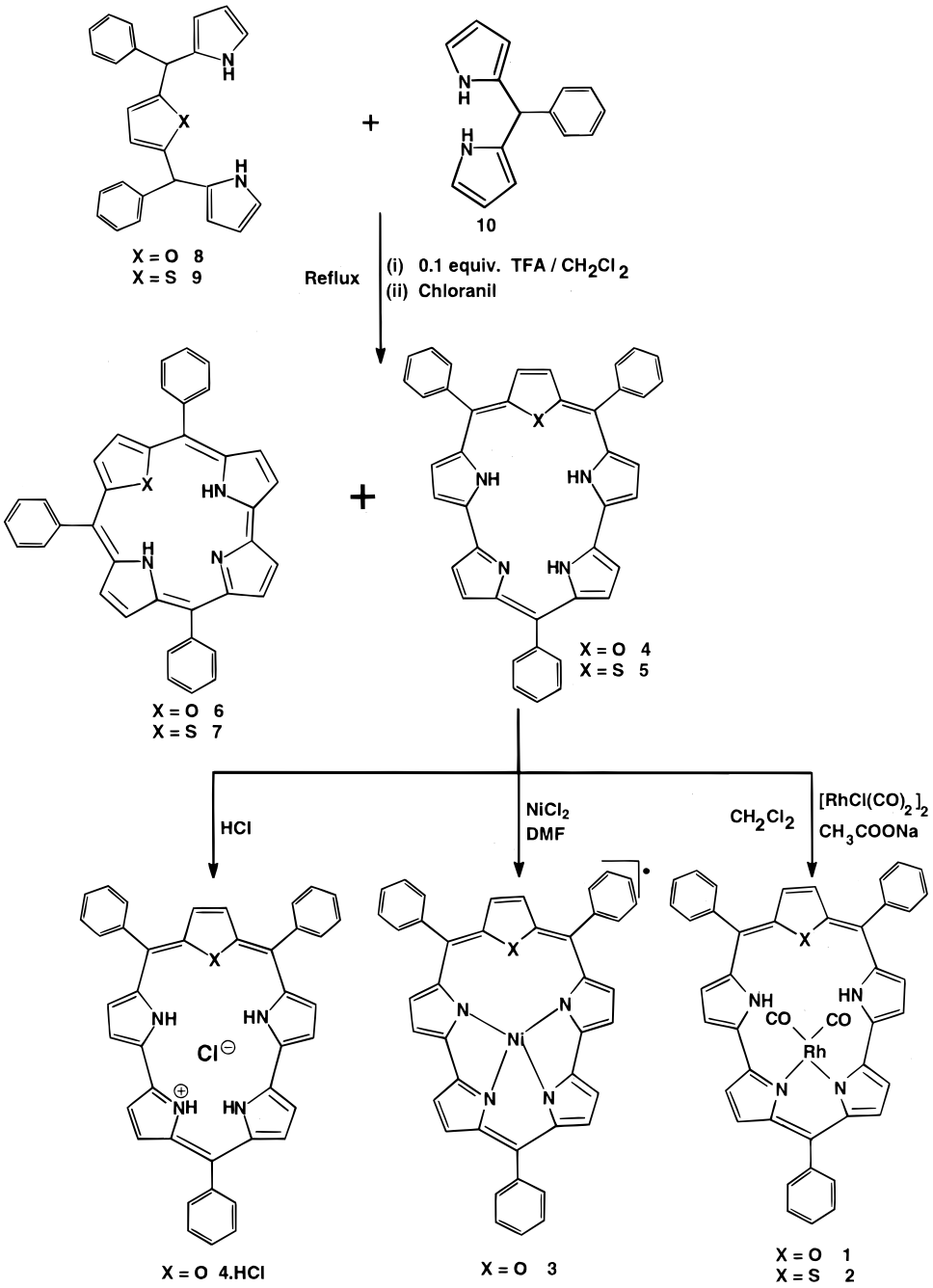
Scheme 2. Synthesis of *meso*-Aryl-Core-Modified Smaragdyrins and Their Cation and Anion Complexes



synthesized by a reaction of a dichloromethane solution of free base with di-μ-chlorobis[dicarbonylrhodium(I)] in the presence of sodium acetate, and the nickel complex was obtained by refluxing the DMF solution of free base with the $NiCl_2$ salt. Purification by column chromatography using neutral alumina proved to be successful in isolating the respective metal complexes in good yield.

Spectral Characterization. The smaragdyrins reported here were characterized by FAB-MS, UV−vis, and proton 1D and 2D NMR spectroscopy. Furthermore, **4·HCl** and **1** were also characterized by X-ray crystallography. The CO stretching frequencies, 2055 and 1985 cm^{-1} for **2** and 2060 and 1995 cm^{-1} for **1**, compare well with those of the rhodium carbonyl complexes of heterosapphyrins.[8c,h,i] The electronic spectra for **4** and **5** show typical intense Soret-like bands[19] at 443 and 453 nm, respectively, and four Q-bands in the range 550−830 nm. All absorption bands were found to be red shifted relative to the corresponding corrole to different extent in agreement with the extension of conjugation in **4** and **5**. In general, thiasmaragdyrin **5** shows more red shift relative to the oxa derivative **4** probably due to the larger distortion upon substitution of bulkier sulfur.[20] The protonation leads to the splitting of the Soret band in both the cases and a small red shift (7−19 nm) of all the bands. The metal derivatives also exhibit the split Soret band (457 and 478 nm for **1**, 471 and 481 nm for **2**, and 452 and 486 nm for **3**). A comparison of the visible spectra of **4**, its protonated salt, and the Rh complex is shown in Figure 1. Changes occurring upon protonation and metalation are in

