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Recognition of Axial Ligands by a Zinc Porphyrin Host on the Basis of Nonpolar Interligand Interaction

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Abstract: A porphyrin host with a preorganized cavity on each face has been synthesized and characterized. The constants for association of the zinc complex of the porphyrin with various amine ligands were determined and compared with those of [*meso*-tetrakis(*p*-methylphenyl)porphyrinato]zinc(II) and of a "picket-fence" porphyrin zinc(II) complex. The selectivity for the amine ligands was not observed for the picket-fence porphyrin complex. Contrary to this, small secondary amines, such as azetidine, pyrrolidine, and diethylamine, that fit the shape of the cavity of the synthesized host complex bind more strongly to the host than less hindered amines, such as butylamine and propylamine; the recognition parameters for azetidine versus butylamine were found to be $K = 22$, $\Delta H^\circ = -2.6$ kcal/mol, and $T\Delta S^\circ = -0.8$ kcal/mol at 25 °C in toluene. However, the binding of the larger secondary amines such as dipropylamine and diisopropylamine to the host was weakened due to greater steric repulsions from the cavity. It was concluded that, in this case, the stabilization of the ligand binding by the geometrical complementarity between the amines and the cavity of the host is ascribed mainly to attractive interligand interactions such as the London force or CH–π interaction.

Introduction

Transition-metal host–guest complexes have received much attention in studies attempting to gain a fundamental understanding of metalloenzyme–substrate binding.[1-4] Binding of an organic ligand to superstructured porphyrin complexes has provided useful information on such host–guest association phenomena.[4d,5-8] The first example of the stabilization of axial-ligand binding by a superstructure was observed for "capped" porphyrin complexes by Basolo and co-workers.[5] Recently, Collman et al.[6] have reported that, in "picnic-basket" porphyrin complexes, an axial ligand binds more tightly to the "in-cavity" side than to the unprotected side. In an earlier work, we[7] have reported that the binding of isoquinoline to the $\alpha,\beta,\alpha,\beta$ atropisomer of the zinc "picket-fence" porphyrin complex is more stabilized than the binding of pyridine in terms of increased van der Waals contacts within the cavity. More recently, Bonar-Law and Sanders[8] have also reported that a larger axial ligand binds more strongly to a capped porphyrin complex. These facts suggest that complementary geometries between an axial ligand and a superstructure may practically enhance the ligand binding.

Complementarity between host and guest dominates molecular recognition that is critical to enzyme functions, where various polar, nonpolar, and steric interactions apparently act as driving forces for the recognition.[3c,9,10] For the binding of an axial ligand to a protected porphyrin complex, some interaction between the axial ligand and the cavity can be regarded as the second recognition factor in addition to the coordination bond.[3c] Recent attention has also been directed toward such multiple recognition on the basis of various host–guest interactions.[4d,11,12] Although one of the major interactions is thought to be the London force,[13,14] experimental results have not provided definitive evidence because of the greater polar interactions as well as solvent effects in polar solvents.

In this work, we designed and synthesized a zinc porphyrin host that contains a preorganized cavity on each face on the porphyrin plane (Figure 1). Thermodynamic values for the binding of various amine ligands to the host complex were then determined photometrically. We also examined the binding behavior of [*meso*-tetrakis(*p*-methylphenyl)porphyrinato]zinc(II), Zn(T-*p*-CH_3PP),[15] and of the zinc picket-fence porphyrin Zn(TpivPP) for comparison. These results confirm shape-selective binding of amine ligands by the host cavity and also allow us to explore the possible interligand interactions between the amines and the cavity.

Results and Discussion

Ligand Design. Effective incorporation of an organic axial ligand into a superstructured porphyrin requires a somewhat large and rigid cavity. A large cavity under a long "strap" or a tall "cap" might be less appropriate to accommodate such organic ligands, because of cavity collapse before the ligation of the axial ligand. Some of the most suitable hosts containing a rigid and preor-

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(15) Abbreviations: pa, propylamine; ba, butylamine; cha, cyclohexylamine; tba, *tert*-butylamine; az, azetidine; pyr, pyrrolidine; pip, piperidine; thiq, 1,2,3,4-tetrahydroisoquinoline; dea, diethylamine; dpa, dipropylamine; dipa, diisopropylamine; py, pyridine; 1-MeIm, 1-methylimidazole; T-*p*-CH_3PP, dianion of *meso*-tetrakis(*p*-methylphenyl)porphyrin; TpivPP, dianion of picket-fence porphyrin, $\alpha,\alpha,\alpha,\alpha$-*meso*-tetrakis(*o*-pivalamidophenyl)porphyrin; BRP, dianion of "bis-roof" porphyrin.

