Comparative Thermochemistry of Metalloporphyrin Isomers as a Function of Metal Ion Size. A Possible Insight into Nature's Choice of Porphyrin over Isomeric Ligands

Abhik Ghosh* and Torgil Vangberg

Institute of Chemistry, Faculty of Science, University of Tromsø, N-9037 Tromsø, Norway

Received July 10, 1998

Nonlocal density functional calculations have been used to compare the stabilities of metalloporphyrin isomers as a function of metal ion size, divalent Ni, Zn, Pd, and Cd ions having been examined. Ordinary porphyrin is found to form the most stable bis-*N*-deprotonated dianions and metal complexes compared to the other isomeric ligands, a finding of potential relevance to the question of why Nature has chosen porphyrin-based cofactors. The various dianionic ligands may be ranked as follows in increasing order of relative energy: [1.1.1.1] < [2.1.1.0] < [2.0.2.0] < [2.1.0.1] < *trans*-[3.0.1.0] < *cis*-[3.0.1.0]. This order differs from that of the stabilities of the free bases. An interesting result reminescent of a recent study of corrole isomers is that the order of stabilities of the isomeric metalloporphyrins is metal-dependent and undergoes reversals with changing size of the coordinated metal ion. Thus, the small Ni(II) ion forms the most stable complex with the [2.0.2.0] porphyrin isomer (with the exception of normal porphyrin) and relatively higher-energy complexes with the [2.1.0.1] ligand. In contrast, the Cd(II) ion forms relatively stable complexes with the [2.1.0.1] porphyrin isomer and relatively unstable complexes with the [2.0.2.0] ligand. Another interesting result concerns cis−trans isomerism of the [3.0.1.0] skeleton: the *trans*-[3.0.1.0] ligand forms increasingly more stable complexes relative to the cis stereoisomeric ligand with increasing size of the coordinated metal ion.

Introduction

The chemistry of porphyrin isomers and analogs is an exciting new direction in porphyrin-related research.[1] Six porphyrin isomers with N_4 cores (Figure 1) have been prepared so far,[2] in addition to the inverted porphyrins which have the remarkable property of forming complexes with metal−carbon bonds.[3,4] Quantum chemical studies have furnished valuable insights into the chemistry of porphyrin isomers, a key contribution being the development of a broad picture of the relative thermodynamic stabilities of the free-base forms of the various isomers.[5,6] These relative stabilities have been correlated with structural features of the molecular skeleton such as strained bond lengths and angles and with the presence of hydrogen-bonding interactions and H···H repulsions in the central regions of the macrocycle.[5,6]

For corrole isomers with N_4 cores, theoretical studies have gone a step further and uncovered interesting correlations between the size of the central metal-binding cavities of the different macrocycles and the ionic radii of coordinated metal ions.[7] An interesting finding was that the relative stabilities of two corrole isomers undergo a reversal with increasing size of the coordinated metal ion. A similar study has not been reported for metalloporphyrin isomers. Given the diversity of electronic structures, oxidation states, and chemical reactivity of transition metal centers coordinated to normal porphyrin ligands, it is reasonable to expect that a similarly rich coordination chemistry should be found for transition metal complexes of the porphyrin isomers as well. However, before undertaking detailed studies of such issues as spin states and electron distributions, it is desirable to develop an understanding of a more basic issue, viz. the stability of metalloporphyrin isomers as a function of metal ion size. Here we present a study of this topic, based on nonlocal density functional theoretical (DFT) calculations[8,9] on the relative stabilities of Ni(II), Zn(II), Pd(II), and Cd(II) complexes of the six porphyrin isomers with N_4 cores that have

---

* To whom correspondence should be addressed. Fax: +47 77644765. E-mail: abhik@chem.uit.no.

(1) (a) Vogel, E. *J. Heterocycl. Chem.* **1996**, *33*, 1461. (b) Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted and Isomeric Porphyrins*; Elsevier: Amsterdam, 1997.