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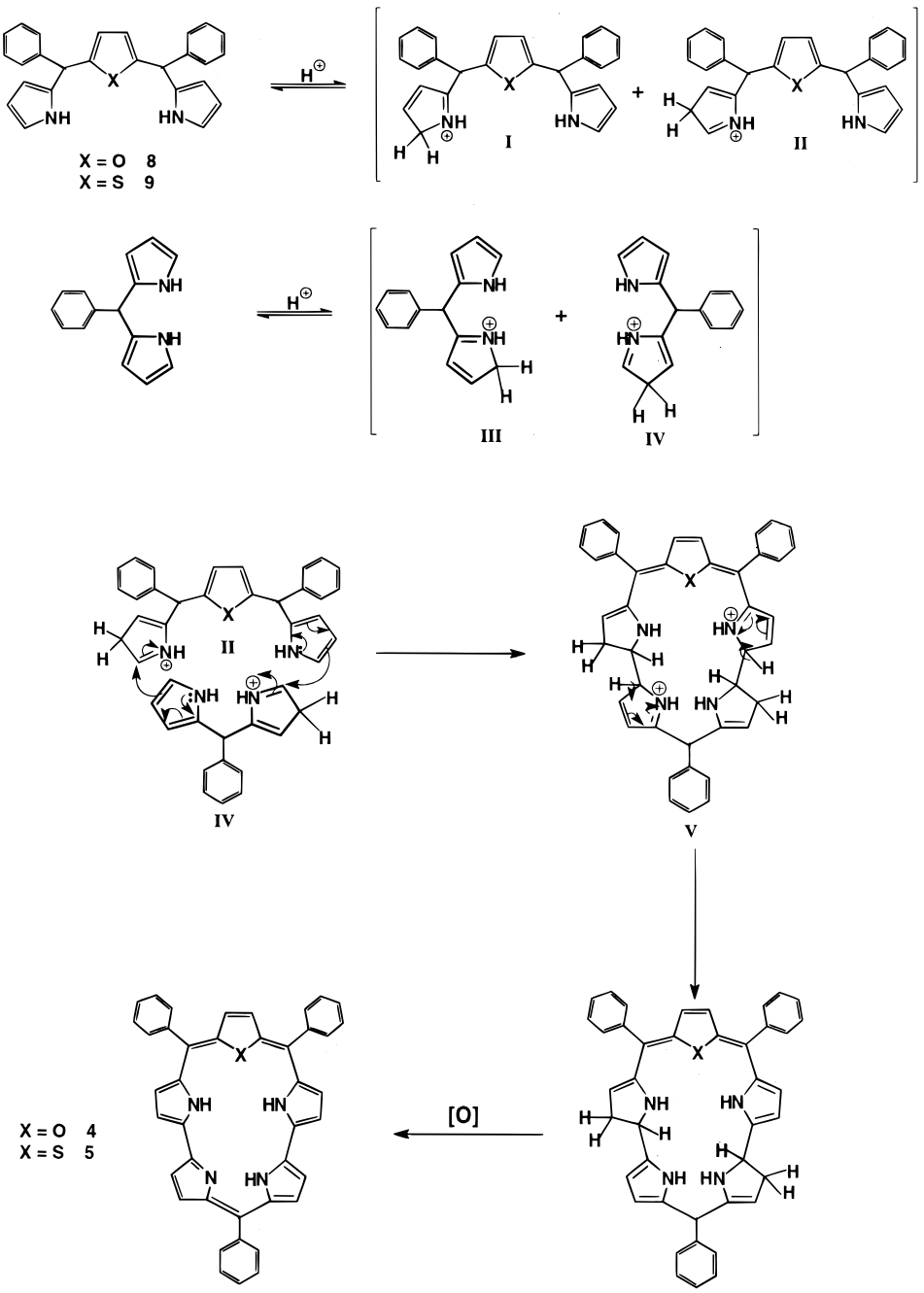
Scheme 3. Possible Mechanism for the Formation of Smaragdyrins



general agreement with the behavior of *meso*-aryl-expanded porphyrins,[21,22] and the splitting of the Soret band is indicative of the lowering of the symmetry due to the distortion as shown by the crystal structures of the protonated salt and metal complexes (vide infra).

^{1}H NMR. A comparison of the ^{1}H NMR spectra of **4**, **1**, and **4·HCl** is made in Figure 2. The ^{1}H NMR spectra of **4** show four doublets with coupling constants 4−4.4 Hz assigned to the bipyrrole protons (b, c, d, e) and a singlet at 8.72 ppm assigned to the furan protons (a). These assignments were made on the basis of the correlations observed in the 2D ^{1}H−^{1}H COSY spectrum and the observation that the outer bipyrrole protons (b, e) are more shielded relative to the inner bipyrrole protons (c, d) because of the upfield ring current contribution of the *meso*-phenyl rings.[21c] The phenyl protons resonate as three multiplets in the region 8.40−7.83 ppm. The equivalence of the bipyrrole protons (e, e′; d, d′; c, c′; b, b′) in the ^{1}H NMR spectrum suggests that the three −NH protons exchange sites between four bipyrrole nitrogen centers, indicating that the molecule adopts a symmetric conformation in solution with respect to the mirror plane passing through the methine bridge and the furan oxygen atom. This is possible only if there is a rapid tautomerism between the inner −NH protons. Indeed failure to see the signals for the inner −NH protons down to −60 °C suggests the presence of rapid tautomerism between the −NH protons in the smaragdyrin skeleton.[21,23]

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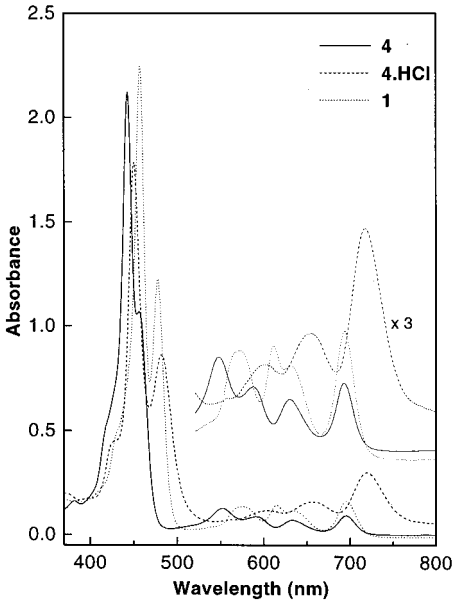

Figure 1. UV−vis spectra for **4**, **4·HCl**, and **1** in CH_2Cl_2 in the Q-band and Soret band region.