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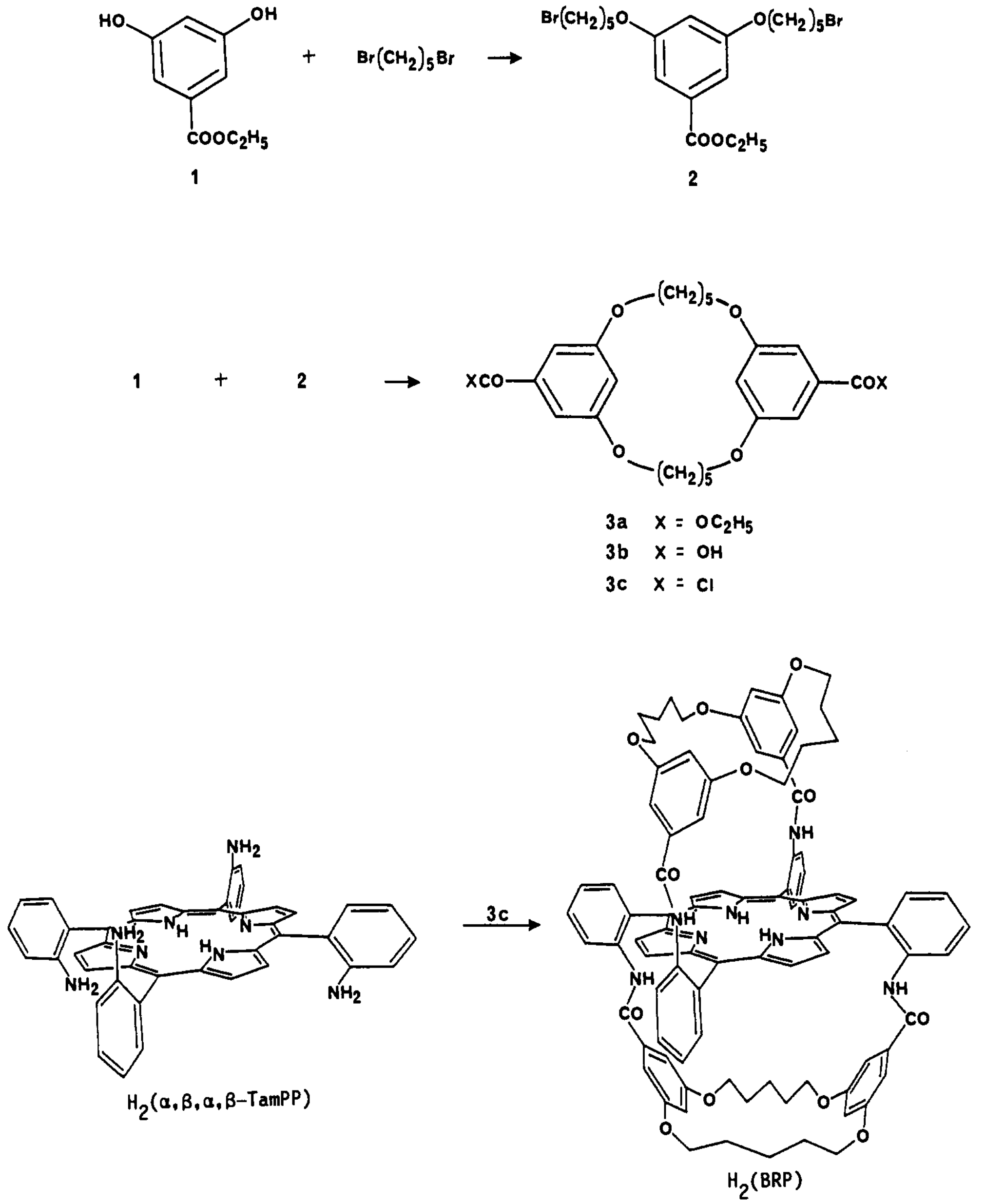
Scheme I



ganized cavity are a series of "picnic-basket" porphyrin complexes developed by Collman and co-workers.[6] There are, however, two regioisomers for the coordination of an axial ligand due to the one-face protection on the porphyrin plane by the cavity in these complexes. This apparently involves two different types of equilibria and may interfere with the accurate estimation of binding constants for axial ligation to the protected side.

On the basis of these considerations, we designed a superstructured porphyrin that contains (1) the same cavity on each face of the porphyrin plane, (2) rigid phenyl groups as the "side-wall" part of the cavity, preventing collapse, and (3) two bridging chains that link the two phenyl walls, which hinder rotation of the phenyl groups. The second and last factors actually provide preorganization of the cavity.