(2) (a) Porphycene: Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257. (b) (i) Corrphycene: Sessler, J. L.; Brucker, E. A.; Weghorn, S. J.; Kisters, M.; Schäfer, M.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2308. (ii) Aukaloo, M. A.; Guilard, R. *New J. Chem.* **1994**, *18*, 1205. (iii) Falk, H.; Chen, Q.-Q. *Monatsh. Chem.* **1996**, *127*, 69. (c) Hemiporphycene: Callot, H. J.; Rohrer, A.; Tschamber, T.; Metz, B. *New J. Chem.* **1995**, *19*, 155. (d) Isoporphycene: Vogel, E.; Broring, M.; Erben, C.; Demuth, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 353.

(3) For a review on carbaporphyrins, see: Nilsen, H. J.; Ghosh, A. *Acta Chem. Scand.* **1998**, *52*, 827.

(4) (a) Chmielewski, P. J.; Latos-Grazynski, L.; Glowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690 and references therein. (b) For a theoretical study, see: Ghosh, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1028.

(5) Ghosh, A.; Jynge, K. *J. Phys. Chem. B* **1997**, *101*, 5459.

(6) Wu, Y.-D.; Chan, K. W. K.; Yip, C.-P.; Vogel, E.; Plattner, D. A.; Houk, K. N. *J. Org. Chem.* **1997**, *62*, 9240.

(7) Ghosh, A.; Jynge, K. *Chem. Eur. J.* **1997**, *3*, 823.

(8) All calculations were carried out with the ADF program system, using the VWN local exchange-correlation functional (Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200), the Perdew−Wang 1991 nonlocal corrections (Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671), triple-ζ plus polarization Slater-type basis sets, a fine mesh for numerical integration of matrix elements, a spin-restricted formalism, and full geometry optimizations within the symmetry constraints shown in Table 2. For additional technical details, the reader is referred to the ADF program manual which can be obtained from Scientific Computing and Modelling, Department of Theoretical Chemistry, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands. Except for the *trans*-[3.0.1.0] dianion and complexes, all molecules were required to be planar as a result of the symmetry constraints. The mirror plane in the *trans*-[3.0.1.0] systems is perpendicular to the mean molecular plane and thus permits nonplanarity.

(9) For a review of the performance of density functional calculations on porphyrins, see: Ghosh, A. *Acc. Chem. Res.* **1998**, *31*, 189.