The protonation of **4** leads to a downfield shift (0.1−0.5 ppm) of all the peaks, suggesting delocalization of the positive charge in the macrocycle. Furthermore, the protonation prevents tautomerism, and all the −NH protons are localized. Actually two kinds of −NH signals are observed at −1.06 and −2.06 ppm. The bipyrrole protons (c, d, e, b) now appear as quartets in contrast to the doublet observed for the free base. This is attributed to the weak coupling between the bipyrrole protons and the −NH protons ($^4J_{H,H}$ = 1.7 Hz).

Metalation of **4** and **5** leads to interesting changes in the NMR spectrum. Specifically, (i) the bipyrrole protons (d, e) which are in the dipyrromethane unit experience an upfield shift (0.20 and 0.15 ppm for **1**; 0.06 and 0.16 ppm for **2**), (ii) the bipyrrole protons (b, c) which are in the tripyrrane unit experience a small downfield shift (0.02 and 0.06 ppm for **1** and 0.04 and 0.07 ppm for **2**), (iii) the bipyrrole protons (b, c) appear as quartets ($^4J_{H,H}$ = 2.4 Hz) while the bipyrrole protons (d, e) appear as doublets (J_{AB} = 4.4 Hz), (iv) the furan/thiophene protons also experience a downfield shift and appear as a singlet (8.81 ppm for **1** and 9.24 ppm for **2**), and (v) the −NH proton signals appear as a singlet (−1.71 ppm for **1** and −1.22 ppm for **2**). The fact that the inner −NH proton signals are still observed in the metal complex suggests that the coordination of metal does not involve all four nitrogens. Infact, only the two nitrogens of the dipyrromethane unit coordinate to the metal in an η^2 fashion (as revealed by X-ray crystallography vide infra). This kind of coordination should affect the bipyrrole protons of the dipyrromethane unit (e, d) more relative to the bipyrrole protons (b, c) as observed in the present study. Furthermore, the appearance of quartets for bipyrrole protons (b, c) suggests that these bipyrrole nitrogens are still protonated and are not involved in the coordination to the metal.

The ^{1}H NMR spectrum of the nickel complex **3** is quite different from that observed for the corresponding rhodium complex **1**. Specifically, there are no peaks in the high-field region, suggesting the absence of inner −NH protons. This would lead to the coordination of all four bipyrrole nitrogens with the Ni(II) ion. However, since **4** has three ionizable protons similar to β-substituted corroles, one would expect stabilization of the metal ion in the +3 oxidation state. However, spectroscopic studies on **3** reveal that nickel is in the Ni(II) state. Thus, this complex is expected to be paramagnetic with an unpaired electron localized on one of the meso carbons. The paramagnetic nature of **3** is strongly supported by the appearance of broad signals in the ^{1}H NMR spectrum and an appearance of a strong EPR signal at both room temperature and liquid nitrogen temperature with a line width of 11 G (g = 2.0031). Consequently, the nickel complex of smaragdyrin contains an oxidized smaragdyrin ligand, and we formulate this complex as a π cation radical of nickel(II) smaragdyrin coordinated to only four bipyrrole nitrogens. Strong support for such a conclusion also comes from the recent work on the nickel complex of octaethyl corrole from Vogel and co-workers.[24] Specifically, they have shown that the nickel corrole exists as a Ni(II) complex and the unpaired electron is centered on one of the meso carbons.

X-ray Crystal Structure. The solid-state structure of **4·HCl** shown in Figure 3 clearly shows coordination of the chloride ion above the plane of the macrocycle. Specifically, out of the four pyrrole −NH groups available, only three −NH groups are involved in the N−H···Cl hydrogen bonds. The hydrogen bond distances N1−Cl1 3.0902(17), N2−Cl1 3.119(17), and N4−Cl1 3.1400(17) suggest that the chloride anion is bound strongly by only three N−H···Cl hydrogen bonds which are pointed toward the chloride atom. The pyrrole rings N1, N2, and N4 which are involved in the bonding are tilted above the plane of the macrocycle defined by the meso carbons while the pyrrole ring N3 is in the plane. This is reflected in the different torsional angles observed for the pyrrole rings in the dipyrromethane unit, N2−C8−C9−C16−14.4° and N3−C16−C9−C8−6.4°. These hydrogen-bonding distances compare well (3.176, 3.039, and 3.200 Å)[6e] with that observed for the monoprotonated chloride salt of a β-substituted dioxasapphyrin. However, the binding seen here is slightly different from that observed for the monoprotonated chloride salt of the smaragdyrin isomer where all four nitogens are involved in binding to the chloride anion.[12]

The X-ray structure of **1** shown in Figure 4 shows that the rhodium atom is attached to the smaragdyrin skeleton in an η^2 fashion involving one amino and one imino nitrogens of the dipyrromethane unit (N2 and N3). The other two coordination sites of the rhodium are occupied by the carbonyl groups. Thus, Rh(I) metal forms an out-of-plane complex, and the observed bond lengths and angles indicate an approximate square planar geometry about the metal center with a metal plane at an angle of 57.69° to the plane of the smaragdyrin (Rh−N3 2.034 Å, Rh−N4 2.042 Å, Rh−C42 1.871 Å, Rh−C43 1.856 Å, N3−Rh−N4 82.45°, C42−Rh−C43 89.32°, N3−Rh−C42 93.73°, N4−Rh−C43 94.27°). This metal environment is analogous to that observed for the Rh(I) complexes of heterosapphyrins.[8c,h,i] Even though both the dipyrromethane and the bipyrrole units have one amino nitrogen and one imino nitrogen (N3 and N2 for dipyrromethane and N3 and N4 for the bipyrrole unit), which are necessary for Rh(I) coordination,[8c,h,i] only the dipyrromethane unit is bound to the Rh(I) ion. This is attributed to the fact that the formation of an out-of-plane square planar complex with a bipyrrole unit having a direct α−α link may cause severe distortion, destabilizing the complex.