Synthesis and Characterization. Scheme I outlines the procedure used to introduce the cavity into a porphyrin to synthesize the "bis-roof" porphyrin, H_2(BRP). In the course of preparing the bibridged diester, **3a**, direct coupling of **1** and 1,5-dibromopentane in an equimolar ratio gave various byproducts; therefore, purification could not be accomplished. A two-step coupling using **2** was then devised as shown in Scheme I and afforded **3a** in fair yield. Upon treatment with basic aqueous acetone, diester **3a** was hydrolyzed to the diacid **3b**, which was then easily converted to the diacid chloride **3c** with thionyl chloride. The final high-dilution coupling between the diacid chloride and H_2(α,β,α,β-TamPP) gave the desired porphyrin, H_2(BRP). A satisfactory yield of greater than 30% for the porphyrin may result from the complementary geometries of the diacid chloride and the amino groups of H_2(TamPP). The synthetic procedure presented here provides a general route to construct a series of superstructures on the porphyrin plane using the appropriate dibromide instead of 1,5-dibromopentane.

The ^{1}H NMR spectrum for H_2(BRP) (Figure S1, supplementary material) is not very complicated because of the high symmetry of the porphyrin. The porphyrin internal NH protons give a chemical shift at −3.17 ppm. The pentyl CH_2 signals appear at 1.02, 1.29, and 3.44 ppm with a ratio of 1:2:2. The two signals at 5.84 and 5.94 ppm in a 1:2 ratio are assigned to the protons of the phenyl groups that comprise the cavities. The singlet at 6.86 ppm is assignable to the amide protons. The meso-phenyl signals appear at 7.60–8.43 ppm as a doublet or triplet. The singlet at 8.89 ppm is assigned to the pyrrolic protons.

The zinc ion was inserted into H_2(BRP) by a method similar to one previously described.[7] The ^{1}H NMR spectrum of Zn(BRP) (not shown) was essentially similar to that of H_2(BRP). It is interesting to note that the visible spectrum of Zn(BRP) in toluene is obviously different from that in chloroform (see Experimental Section). The red shifts in toluene suggested that a water molecule

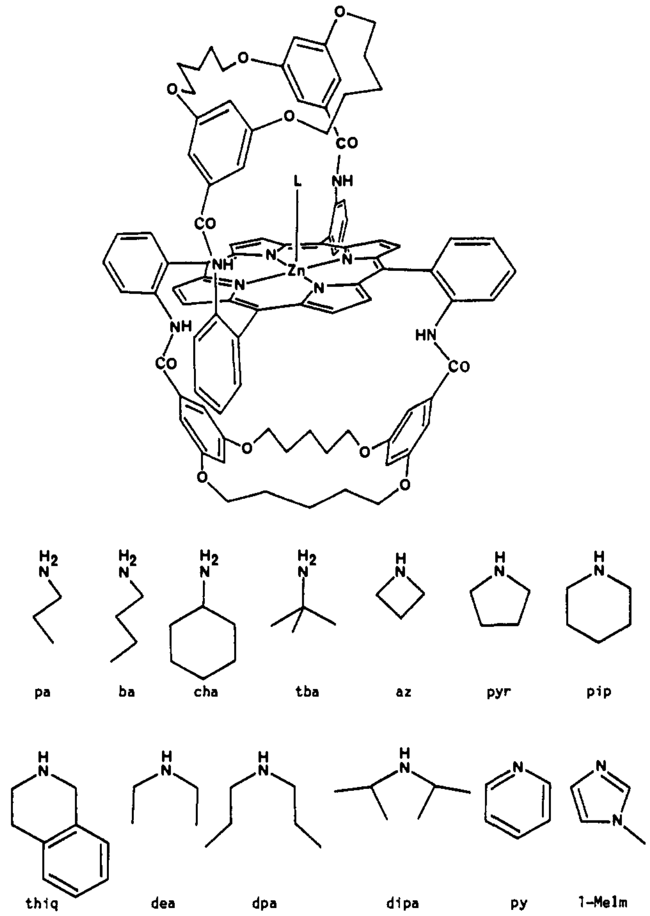


Figure 1. Zinc "bis-roof" porphyrin Zn(BRP) and amine ligands.

may tightly ligate to the metal ion in toluene. This phenomenon is observed for the $\alpha,\beta,\alpha,\beta$ atropisomer of Zn(TpivPP)[7] but not for Zn(TPP) even in wet toluene.[16]