10.1021/ic9807994 CCC: $15.00

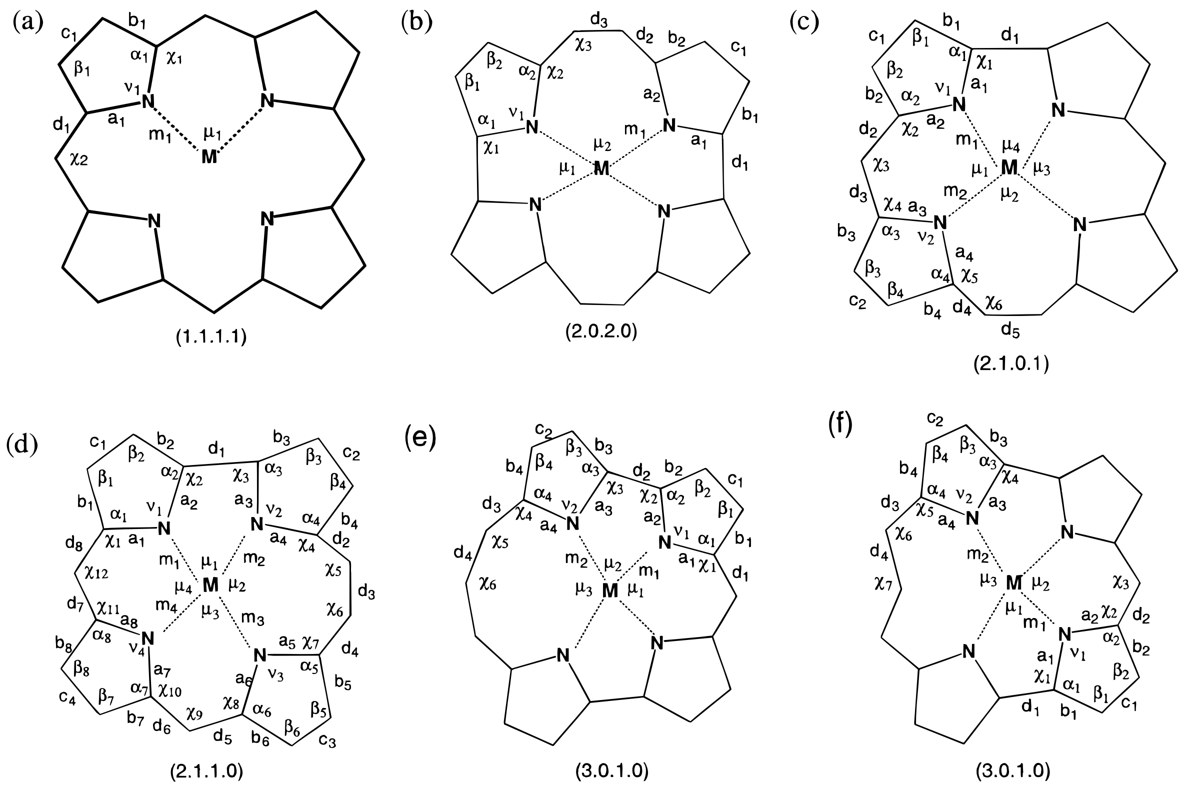

Figure 1. Molecular skeletons of different metalloporphyrin isomers. The isomers are described by the standard notation, (*p*.*q*.*r*.*s*), where *p*, *q*, *r*, and *s* are the numbers of methine units in the interpyrrole linkers around the macrocycle. Thus, *p*, *q*, *r*, and *s* can assume values of 0, 1, 2, 3, and 4, with the constraint that $p + q + r + s = 4$. Table 1 presents selected optimized geometry parameters (Å, deg).

been prepared to date. Figure 1 includes diagrams of the different porphyrin isomer skeletons, and Table 1 includes relevant bond lengths and angles.

Results and Discussion

Table 2 presents the relative energies of various metalloporphyrin isomers as well as the relative energies of the bis-*N*-deprotonated dianionic forms of the free base porphyrin isomers. Table 2 also includes semiempirical PM3 relative energies for certain zinc complexes of porphyrin isomers, recently reported by Zandler and D'Souza.[10] Table 3 presents a measure of the metal ion affinities of the various porphyrin isomer dianions. The entries in Table 3 are given by $|E_b(P_iM) - E_b(P_i^{2-})|$, where E_b refers to the total bonding energy of a species (defined as the total energy of the species relative to the total energies of the constituent atoms), P_iM is a metalloporphyrin isomer, and P_i^{2-} is a porphyrin isomer dianion. The subtraction of the dianion energies is necessary for projecting out differences in stability of the ligand skeleton from the metal ion affinity data in Table 3. The higher an entry in Table 3, the higher the metal ion affinity. Table 1 presents selected optimized structural data on the various molecules studied. In general, the optimized geometrical parameters of the metalloporphyrin isomers are in excellent agreement with experimental crystallographic results on closely similar molecules. Such agreement between theory and experiment is precedented in many nonlocal density functional theoretical studies,[9] and, accordingly, we shall skip a tedious comparison of various calculated and experimental geometrical parameters. The results of this study afford many insights into the thermochemistry of metalloporphyrin isomers, as discussed below.