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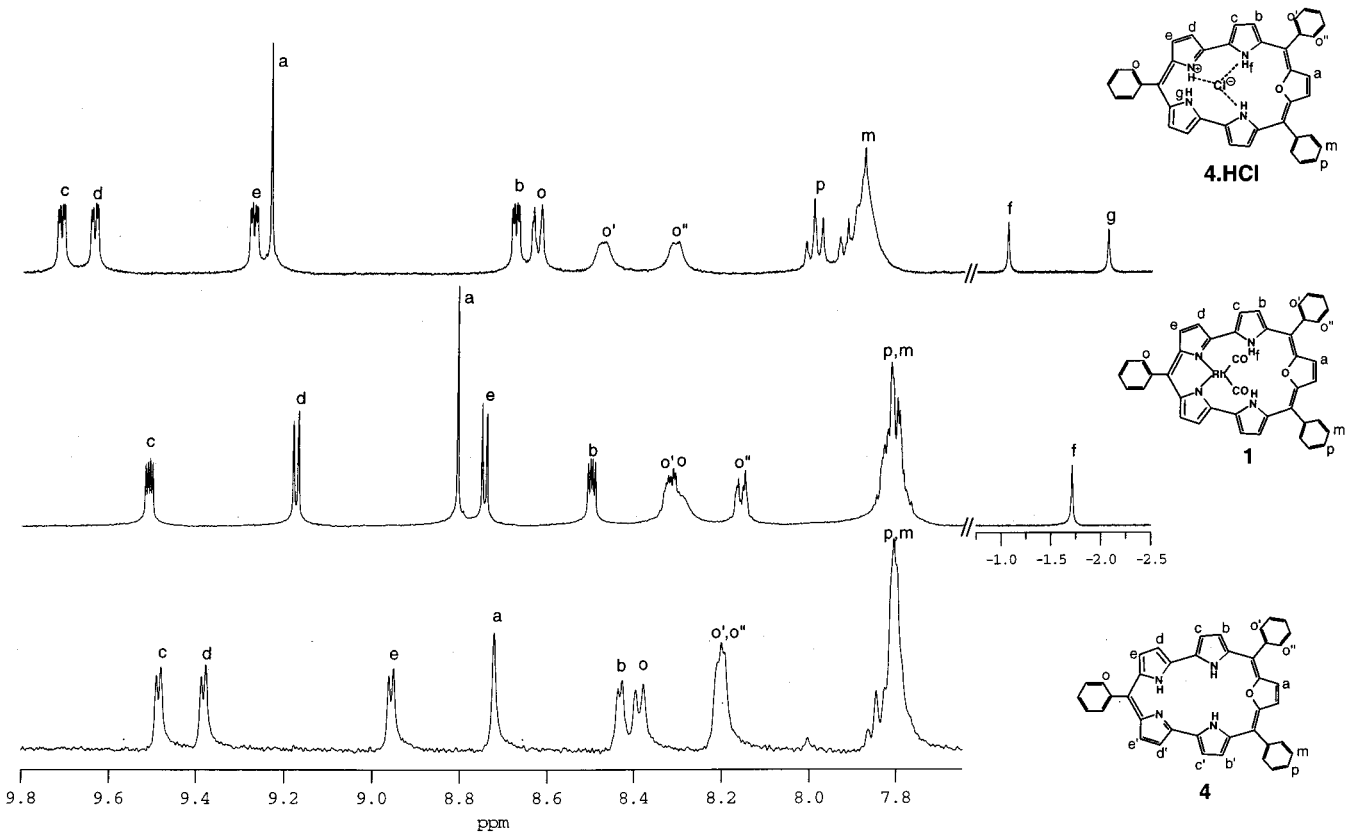


Figure 2. A stack plot showing ^{1}H NMR spectra of **4**, **4·HCl**, and **1** in $CDCl_3$.

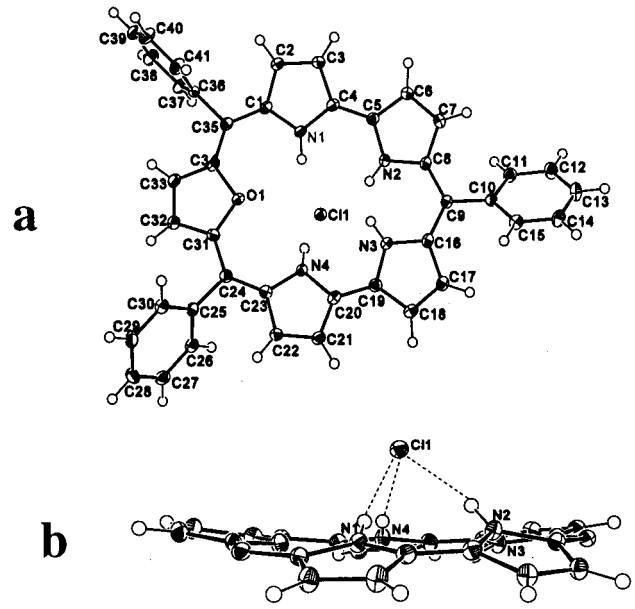


Figure 3. ORTEP diagram illustrating the structure of the chloride anion complex **4·HCl**: top, plane view; bottom, side view (phenyl rings are omitted for clarity).