Criterion of Recognition. It is generally accepted that zinc porphyrins (ZnP) show a well-defined equilibrium between four- and five-coordination:

$$\mathrm{ZnP} + \mathrm{L} \overset{K}{\rightleftharpoons} \mathrm{ZnP{\cdot}L} \qquad (1)$$

where L is an axial ligand. From a comparison of the thermodynamic values for the binding of two axial ligands (L_1 and L_2) between two porphyrin systems (P_1 and P_2), the thermodynamic parameters for the recognition of axial ligands can be obtained as follows:

$$K_{\mathrm{recog}} = [K(\mathrm{P_1{-}L_1})/K(\mathrm{P_1{-}L_2})]/[K(\mathrm{P_2{-}L_1})/K(\mathrm{P_2{-}L_2})] \qquad (2)$$

$$\Delta G^\circ_{\mathrm{recog}} = -RT \ln K_{\mathrm{recog}} = \Delta H^\circ_{\mathrm{recog}} - T\Delta S^\circ_{\mathrm{recog}} \qquad (3)$$

$$\Delta H^\circ_{\mathrm{recog}} = \Delta H^\circ(\mathrm{P_1{-}L_1}) - \Delta H^\circ(\mathrm{P_1{-}L_2}) - \Delta H^\circ(\mathrm{P_2{-}L_1}) + \Delta H^\circ(\mathrm{P_2{-}L_2}) \qquad (4)$$

$$\Delta S^\circ_{\mathrm{recog}} = \Delta S^\circ(\mathrm{P_1{-}L_1}) - \Delta S^\circ(\mathrm{P_1{-}L_2}) - \Delta S^\circ(\mathrm{P_2{-}L_1}) + \Delta S^\circ(\mathrm{P_2{-}L_2}) \qquad (5)$$

When there is no special interaction in any combination of P and L, the K_{recog} value equals unity. However, if the porphyrin complex P_1 prefers axial ligand L_1 and the binding of P_1–L_1 is specifically more stabilized than the others, the observed K_{recog} value becomes larger than unity. It should be emphasized that the differences in metal–L bond strength that depend on the pK_a of L are canceled by each other and that solvation of the binding sites or ligation of H_2O cannot affect the values of K_{recog}, $\Delta H^\circ_{\mathrm{recog}}$, and $\Delta S^\circ_{\mathrm{recog}}$.

In the present work, P_1 is Zn(BRP). For comparison, in porphyrin P_2, there must be essentially no interaction between the porphyrin substituent(s) and the bound L_1 or L_2. Thus, flat TPP derivatives are appropriate as P_2. We chose Zn(T-*p*-CH_3PP) because its solubility in organic solvents is higher than those of other flat porphyrins, forming no precipitation of ZnP·L. As the axial ligand for comparison (L_2), a less hindered primary amine is preferred in terms of inducing less interactions with the cavity of Zn(BRP). Hence, we chose butylamine, ba, as L_2. This is, however, a measure for other amines, and K_{recog} can easily be converted using a value for another reference amine L_3, as follows:

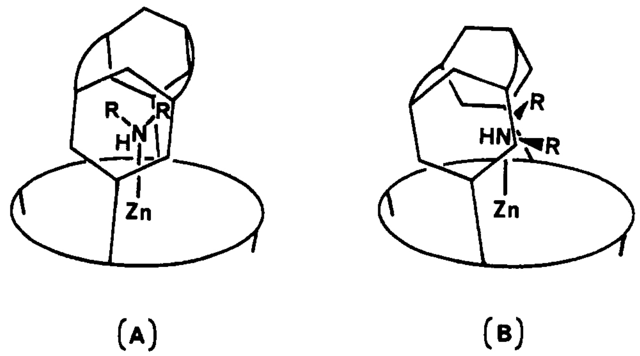
$$K_{\mathrm{recog}}(\mathrm{L_1\ vs\ L_3}) = K_{\mathrm{recog}}(\mathrm{L_1\ vs\ ba})/K_{\mathrm{recog}}(\mathrm{L_3\ vs\ ba}) \qquad (6)$$

Table I. Constants[a] for Binding of Amines to Zinc Porphyrins

	Zn(BRP)		Zn(TpivPP)		Zn(T-*p*-CH_3PP)
amine	K, M^{-1}	K_{recog}	K, M^{-1}	K_{recog}	K, M^{-1}
pa	1.7×10^4	1.5	7.6×10^4	0.94	1.9×10^4
ba	$1.5 \times 10^{4\,b}$	1	1.1×10^5	1	$2.5 \times 10^{4\,b}$
cha	7.1×10^3	0.78	8.2×10^4	1.2	1.5×10^4
tba	1.6×10^3	0.50			5.3×10^3
az	$4.1 \times 10^{6\,b}$	22	1.6×10^6	1.2	$3.2 \times 10^{5\,b}$
pyr	8.6×10^5	6.9			2.1×10^5
pip	4.7×10^4	1.2	$4.1 \times 10^{5\,c}$	1.4	6.9×10^4
thiq	1.9×10^4	0.79	1.7×10^5	0.97	4.0×10^4
dea	8.2×10^3	10	7.2×10^3	1.2	1.4×10^3
dpa	1.1×10^2	0.13			1.4×10^3
dipa	$\sim 0^d$				
py	2.9×10^3	1.5	$2.4 \times 10^{4\,c}$	1.7	3.3×10^3
1-MeIm	5.1×10^4	1.9			4.6×10^4

[a] At 25 °C in toluene; errors are smaller than 10% where $K < 2 \times 10^6$ and smaller than 20% for the larger values of K, except for those calculated from van't Hoff plots. [b] Calculated at 25 °C from van't Hoff plots. [c] Reference 7. [d] Little spectral change was observed upon addition of dipa to the complex solution.