Stability Trends of Free Bases versus Dianions. The relative energies of the dianions reflect the intrinsic stabilities of the skeletons of the different porphyrin isomers. In increasing order of relative energy (kcal/mol), the porphyrin isomer dianions may be ranked as follows: [1.1.1.1] (0.00) < [2.1.1.0] (6.54) < [2.0.2.0] (7.34) < [2.1.0.1] (9.75) < *trans*-[3.0.1.0] (14.00) < *cis*-[3.0.1.0] (21.34). This order differs from that of the relative energies (kcal/mol) of the most stable tautomers of the free bases, which is as follows: [2.0.2.0] (−1.5) < [1.1.1.1] (0.0) < [2.1.1.0] (5.1) < [2.1.0.1] (12.0) < *cis*-[3.0.1.0] (19.0) < *trans*-[3.0.1.0] (26.2).[6] The free-base energies reflect not only the strain energies of the molecular skeletons but also N−H···N hydrogen bonding interactions and H···H repulsions in the interior of the macrocycles.[5,6] For the free bases, the [2.0.2.0] system is the most stable porphyrin isomer, even more stable than porphine, which is a result of extremely short, strong hydrogen bonds in the [2.0.2.0] free base.[6] Among the dianions, both the [1.1.1.1] and [2.1.1.0] ring systems are more stable than the [2.0.2.0] system, presumably reflecting less skeletal strain in the former. Note also that the *cis*-[3.0.1.0] free base is significantly more stable than the trans free base, but the trend is reversed for the dianions.

Global Stability of Porphine. An important result is that ordinary porphyrin forms the most stable dianion and also the most stable metal complexes, for each metal considered, compared to the other isomeric ligands. This may not be surprising, but, to our knowledge, this result has not been reported elsewhere in the literature. Indeed, Zandler and D'Souza report that Mg(II) porphine is *less stable* than the magnesium complexes of all the porphyrin isomers (except *trans*-[3.0.0.0] porphyrin, which they did not consider) considered here.[10] In light of the present results, these results of Zandler and D'Souza seem to be unrealistic.[11] In addition, the

---

(10) Zandler, M. E.; D'Souza, F. D. *J. Mol. Struct. (THEOCHEM)* **1997**, *401*, 301.

Table 1. Distances (Å) and Angles (deg) for the Metalloporphyrin Isomers Shown in Figure 1; Roman Letters Denote Distances and Greek Letters Denote Angles