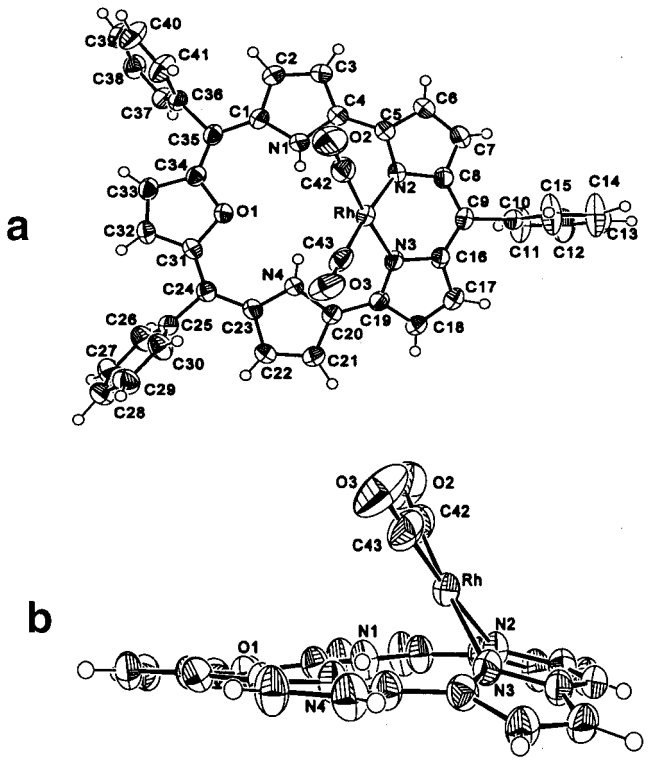


Figure 4. Two views of the molecular structure of **1** showing η^2 binding of the Rh(I) cation. In the side view the phenyl rings are omitted for clarity.

A comparison of the important bond distances and bond angles of **4**, **4·HCl**, and **1** is listed in Table 1. In general, in all the cases, the $C_\alpha-C_\beta$ distances of heterocyclic rings are greater than the $C_\beta-C_\beta$ distances, suggesting the aromatic nature of the smaragdyrin skeleton in its free base, protonated, and metal complexes.[1,2] However, the planarity of the smaragdyrin skeleton is significantly affected on going from the free base to the metal and anion complexes. This is reflected in the variation in the dihedral angles between the planes constructed using individual heterocyclic rings and the plane with the inner peripheral atoms (excluding β-carbon and phenyl ring atoms). These angles listed in Table 2 show an interesting variation. Specifically, (i) the furan ring, which is not involved in

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**, **4·HCl**, and **1**

bond	**4**	**4·HCl**	**1**
O1−C31	1.406(3)	1.401(2)	1.407(4)
O1−C34	1.399(2)	1.401(2)	1.399(4)
C31−C32	1.413(3	1.415(3)	1.410(4)
C33−C34	1.419(3)	1.420(3)	1.420(4)
C32−C33	1.354(3)	1.353(3)	1.341(5)
C1−N1	1.378(3)	1.377(2)	1.370(4)
C4−N1	1.380(2)	1.380(2)	1.373(4)
C1−C2	1.411(3)	1.418(3)	1.400(5)
C3−C4	1.394(3)	1.413(3)	1.388(5)
C2−C3	1.384(3)	1.382(3)	1.376(5)
C4−C5	1.421(3)	1.415(3)	1.422(4)
C19−C20	1.432(3)	1.421(3)	1.416(4)
N2−C5	1.353(3)	1.376(3)	1.349(4)
N2−C8	1.386(3)	1.395(2)	1.389(4)
N3−C16	1.391(3)	1.390(2)	1.391(4)
N3−C19	1.346(3)	1.360(2)	1.350(4)
C8−C9	1.411(3)	1.415(3)	1.398(4)
C9−C16	1.404(3)	1.414(3)	1.395(4)
C31−O1−C34	107.10(15)	107.07(14)	107.1(2)
C31−C24−C23	130.15(19)	130.21(18)	129.6(3)
C34−C35−C1	128.11(19)	129.08(18)	130.3(3)
C1−N1−C4	109.57(17)	109.79(16)	111.0(3)
N1−C4−C5	124.00(18)	124.73(17)	124.5(3)
C4−C5−N2	123.85(18)	124.59(17)	123.0(3)
C8−C9−C16	122.16(18)	122.83(17)	123.3(3)
N4−C20−C19	122.84(19)	123.10(18)	124.4(3)
C20−C19−N3	121.62(19)	122.93(18)	123.5(3)

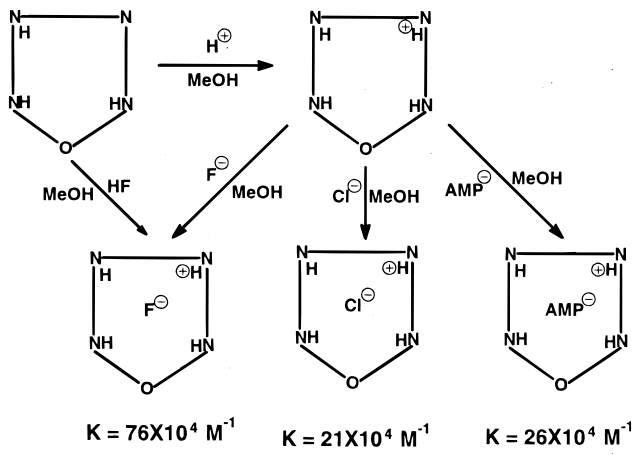
Table 2. Deviation Angles (deg) between the Plane Constructed with the Inner Periphery Atoms and the Plane of Individual Heterocyclic Rings

heterocyclic ring	**4**	**4·HCl**	**1**
furan ring	12.85	9.10	5.67
N1 pyrrole ring	19.66	17.66	4.98
N2 pyrrole ring	8.16	22.72	15.85
N3 pyrrole ring	6.91	7.40	22.40
N4 Pyrrole ring	15.24	10.31	3.75

coordination to the metal nor the binding of the chloride ion, shows a decrease on going from the free base to the metal complex, suggesting that the furan ring is more planar in **1** than in **4**, (ii) the pyrrole rings having nitrogens N1 and N4, which are not involved in binding to the metal, also become more planar in **1** relative to the free base **4**, while the pyrrole rings having nitrogens N1 and N3, which are involved in the metal binding, show the opposite trend, (iii) in **4**, the pyrrole rings containing N1 and N4 are deviated much more relative to the pyrrole rings containing N2 and N3 (this can be understood in terms of steric crowding because of the presence of two hydrogens on N1 and N4), and (iv) in **4·HCl**, the pyrrole ring which are involved in binding of the chloride ion are deviated much more relative to the pyrrole ring N3, which is not involved in the binding. These observations clearly suggest that the smaragdyrin skeleton is quite flexible and is able to adjust itself to different environments involved in the binding of an anion and a metal cation.