Chart I



Binding Behavior. Table I lists the binding constants obtained by photometric titration of a complex solution with amine ligands. The K_{recog} values for the picket-fence porphyrin complex, Zn(TpivPP), are fairly close to unity, irrespective of the kind of amine, i.e., primary, secondary, or aromatic. Since the axial ligands will preferentially bind to the flat side of the porphyrin plane of Zn(TpivPP),[7] the lack of selectivity for these amines is quite reasonable. Further, this result warrants the application of eq 2 between two different porphyrin systems.

In the case of Zn(BRP), the binding behavior is quite different from that of Zn(TpivPP). For the binding of primary amines to Zn(BRP), the K_{recog} values are in the range between 0.50 and 1.5, and little selectivity exists among these amines. This is probably due to small interactions between the cavity of Zn(BRP) and the primary amines examined. Contrary to this, the binding of secondary amines to Zn(BRP) is evidently shape-selective. A striking feature of our data is that the K_{recog} values of Zn(BRP) for az, dea, and pyr are 22, 10, and 6.9, respectively; the binding of these amines is specially stabilized with respect to the binding of the other amines. On the other hand, a (CPK) model-building study has shown that two structures for amine adducts are probable, as schematically shown in Chart I. The small secondary amines, az, dea, and pyr, can bind to Zn(BRP) as shown in structure A

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Table II. Thermodynamic Values for the Binding of Amines[a]

system	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol K)[b]
Zn(BRP)–az	−11.0 ± 0.4	−6.6 ± 1.3
Zn(BRP)–ba	−7.9 ± 0.1	−7.6 ± 0.2
Zn(T-*p*-CH_3PP)–az	−12.1 ± 0.3	−15.4 ± 0.9
Zn(T-*p*-CH_3PP)–ba	−11.7 ± 0.1	−19.0 ± 0.3

[a] In toluene. [b] At 25 °C.

Table III. Binding Constants in Chloroform[a]

	Zn(BRP)		Zn(T-*p*-CH_3PP)
amine	K, M^{-1}	K_{recog}	K, M^{-1}
ba	7.7×10^4	1	1.1×10^4
az	1.4×10^7	18	1.1×10^5
pyr	2.7×10^6	4.4	8.7×10^4
pip	2.2×10^5	0.70	4.5×10^4

[a] At 25 °C.

without steric repulsions from the cavity. In constrast, bulkier cyclic amines, pip and thiq, are too large to be accommodated by the cavity and will prefer structure B rather than structure A with slight steric repulsions. This reflects the fact that the K_{recog} values for these amines are fairly close to unity. However, the model building has also suggested that noncyclic secondary amines in structure B obviously cause greater steric repulsions from the cavity because of the larger C–N–C or C–(C)–N–(C)–C bond angles[17] than those of cyclic amines. Then, dea, dpa, and dipa adducts of Zn(BRP) will prefer structure A, where a slight increment in molecular dimensions of the amines causes substantial steric repulsions from the cavity. Thus, the binding of these amines to Zn(BRP) drastically decreases in the order dea > dpa > dipa. The K_{recog} value for dea versus dpa is estimated to be 77.

In the case of the binding of aromatic amines, py and 1-MeIm, the K_{recog} values of Zn(BRP) do not deviate significantly from unity. This result would come from the balance of attraction against repulsion between the bound amine ligand and the cavity. The attractive forces probably involve π–π interaction.[12,18,19] However, these data may be insufficient to explain such an interaction in detail.

For the recognition of az compared with ba by Zn(BRP), the thermodynamic contribution was found to be $\Delta H°_{recog} = -2.6 \pm 0.9$ kcal/mol and $T\Delta S°_{recog}(25\ °C) = -0.8 \pm 0.8$ kcal/mol (Table II).[20] Thus, it is evident that the increased binding energy stabilizes the binding of az, while the entropy factor hardly affects the value of K_{recog}. Table III lists binding constants in chloroform. The values of K_{recog} in toluene are very similar to those in chloroform, suggesting that solvents only slightly affect the thermodynamic values for the recognition. Therefore, the stability enhancements in this case are best related to the number of van der Waals contacts between the cavity and the axial ligands in structure A[21] and are also explained by the geometrical complementarity between the host and the axial-ligand guests (Figure 2). Thus, we concluded that the special stabilization of the binding of az, dea, and pyr has mainly come from nonpolar interligand interactions such as the London force or CH–π interaction.[22] This also supports our earlier suggestion[7] that attractive interligand interactions occur in nonpolar organic solvents. These interactions may be too weak to accompany the reorganization of the cavity or the bound axial ligand, thus giving rise only to an increase in the binding energy, $-\Delta H°$.