	Ni	Zn	Pd	Cd
(a) For 1.1.1.1				
m1	1.972	2.058	2.047	2.153
a1	1.380	1.372	1.372	1.369
b1	1.438	1.446	1.443	1.451
c1	1.360	1.366	1.363	1.371
d1	1.380	1.398	1.392	1.417
μ1	90	90	90	90
ν1	104.79	107.13	107.25	109.97
α1	110.93	109.52	109.32	107.56
β1	106.68	106.92	107.06	107.45
χ1	125.53	125.07	129.51	124.90
χ2	123.72	126.99	126.23	130.17
(b) For 2.0.2.0				
m1	1.917	2.011	2.010	2.126
a1	1.372	1.363	1.374	1.366
a2	1.372	1.360	1.361	1.355
b1	1.428	1.435	1.434	1.442
b2	1.447	1.449	1.450	1.453
c1	1.369	1.376	1.372	1.381
d1	1.395	1.425	1.408	1.449
d2	1.402	1.415	1.411	1.430
d3	1.385	1.399	1.395	1.416
μ1	84.02	82.654	80.94	77.84
μ2	95.98	97.346	99.07	102.16
ν1	106.76	109.02	109.10	111.23
α1	111.02	109.25	108.94	107.37
α2	108.54	107.81	107.43	106.68
β1	105.63	106.30	106.36	107.00
β2	108.05	107.62	108.16	107.73
χ1	115.28	116.86	115.92	116.58
χ2	129.65	127.40	128.43	126.08
χ3	131.83	134.77	134.76	138.57
(c) For 2.1.0.1				
m1	1.918	2.073	2.008	2.175
m2	2.010	2.045	2.085	2.138
a1	1.362	1.349	1.361	1.351
a2	1.365	1.358	1.358	1.359
a3	1.395	1.389	1.388	1.383
a4	1.380	1.369	1.367	1.362
b1	1.426	1,438	1.432	1.443
b2	1.438	1.446	1.440	1.449
b3	1.434	1.438	1.439	1.444
b4	1.441	1.440	1.443	1.444
c1	1.377	1.381	1.380	1.384
c2	1.358	1.367	1.362	1.374
d1	1.403	1.432	1.423	1.459
d2	1.380	1.395	1.393	1.413
d3	1.390	1.406	1.403	1.422
d4	1.404	1.417	1.413	1.436
d5	1.370	1.386	1.380	1.403
μ1	78.92	75.36	77.23	73.19
μ2	88.84	87.91	89.51	87.29
μ3	103.41	108.81	103.77	112.06
ν1	107.13	109.02	109.67	111.09
ν2	104.43	106.98	106.81	109.62
α1	110.47	109.33	108.42	107.71
α2	109.25	108.48	107.80	107.06
α3	110.95	109.01	109.22	107.32
α4	110.85	109.64	109.67	108.08
β1	106.15	106.43	106.82	107.02
β2	107.00	106.73	107.29	107.16
β3	106.73	107.25	107.17	107.65
β4	107.04	107.12	107.14	107.38
χ1	112.35	114.11	113.45	114.80
χ2	120.79	119.79	120.83	120.87
χ3	123.50	126.52	126.54	129.35
χ4	128.56	128.53	128.70	127.12
χ5	132.11	129.80	130.56	128.21
χ6	134.25	137.25	136.40	140.31
(d) For 2.1.1.0				
m1	1.895	2.027	1.988	2.154
m2	1.986	2.104	2.062	2.163
m3	1.967	2.006	2.055	2.113
m4	1.950	2.039	2.038	2.150
a1	1.370	1.363	1.362	1.361
a2	1.358	1.347	1.358	1.351
a3	1.373	1.364	1.375	1.365
a4	1.374	1.360	1.362	1.356
a5	1.388	1.373	1.374	1.363
a6	1.389	1.385	1.382	1.381
a7	1.372	1.365	1.364	1.366
a8	1.383	1.372	1.375	1.368
b1	1.442	1.448	1.446	1.456
b2	1.432	1.441	1.438	1.447
b3	1.423	1.433	1.428	1.438
b4	1.440	1.443	1.443	1.447
b5	1.447	1.446	1.450	1.451
b6	1.435	1.440	1.442	1.447
b7	1.436	1.444	1.441	1.448
b8	1.437	1.446	1.442	1.450
c1	1.373	1.378	1.375	1.381
c2	1.371	1.378	1.374	1.383
c3	1.355	1.364	1.359	1.370
c4	1.365	1.370	1.368	1.374
d1	1.379	1.396	1.392	1.413
d2	1.395	1.424	1.412	1.451
d3	1.395	1.410	1.405	1.427
d4	1.376	1.390	1.388	1.408
d5	1.405	1.419	1.414	1.433
d6	1.382	1.400	1.393	1.415
d7	1.384	1.402	1.399	1.423
d8	1.392	1.409	1.405	1.426
μ1	86.68	86.23	87.99	85.99
μ2	81.04	77.84	78.63	74.71
μ3	97.38	99.70	100.34	105.32
μ4	94.91	96.24	93.05	93.98
ν1	107.28	109.28	109.86	111.42
ν2	105.45	107.62	107.81	110.51
ν3	104.71	107.38	107.10	109.94