Anion Complexes of Smaragdyrin in Solution. The complexation of anions by the protonated form of smaragdyrin **4·HCl** in solution is further probed by UV−vis spectroscopy because of the strong absorption of the smaragdyrins. Three different anions, F^-, Cl^-, and adenosine monophosphate (AMP^-), were chosen for study. In a typical experiment, a constant volume of smaragdyrin in its protonated form (~5.2 × 10^{-6} M) was taken in 10 mL volumetric flasks. An increasing amount of the required anion salt solution (0.5 × 10^{-6} to 1 × 10^{-4} M) in methanol was transferred to each flask. Then in each flask, 1 mL of 0.5 M 18-crown-6 was added so that the cation was complexed by the crown ether, leaving the naked anion for binding. The remaining volume was made up with the solvent up to the mark. The solution was shaken well, and immediately the absorption spectra of these solutions in the desired region were recorded. The addition of an increasing amount of salt results in a small increase in the absorbance of the smaragdyrin due to complexation, and this increase in the absorbance was analyzed using the Nash equation[25] (1) to

Scheme 4. Binding Constants of Various Anions with the Protonated Form of Smaragdyrin



$$1/C_A = [(d^o/(d^o - d))(K - (\epsilon_{AD}/\epsilon_D)) - K] \quad (1)$$

evaluate the binding constants. Here d^o is the optical density of smaragdyrin at a particular wavelength in the absence of any salt while d is the optical density of the anion complex of the smaragdyrin at a particular concentration of the salt solution. C_A is the concentration of the anion, ϵ_D represents the molar absorptivity of the protonated smaragdyrin, ϵ_{AD} represents the molar absorptivity of the anion complex of smaragdyrin, and K is the binding constant. The physical significance of this equation is quite clear when the reciprocal of the acceptor concentration is plotted against $d^o/(d^o - d)$. The intercept of the straight line should be the negative of the binding constant, and the slope is related to the molar absorptivity of the complex.

The summary of the binding data is shown in Scheme 4. A comparison of the binding constants observed here shows that they are approximately an order of magnitude lower relative to those of the similar ions by the protonated form of N5 sapphyrin reported by Sessler and co-workers.[6d] Relative to N5 sapphyrin the oxasmaragdyrin **4** reported here is different in the following aspects: (a) The cavity size available for anion binding in the smaragdyrin is slightly smaller because of the presence of two direct pyrrole−pyrrole links and the furan oxygen atom instead of the pyrrole nitrogen. (b) The N5 sapphyrins reported by Sessler[6d] have β-alkyl substituents with free meso carbons, while the smaragdyrins have *meso*-phenyl substituents. (c) The number of hydrogen-bonding sites which are mainly responsible for anion binding[6d] in the protonated form of oxasmaragdyrin is only four relative to five such sites in N5 sapphyrin. These structural differences probably could account for the small lowering of the binding constants in the present study.

Conclusions

The synthesis of stable *meso*-aryl smaragdyrins has been achieved in moderately good yields using easily available

(25) Nash, C. J. *Phys. Chem.* **1960**, *64*, 950.

Table 3. Crystallographic Data for **1** and **4·HCl**

crystallographic information	**4·HCl**	**1**
solvent for crystallization	dichloromethane/*n*-heptane	dichloromethane/methanol
empirical formula	$C_{41}H_{29}N_4O_1Cl$	$C_{41}H_{27}N_4O_3Rh$
temp (K)	93(2)	293(2)
crystal system	monoclinic	triclinic
space group	*P*2(1)/*c*	*P*-1
vol (Å)	3115.47(11)	1692.1(17)
a (Å)	11.8783(2)	11.836(8)
b (Å)	17.3787(4)	12.495(9)
c (Å)	16.0151(3)	12.670(2)
α (deg)	90	69.09(6)
β (deg)	109.5460(10)	78.78(6)
γ (deg)	90	77.02(5)
Z	4	2
density(calcd) (mg/m^3)	1.341	1.473
no. of unique reflns collected	24 139	6259
	7601	5945
R(int)	0.0565	0.0164
F(000)	1312	764
limiting indices	$-15 \le h \le 14$, $-14 \le k \le 23$, $-19 \le l \le 20$	$0 \le h \le 14$, $-14 \le k \le 14$, $-14 \le l \le 15$
goodness of fit (F^2)	1.015	0.832
final *R* indices $\{I > 2\sigma(I)\}$	R1 = 0.0497 wR2 = 0.1071	R1 = 0.0303 wR2 = 0.0902
R indices (all data)	R1 = 0.0850 wR2 = 0.1211	R1 = 0.0471 wR2=0.1047

precursors. The formation of stable metal complexes in the free base form and anion complexes in the protonated form reveal that these molecules are capable of exhibiting rich and diverse coordination chemistry like sapphyrins and rubyrins. Furthermore, despite the presence of two direct pyrrole−pyrrole links, the smaragdyrin ring system is quite flexible and comparable to other tetrapyrrole pigments. It is hoped that the availability of these stable smaragdyrins will now allow development of their rich and diverse chemistry. Studies in this direction are in progress in this laboratory.

Experimental Section

Instrumentation. Electronic spectra were recorded on a Perkin-Elmer Lamda 20 UV−vis spectrophotometer. IR spectra were obtained from a Perkin-Elmer 1320 Infrared spectrophotometer. Chemical analyses (C, H, N) were done on a Heraeus Carlo Erba 1108 elemental analyzer. Proton NMR spectra were obtained on either a 300 or a 500 MHz Bruker spectrometer or a 400 MHz JEOL spectrometer using $CDCl_3$ as solvent. Chemical shifts are expressed in parts per million relative to residual $CHCl_3$ (7.258 ppm). FAB-mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer. The electrospray mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer.

Chemicals. Dipyrromethane **10**, 16-oxatripyrrane **8**, and 16-thiatripyrrane **9** were prepared according to the published procedure[16,26] and stored under inert atmosphere at −10 °C.