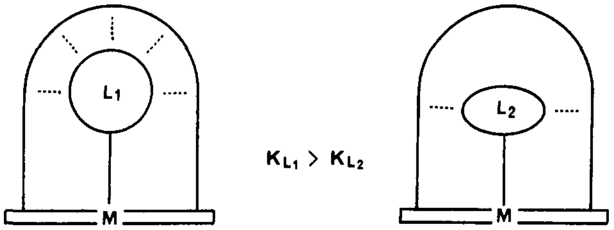

Figure 2. Schematic representation for complementarity between the cavity and axial ligands. The binding of the axial ligand becomes strong with an increase in the number of van der Waals contacts.

The complementarity between axial ligands and the cavity of Zn(BRP) presented here provides both substantial stability enhancements and the shape-selective recognition for axial ligands without specific polar interactions. Contrary to the well-known hydrophobic interactions,[14,23] this stabilization occurs even in nonpolar organic solvents. However, this phenomenon requires a subtle condition in which the geometry of an axial ligand fixed by the coordination bond affords to some extent van der Waals contacts with the preorganized cavity without steric repulsions.

Experimental Section

Measurements. Proton NMR spectra were recorded on a JEOL JMN-FX-100 or a JEOL-GSX-400 spectrometer. Visible absorption spectra were obtained with a Hitachi 340 or a Hitachi U-3000 spectrophotometer. The equilibrium constants for N-donor axial ligands were determined from the Hill equation on the basis of spectrophotometric titrations of porphyrin complexes with ligand solutions as previously described.[7] The thermodynamic values for the binding of az and ba were estimated from the temperature dependence of the equilibrium constants.

Materials. Amine ligands, except for az, were of reagent grade quality and were purified by distillation from KOH. Azetidine (Aldrich) was dried over molecular sieves (4 Å). Toluene was distilled from molecular sieves (4 Å). Chloroform was ethanol-free (HPLC grade, Merck) and was dried over molecular sieves (4 Å). 2,6-Lutidine was distilled from KOH. Dichloromethane, DMF, and THF were of reagent grade quality and were dried over molecular sieves (4 Å). The porphyrins, H_2(T-*p*-CH_3PP)[24] and H_2(TpivPP),[25] were synthesized according to the literature. The zinc ion was incorporated into the porphyrins as described elsewhere.[7]

Ethyl 3,5-Bis((5-bromopentyl)oxy)benzoate (2). To a mixture of 29 mL (214 mmol) of 1,5-dibromopentane in 250 mL of DMF and 30 g of K_2CO_3 maintained at 80 °C under N_2 was added dropwise a solution of 10 g (55 mmol) of ethyl 3,5-dihydroxybenzoate (**1**) in 100 mL of DMF over 1 h. The mixture was then stirred for 2 h at 80 °C. After filtration, the reactant solution was reduced in volume on an evaporator. The residual oily mixture was dissolved in 500 mL of benzene, and the benzene solution was washed twice with 300 mL of H_2O. The organic layer was dried over anhydrous Na_2SO_4, filtered, and reduced to an oil on an evaporator. The oil was chromatographed on a silica-gel column (4 × 35 cm, benzene) and eluted with benzene. The first band contained the desired benzoate and unreacted 1,5-dibromopentane. Removal of 1,5-dibromopentane from the eluant under vacuum at 80 °C gave a colorless oily product, yield 10.4 g (39%): ^1H NMR ($CDCl_3$) δ 1.39 (t, 3 H), 1.5–2.0 (br m, 12 H), 3.44 (t, 4 H), 4.00 (t, 4 H), 4.36 (q, 2 H), 6.62 (t, 1 H), 7.17 (d, 2 H).