ν4	105.61	107.99	108.07	110.10
α1	108.89	107.91	107.36	106.59
α2	110.50	109.31	108.44	107.56
α3	111.78	110.14	109.69	107.82
α4	109.71	109.08	108.59	107.31
α5	110.00	108.77	108.88	107.50
α6	111.26	109.17	109.50	107.36
α7	110.78	109.38	109.24	107.76
α8	110.06	108.69	108.46	107.35
β1	107.28	107.21	107.62	107.44
β2	106.06	106.30	106.71	107.00
β3	105.59	106.04	106.35	106.93
β4	107.46	107.12	107.56	107.44
β5	107.61	107.72	107.65	107.77
β6	106.43	106.96	106.86	107.45
β7	106.50	106.71	106.81	107.20
β8	107.05	107.25	107.42	107.57
χ1	121.56	121.45	121.90	121.89
χ2	113.73	114.73	114.33	115.10
χ3	115.03	116.49	115.67	115.88
χ4	128.58	126.01	127.21	125.54
χ5	130.40	133.35	133.56	137.92
χ6	134.56	137.61	137.15	140.15
χ7	134.00	131.89	132.34	129.27
χ8	127.41	127.41	127.20	126.44
χ9	125.90	129.21	127.99	131.47
χ10	124.25	123.49	124.14	124.34
χ11	126.06	125.41	126.35	125.30
χ12	121.56	125.22	125.00	128.66
(e) For 3.0.1.0				
m1	1.858	2.029	1.970	2.181
m2	1.969	2.007	2.064	2.103
a1	1.371	1.363	1.363	1.363
a2	1.353	1.344	1.428	1.352
a3	1.375	1.370	1.377	1.365
a4	1.380	1.368	1.367	1.360
b1	1.440	1.449	1.446	1.450
b2	1.431	1.440	1.438	1.442
b3	1.421	1.428	1.428	1.436
b4	1.448	1.445	1.448	1.447
c1	1.379	1.383	1.381	1.384
c2	1.369	1.377	1.392	1.382
d1	1.394	1.410	1.408	1.422
d2	1.409	1.437	1.427	1.458
d3	1.401	1.410	1.407	1.421
d4	1.396	1.412	1.408	1.432
μ1	86.11	82.06	88.15	81.36
μ2	83.44	81.16	79.79	75.87
μ3	107.01	115.61	112.27	126.90
ν1	108.75	110.20	111.37	111.04
ν2	105.80	108.25	107.95	110.89
α1	107.72	107.20	106.17	106.70
α2	109.68	108.92	107.71	107.92
α3	111.83	109.68	109.75	107.52
α4	108.81	108.03	108.05	106.77
β1	107.72	107.43	108.04	107.55
β2	106.13	106.26	106.71	106.80
β3	105.55	106.34	106.33	107.13
β4	108.01	107.71	107.92	107.68
χ1	122.03	121.60	122.72	122.27
χ2	113.29	114.35	113.70	114.85
χ3	116.07	117.59	116.65	116.45
χ4	133.60	130.14	131.16	127.00
χ5	139.85	141.10	141.30	143.17
χ6	138.76	143.24	142.77	148.67
(f) For 3.0.1.0				
m1	1.871	2.047	1.971	2.166
m2	2.090	2.084	2.159	2.180
a1	1.361	1.348	1.358	1.353
a2	1.374	1.364	1.365	1.366
a3	1.363	1.361	1.365	1.359
a4	1.391	1.380	1.380	1.373
b1	1.427	1.438	1.435	1.439
b2	1.438	1.447	1.444	1.448
b3	1.428	1.432	1.433	1.435
b4	1.434	1.435	1.438	1.440
c1	1.379	1.382	1.381	1.385
c2	1.377	1.382	1.378	1.387
d1	1.410	1.434	1.426	1.460
d2	1.394	1.408	1.406	1.422
d3	1.408	1.415	1.418	1.429
d4	1.383	1.392	1.387	1.406
μ1	80.04	78.291	77.237	74.752
μ2	88.11	83.154	89.689	83.173
μ3	111.81	120.099	115.835	127.266
ν1	108.32	109.634	110.822	110.741
ν2	105.96	108.051	107.948	110.337
α1	109.70	109.201	107.864	108.163
α2	107.96	107.512	106.477	106.732
α3	111.28	109.536	109.612	107.847
α4	109.34	108.473	108.334	107.100
β1	106.32	106.220	106.822	106.668
β2	107.69	107.431	108.014	107.692
β3	106.09	106.730	106.572	107.211
β4	107.27	107.165	107.507	107.424
χ1	114.35	114.715	114.571	115.175
χ2	122.65	122.240	123.248	122.584
χ3	121.69	124.810	125.365	128.202
χ4	115.23	116.660	115.679	116.303
χ5	121.78	120.061	121.546	119.212
χ6	113.21	114.964	114.384	118.722
χ7	136.44	138.067	141.912	136.665