X-ray Structure Determinations. X-ray-quality crystals for all compounds were grown using the solvent mixture given in Table 3 by the diffusion method. The crystals were removed from the Schlenk tube under a steam of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected with the aid of a microscope attached to a glass fiber, and immediately placed in the low-temperature N_2 stream of the diffractometer.[27] Data sets for **4·HCl** were collected using a Siemens SMART system, complete with a three-circle goniometer and CCD detector operating at −54 °C. The data set was collected at 93 K, by employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The data collection nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle, and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections; no decay was observed. An absorption correction was applied utilizing the program SADABS.[28] The data set for **1** was collected using the Enraf Nonius XCAD 4 instrument. The crystal structures of all compounds were solved by direct methods, as included in the SHELX program package. Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures were refined by full-matrix least-squares refinement on F^2 (SHELX-93).[29,30] Hydrogen atoms for **1** were located in difference Fourier cycles and included in the refinement. Hydrogen atoms for **4·HCl** were placed geometrically and refined using a riding model. The hydrogen atoms in all compounds were refined with U_{iso} constrained at $1.2U_{eq}$ of the carrier C atom. Scattering factors were those provided by the SHELX program. All non-hydrogen atoms were refined anisotropically. Further details about the refinements are outlined in the Supporting Information. Crystallographic parameters for compounds **4·HCl** and **1** are summarized in Table 3.

Syntheses. 5,10,19-Triphenyl-25-oxasmaragdyrin (4). 16-Oxatripyrrane **8** (0.475 g, 1.263 mmol) and dipyrromethane **10** (0.278 g, 1.263 mmol) were dissolved in 500 mL of dry dichloromethane and stirred under a nitrogen atmosphere for 5 min. TFA (0.012 mL, 0.126 mmol) was added, and the stirring was continued for a further 90 min. Then chloranil (0.932 g, 3.789 mmol) was added, and the reaction mixture was heated at reflux for an additional 90 min. After removal of the solvent, the residue was purified by chromotography on basic alumina (grade 3). The pink fraction which eluted with petroleum ether/dichloromethane (5:1) was identified as **6** (0.019 g, 3%); **4** (0.380 g, 51%) eluted as a green band when the eluent was dichloromethane.[1]H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.49 (d, 2H, $J = 4.4$ Hz), 9.38 (d, 2H, $J = 4.0$ Hz), 8.96 (d, 2H, $J = 4.4$ Hz), 8.72 (s, 2H), 8.44 (d, 2H, $J = 4.2$ Hz), 8.39 (m, 2H), 8.20 (m, 4H), 7.83 (m, 9H). UV−vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-4}$ (mol^{-1} dm^3 cm^{-1})) 443 (33.0), 456sh (16.0), 552 (2.0), 591 (1.4), 633 (1.0), 696 (1.4). Emission (CH_2Cl_2): $\lambda =$ 701 nm. FAB-MS: *m*/*z* 593 [M$^+$]. Anal. Calcd for $C_{41}H_{28}N_4O$: C, 83.09; H, 4.76; N, 9.45. Found: C, 83.14; H, 4.72; N, 9.49.

Monohydrochloride Salt of 5,10,19-Triphenyl-25-oxasmaragdyrin (4·HCl). Oxasmaragdyrin **4** (0.020 g, 0.034 mmol) was dissolved in 15 mL of dichloromethane. The solution was worked up in a separating funnel with 15 mL of 10% HCl solution. The organic layer was separated and quickly dried with $MgSO_4$. Evaporation of solvent yielded

(26) Sridevi, B.; Narayanan, S. J.; Srinivasan, A.; Reddy, M. V.; Chandrashekar, T. K. *J. Porphyrins Phthalocyanines* **1998**, *2*, 69−78.
(27) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1.
(28) SADBS: Sheldrick, G. M., University of Gottingen, Germany, 1996, using redundant data by the method described by Blessing, *Acta Crystallogr.* **1995**, *A51*, 33.
(29) Sheldrick, G. M. SHELXL-93, Program for crystal structure solution and refinement, University of Gottingen, Germany, 1993.
(30) Sheldrick, G. M. SHELXTL-Plus, Program for crystal structure solution and refinement, University of Gottingen, Germany, 1990.

a blue-green solid (0.0195 g, 91%). This was further recrystallized from a dichloromethane and *n*-heptane mixture. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.71 (dd, 2H, J_{AB} = 4.12 Hz, $^4J_{H,H}$ = 1.7 Hz), 9.64 (dd, 2H, J_{AB} = 4.2 Hz, $^4J_{H,H}$ = 1.7 Hz), 9.27 (dd, 2H, J_{AB} = 4.4 Hz, $^4J_{H,H}$ = 1.7 Hz), 9.24 (s, 2H), 8.68 (dd, 2H, J_{AB} = 4.2 Hz, $^4J_{H,H}$ = 1.7 Hz), 8.63 (m, 2H), 8.47 (m, 2H), 8.30 (m, 2H), 7.99 (m, 3H), 7.92 (m, 6H), −1.06 (s, 2H), −2.06 (s, 2H). UV−vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-4}$ (mol^{-1} dm^3 cm^{-1})) 450 (27.9), 482 (13.5), 605 (1.8), 657 (2.4), 720 (4.6).

5,10,19-Triphenyl-25-thiasmaragdyrin (5). 5 was prepared by the reaction of 16-thiatripyrrane **9** (0.200 g, 0.51 mmol) and dipyrromethane **10** (0.113 g, 0.51 mmol) with TFA (0.004 mL, 0.051 mmol) followed by oxidation with chloranil (0.376 g, 1.53 mmol) by a procedure similar to that described above. The crude product upon chromatographic separation on basic alumina with petroleum ether and dichloromethane (1:4) gave **5** as a purple solid. yield: 0.013 g, 4%. ^{1}HNMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 9.38 (d, 2H, J = 4.5 Hz), 9.36 (d, 2H, J = 4.0 Hz), 9.22 (s, 2H), 8.91 (d, 2H, J = 4.0 Hz), 8.63 (d, 2H, J = 4.0 Hz), 8.35 (m, 2H), 8.32 (m, 4H), 7.85 (m, 9H). UV−vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-4}$) (mol^{-1} dm^3 cm^{-1})) 453 (12.6), 557 (1.11), 590 (0.77), 643 (0.57), 710 (0.46), 823 (0.19). UV−vis (CH_2Cl_2/HCl): λ_{max} (nm) ($\epsilon \times 10^{-4}$); 478 (10.85), 616 (0.86), 671 (0.86), 878sh (0.95), 927 (1.34). Emission (CH_2Cl_2): λ = 725 nm. MS (electron spray): *m*/*z* (%) 609 (85) [M^+]. Anal. Calcd for $C_{41}H_{28}N_4S$: C, 80.89; H, 4.64; N, 9.20. Found: C, 80.82; H, 4.68; N, 9.28.