Diethyl 3,3′,5,5′-Bis(1,5-pentanediyldioxy)dibenzoate (3a). To a solution of 10.2 g (21 mmol) of ethyl 3,5-bis((5-bromopentyl)oxy)benzoate (**2**) in 400 mL of DMF and 30 g of K_2CO_3 was added 3.9 g (21 mmol) of ethyl 3,5-dihydroxybenzoate (**1**). The mixture was stirred for 3 h at 80 °C under N_2. After filtration, the reactant solution was reduced in volume on an evaporator. The residual oil was dissolved in 300 mL of benzene, and the benzene solution was washed twice with 200 mL of H_2O. The organic layer was dried over anhydrous Na_2SO_4, filtered, and reduced in volume to an oil. The oil was chromatographed on a silica-gel

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(17) The larger C–N–C or C–(C)–N–(C)–C bond angle in secondary amines also lowers the binding constant by increased steric interactions with the porphyrin plane: the binding constants for Zn(T-*p*-CH_3PP) decrease in the order az > pyr > pip > dea ≑ dpa, mainly due to the increased C–N–C bond angle, where the donor abilities (pK_a values) of these amines are fairly close.

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(20) The larger $\Delta S°$ values of Zn(BRP) compared to Zn(T-*p*-CH_3PP) may result from the release of the coordinated water molecule upon amine binding to Zn(BRP).

(21) This explanation might be better supported by comparing the binding constants for much smaller amines such as methylamine or dimethylamine, which could not be determined experimentally because of their low boiling points.

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column (5 × 30 cm, benzene) and eluted with benzene. After unreacted benzoate **2** passed through the column, elution with benzene/ether (50/1) eluted the desired dibenzoate. Removal of the solvent gave white crystals, yield 1.8 g (19%): mp 128–129 °C; ^{1}H NMR ($CDCl_3$) δ 1.37 (t, 6 H), 1.6–2.0 (br m, 12 H), 4.06 (t, 8 H), 4.34 (q, 4 H), 6.58 (t, 2 H), 7.14 (d, 4 H).

3,3′,5,5′-Bis(1,5-pentanediyldioxy)dibenzoic Acid (3b). To a solution of 1.65 g (3.65 mmol) of the precursor diester **3a** in 50 mL of acetone was added a solution of 4.0 g of NaOH in 40 mL of H_2O. The mixture was then stirred for 30 min at 40 °C. To the solution was added 2 N HCl until the pH of the mixture was lowered to about 2; then a white precipitate was obtained. The solid was filtered off, washed well with H_2O, and dried at 80 °C under vacuum; yield 1.40 g (97%): mp 280–283 °C dec; ^{1}H NMR (D_2O/K_2CO_3) δ 1.4–1.8 (br m, 12 H), 4.81 (br s, 8 H), 6.45 (s, 2 H), 7.05 (d, 4 H).

3,3′,5,5′-Bis(1,5-pentanediyldioxy)dibenzoyl Chloride (3c). The precursor diacid **3b** (1.40 g, 3.53 mmol) was heated at reflux for 3 h in 20 mL of $SOCl_2$ containing a drop of DMF. Removal of excess $SOCl_2$ from the mixture under vacuum gave a pale yellow solid, yield 1.45 g (95%): mp 144–147 °C; ^{1}H NMR ($CHCl_3$) δ 1.38 (m, 4 H), 1.78 (m, 8 H), 4.07 (t, 8 H), 6.67 (t, 2 H), 7.19 (d, 4 H).

Bis-Roof Porphyrin, H_2(BRP). To a solution of 0.36 g (0.53 mmol) of $\alpha,\beta,\alpha,\beta$-*meso*-tetrakis(*o*-aminophenyl)porphyrin in 500 mL of dry CH_2Cl_2 containing 0.5 mL of *N*-methylmorpholine in an ice bath was added a solution of 0.50 g (1.2 mmol) of the diacid chloride, **3c**, in 100 mL of dry CH_2Cl_2. The solution was then stirred for 20 h at that temperature. After the volume of the reactant was reduced to 200 mL, the organic solution was washed twice with H_2O and then dried over anhydrous Na_2SO_4. After filtration, the solution was evaporated to dryness. The residue was purified by silica-gel column chromatography (benzene, 3 × 35 cm) and elution with benzene/acetone (30/1), yielding the desired porphyrin, 0.27 g (32%): ^{1}H NMR ($CDCl_3$) δ −3.17 (s, 2 H), 1.02 (m, 8 H), 1.29 (m, 16 H), 3.44 (s, 16 H), 5.84 (t, 4 H), 5.94 (d, 8 H), 6.86 (s, 4 H), 7.60 (t, 4 H), 7.91 (t, 4 H), 8.05 (d, 4 H), 8.43 (d, 4 H), 8.89 (s, 8 H); vis ($CHCl_3$) λ 402 (sh), 421.8 (Soret), 482 (sh), 515.0, 548.8, 587.4, 642.5 nm. Anal. Calcd for $C_{92}H_{82}N_8O_{12}\cdot CHCl_3$: C, 69.33; H, 5.19; N, 6.96. Found: C, 69.98; H, 5.49; N, 7.24.

