

Solvent Effects on Chelate Cooperativity: Comparative Analysis of Intramolecular H-bonding Interactions in Toluene, 1,1,2,2-Tetrachloroethane and Cyclohexanone

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5 Partially Bound States Analysis

One H-bond. For complexes that can make a single intramolecular H-bond, the observed association constant is given by the sum of the equilibrium constants for the fully bound and partially bound states (Equation S1).

$$K_{obs} = K_0(1 + \sigma_1 K_1 EM_1) \quad (S1)$$

where K_0 is intermolecular association constant for formation of the zinc-nitrogen interaction, K_1 is the intermolecular association constant for formation of the H-bonding interaction, EM_1 is the effective molarity for the intramolecular interaction, and σ_1 is a statistical factor that describes the degeneracy of the fully bound state. In the complexes discussed here, the porphyrins all have four identical H-bond donor sites, so $\sigma_1 = 4$.

So, the parameter f required for the determination of EM using the double mutant cycle analysis is given by Equation S2.

$$f = 1 + \sigma_1 K_1 EM_1 \quad (S2)$$

15 The population of the fully bound state, P_b , is given by

$$P_b = \frac{\sigma_1 K_1 EM_1}{1 + \sigma_1 K_1 EM_1} \quad (S3)$$

and the population of the partially bound state, P_f , where the intramolecular H-bond is not made is given by

$$P_f = \frac{1}{1 + \sigma_1 K_1 EM_1} \quad (S4)$$

Two H-bonds. For complexes that can make two identical intramolecular H-bonds, the observed association constant is given by the sum of the equilibrium constants for the fully bound and two partially bound states (Equation S5).

$$f = 1 + \sigma_1 K_1 EM_1 + \sigma_{11} (K_1 EM_1)^2 \quad (S5)$$

We assume that the effective molarity for the formation of the first H-bond is not affected by the formation of the second H-bond, so that $K_1 EM_1$ is a constant (Equation S6).

$$K_1 EM_1 = \frac{-\sigma_1 + \sqrt{\sigma_1^2 - 4\sigma_{11}(1 - e^{-\Delta\Delta G^\circ/RT})}}{2\sigma_{11}} \quad (S6)$$

25 Assumptions about the statistical factors are required in order to deduce values of $K_1 EM_1$. For the partially bound, singly H-bonded complex, $\sigma_1 = 8$. For the fully bound, doubly H-bonded complex, there are two degenerate states in which two H-bonds are made with phenol groups on trans-related meso positions on the porphyrin, and four degenerate states in which two H-bonds are made with phenol groups on cis-related meso positions. Models suggest that all states are equally accessible, so $\sigma_{11} = 6$, but this value may be as low as 2, if the cis states are inaccessible.

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Table S1 Statistical factors for complexes formed with ligands L2a-L6a.

| | Ligand | | | | |
|---------------|--------|-----|-----|-----|-----|
| | L2a | L3a | L4a | L5a | L6a |
| σ_1 | 4 | 8 | 4 | 4 | 8 |
| σ_{11} | | 12 | | | 12 |

Statistically-corrected equilibrium constants for formation of intramolecular H-bonds

Table S2 *K_{EM}* values for formation of an intramolecular phosphonate diester-phenol H-bond.^a

| Porphyrin | Ligand | | | | |
|-----------|--------------|--------------|--------------|--------------|--------------|
| | L2a | L3a | L4a | L5a | L6a |
| P1a | 0.9 | ^b | ^b | 1.2 | ^b |
| P2a | ^b | ^b | ^b | 0.4 | 0.2 |
| P3a | 1.1 | ^b | ^b | ^b | ^b |
| P4a | ^b | ^b | ^b | ^b | ^b |

^a Errors are ±50%.

^b These complexes do not make detectable H-bonds.

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H-bond occupancy

Table S3 Occupancy of the H-bonded state for phosphonate diester-phenol H-bonds (%).

| Porphyrin | Ligand | | | | |
|-----------|--------|-----|-----|-----|-----|
| | L2a | L3a | L4a | L5a | L6a |
| P1a | 78 | | | 82 | |
| P2a | | | | 59 | 40 |
| P3a | 81 | | | | |
| P4a | | | | | |

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