(5,10,19-Triphenyl-25-oxasmaragdyrinato)dicarbonyl rhodium-(I) (1). Oxasmaragdyrin **4** (0.020 g, 0.034 mmol) was dissolved in alcohol-free dichloromethane (50 mL). Anhydrous sodium acetate (0.028 g, 0.340 mmol) was added to the solution followed by di-μ-chlorobis[dicarbonylrhodium(I)] (0.020 g, 0.050 mmol), and the mixture was stirred under reflux for 2 h. The solvent was evaporated and was chromatographed using a silica gel column with petroleum ether/dichloromethane (3:2) solution. Removal of the solvent gave a purple solid (0.025 g, 96%) which was recrystallized from a dichloromethane/*n*-heptane mixture. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.51 (dd, 2H, J_{AB} = 4.2 Hz, $^4J_{H,H}$ = 2 Hz), 9.18 (d, 2H, J_{AB} = 4.4 Hz), 8.81 (s, 2H), 8.75 (d, 2H, J_{AB} = 4.4 Hz), 8.50 (dd, J_{AB} = 4.2 Hz, $^4J_{H,H}$ = 2.4 Hz), 8.31 (m, 4H), 8.15 (m, 2H), 7.81 (m, 9H), −1.71 (s, 2H). UV−vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-4}$) (mol^{-1} dm^3 cm^{-1})) 457 (20.9), 478 (11.5), 574 (1.26), 616 (1.31), 637 (1.06), 696 (1.5). IR (KBr): 2060, 1995 (CO). ES-MS: *m*/*z* (%) 750.1 (18) [M^+], 692.1 (100) [$M^+ - (CO)_2$]. Anal. Calcd for $C_{43}H_{27}N_4O_3Rh$: C, 68.81; H, 3.63; N, 7.46. Found: C, 68.88; H, 3.68; N, 7.51.

(5,10,19-Triphenyl-25-thiasmaragdyrinato)dicarbonyl rhodium-(I) (2). The above procedure was followed using thiasmaragdyrin **5** (0.012 g, 0.020 mmol), anhydrous sodium acetate (0.016 g, 0.20 mmol), and di-μ-chlorobis[dicarbonylrhodium(I)] (0.012 g, 0.030 mmol). **2** was obtained in 53% yield (0.008 g) as a purple solid and was recrystallized from a dichloromethane/*n*-heptane mixture. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.42 (dd, 2H, J_{AB} = 4.2 Hz, $^4J_{H,H}$ = 2.4 Hz), 9.30 (d, 2H, J_{AB} = 4.4 Hz), 9.24 (s, 2H), 8.75 (d, 2H, J_{AB} = 4.4 Hz), 8.70 (dd, J_{AB} = 4.2 Hz, $^4J_{H,H}$ = 2.4 Hz), 8.50 (m, 2H), 8.17 (m, 2H), 7.88 (m, 2H), 7.80 (m, 9H), −1.22 (s, 2H). UV−vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-4}$) (mol^{-1} dm^3 cm^{-1})) 471 (14.23), 489 (9.86), 582 (1.14), 622 (0.56), 655 (0.54), 719 (0.81). IR (KBr): 2055, 1985 (CO). FAB-MS: *m*/*z* (%) 766 (100) [M^+]. Anal. Calcd for $C_{43}H_{27}N_4O_2S_1Rh$: C, 67.37; H, 3.55; N, 7.31. Found: C, 67.32; H, 3.49; N, 7.36.

(5,10,19-Triphenyl-25-oxasmaragdyrinato)nickel(II) Complex (3). The free base **4** (0.19 g, 0.168 mmol) and nickel chloride (0.48 g, 1.68 mmol) were dissolved in 30 mL of freshly distilled dimethylformamide (DMF) and refluxed for 10 h. Solvent was evaporated under reduced pressure, and column chromatography was done in basic alumina. The green band eluted with the 1:1 mixture of dichloromethane/hexane was recrystallized with dichloromethane/*n*-heptane and gave a green solid (0.012 g, 10%). UV−vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-4}$ (mol^{-1} dm^3 cm^{-1})) 452 (13.26), 486 (10.01), 606 (0.83), 651 (0.72), 738 (0.62). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.84 (m, 9H), 8.20 (m, 2H), 8.37 (m, 2H), 8.68 (m, 2H), 8.86 (br d, 2H), 9.347 (br d, 2H), 9.43 (br d, 2H), 9.619 (br s, 2H), 9.83 (br s, 2H). Anal. Calcd for $C_{41}H_{25}N_4ONi$: C, 75.95; H, 3.89; N, 8.64. Found: C, 75.90; H, 3.91; N, 8.68.

Acknowledgment. This work was supported by the Department of Science and Technology (DST; grant to T.K.C) and by the Council of Scientific and Industrial Research (CSIR), Government of India, New Delhi, and the National Science Foundation (K.R.S.; Grant CHE-9702246). Purchase of the X-ray diffractometion equipment was made possible with grants from the NSF (CHE-95-27898), the W.M. Keck Foundation, and Syracuse University. T.K.C. is also grateful to the Alexander Von Humboldt foundation for an equipment grant.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **1** and **4·HCl**, FAB-mass spectra for **1**, ^{1}H NMR spectra for **2**, **3**, and **5**, and 2D ^{1}H−^{1}H COSY spectra for **1**, **2**, **4**, and **4·HCl**. This material is available free of charge via the Internet at http://pubs.acs.org.

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