Zinc Bis-Roof Porphyrin, Zn(BRP). To a solution of 0.11 g (0.068 mmol) of H_2(BRP) in 20 mL of THF was added 0.20 g of $ZnCl_2$ and 0.1 mL of 2,6-lutidine. After being refluxed for 6 h, the reaction mixture was evaporated; then the residue was dissolved in 100 mL of chloroform. The organic layer was washed twice with 200 mL of H_2O and dried over anhydrous Na_2SO_4. After removal of the solvent, the solid was purified on a silica-gel column ($CHCl_3$, 3 × 25 cm), eluting with chloroform/ether (10/1); yield 0.11 g (95%): ^{1}H NMR ($CDCl_3$) δ 1.03 (m, 8 H), 1.30 (m, 16 H), 3.38 (s, 16 H), 5.81 (t, 4 H), 5.87 (s, 8 H), 6.98 (s, 4 H), 7.59 (t, 4 H), 7.88 (t, 4 H), 8.13 (d, 4 H), 8.39 (d, 4 H), 8.91 (s, 8 H); vis (toluene) λ 430.0 (Soret), 553.6, 590.4 nm; vis ($CHCl_3$) λ 422.5 (Soret), 548.5, 585 (sh) nm. Anal. Calcd for $C_{92}H_{80}N_8O_{12}\cdot CHCl_3\cdot 2H_2O$: C, 65.30; H, 5.01; N, 6.55. Found: C, 65.73; H, 5.03; N, 6.18.

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Supplementary Material Available: Table SI, giving equilibrium data for the binding of azetidine and butylamine, and Figure S1, showing the 400-MHz ^{1}H NMR spectrum for H_2(BRP) in $CDCl_3$ (2 pages). Ordering information is given on any current masthead page.

The Question of Metal–Metal Bonding in Edge-Sharing Bioctahedral Mo(III) Complexes. Variable Temperature ^{1}H NMR Study of $Mo_2Cl_6(PMe_xEt_{3-x})_4$ (x = 0–3) and the Mechanism of the Face-Sharing to Edge-Sharing Transformation

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Abstract: Homoleptic (L = L′) and heteroleptic (L ≠ L′) edge-sharing bioctahedral Mo(III) complexes of formula $Mo_2Cl_6L_{4-n}L'_n$ (n = 0–2; L, L′ = PMe_xEt_{3-x}; x = 0–3) have been generated in solution and investigated by paramagnetic ^{1}H NMR spectroscopy. The derivatives have been obtained by interaction of a face-sharing bioctahedral $Mo_2Cl_6L_3$ precursor with L′ or, for the case of n = 0, L = L′ = $PMeEt_2$, by brief reflux of $MoCl_3(THF)_3$ and 2 equiv of the phosphine in toluene. The $Mo_2Cl_6L_3$/L′ interaction occurs regioselectively to afford a single product, and this is followed by other processes, one of them being ligand exchange to generate a single stereoisomer of formula $Mo_2Cl_6L_2L'_2$. A relatively simple mechanistic scheme which is based on the previously proven higher trans effect of phosphine ligands with respect to chlorides for pseudooctahedral Mo(III) coordination compounds allows a rationalization of all stereochemical results. The paramagnetic shift of the phosphine proton resonances for the edge-sharing bioctahedral $Mo_2Cl_6L_{4-n}L'_n$ compounds increases as the Me/Et ratio for the phosphine substituents decreases, and it is found in general that, for a given Me/Et ratio, the system is more paramagnetic when more ethyl groups are located on equatorial phosphines. For instance, $Mo_2Cl_6(PEt_3)_2$(*ax*-$PMe_3)_2$ is more paramagnetic than the isomeric $Mo_2Cl_6(PMe_3)_2$(*ax*-$PEt_3)_2$. Variable temperature ^{1}H NMR measurements have been carried out for $Mo_2Cl_6(PMe_xEt_{3-x})_4$ (x = 0–3) and for $Mo_2Cl_6(PEt_3)_{4-n}$(*ax*-$PMe_3)_n$ (n = 1, 2). These investigations allow considerations on the ground electronic structure of these materials to be made.

Introduction

We have recently discovered a tremendous effect of minor changes in the nature of phosphine substituents on the ability of the Mo atoms in edge-sharing bioctahedral (ESBO) $Mo_2Cl_6(PR_3)_4$ to bind to each other.[1] When PR_3 = PEt_3, the two metals are separated by 3.730 (1) Å,[2] indicating no direct bonding interaction and the metals are communicating only through a weak antiferromagnetic coupling, whereas when PR_3 = PMe_2Ph, the two metals are separated by 2.8036 (8) Å, and the compound is almost completely diamagnetic, consistent with the pairing of the six metal

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