correct, symmetric structures of many porphyrin isomers have large imaginary frequencies with the semiempirical AM1 and PM3 methods used by these authors, showing that, unlike DFT, these theories provide a highly defective picture of the ground-state potential energy surfaces of these compounds.[9]

Table 3 also shows that among all the porphyrin isomers considered, ordinary porphyrin has the highest metal ion affinity for each metal studied. Thus, the high stability of normal metalloporphyrins compared to the other isomers is a combined effect of the low energy and high metal ion affinity of the [1.1.1.1] porphyrin skeleton.

It is interesting to speculate whether the globally highest stability and metal ion affinities of the [1.1.1.1] porphyrin ring system are related to Nature's choice of ordinary porphyrin-

Table 2. Energies (kcal/mol) of Porphyrin Isomer Bis-*N*-deprotonated Dianions and Metal Complexes Relative to Corresponding Normal Porphine Derivative as the Zero Level

isomer	point group	Ni	Zn	Pd	Cd	dianion
[1.1.1.1]	D_{4h}	0.00	0.00 (0.0)[a]	0.00	0.00	0.00
[2.0.2.0]	D_{2h}	10.05	17.05 (29.0)[a]	21.25	25.78	7.34
[2.1.0.1]	C_{2v}	18.36	17.01 (18.0)[a]	22.00	16.04	9.75
[2.1.1.0]	C_s	10.69	12.22 (12.8)[a]	15.69	14.38	6.54
cis-[3.0.1.0]	C_{2v}	25.19	32.32 (39.6)[a]	38.20	36.61	21.34
trans-[3.0.1.0]	C_s	38.86	38.73	44.54	34.99	14.00

[a] The numbers in parentheses are PM3 energies obtained from ref 10.

Table 3. Metal Ion Affinities (kcal/mol) of Porphyrin Isomer Dianions[a]

isomer	Ni	Zn	Pd	Cd
[1.1.1.1]	183.2	98.5	123.4	71.6
[2.0.2.0]	180.4	88.8	108.8	53.1
[2.1.0.1]	174.5	91.3	111.1	65.3
[2.1.1.0]	179.0	92.8	114.2	63.7
cis-[3.0.1.0]	179.3	87.5	106.5	56.3
trans-[3.0.1.0]	158.3	73.8	92.8	50.6

[a] The higher a certain entry, the higher the metal ion affinity.

based cofactors over isomeric systems. Suitably substituted derivatives of all the isomers studied here, with the exception of the [3.0.1.0] isomers, can be regarded as formally derivable from porphobilinogen units. At this point, however, it is not possible to say whether Nature's choice reflects the thermodynamic effect that is studied here or mechanistic considerations.

A parallel to our previous study on corrole isomers may be drawn.[7] Like normal porphyrin, normal corrole also forms the most stable metal complexes, relative to its isomers. This holds for a wide range of metal ion sizes [Ga(III) to In(III)], in spite of the fact that normal corrole has a rather small central cavity. The reason is that the normal corrole skeleton is much more stable and strain-free relative to the isomeric corroles.

Porphycene, Corrphycene, and Hemiporphycene. Table 2 shows that, in general, the dianions and metal complexes of the [2.0.2.0] (porphycene), [2.1.0.1] (corrphycene), and [2.1.1.0] (hemiporphycene) isomers are significantly more stable than analogous derivatives of the two [3.0.1.0] (isoporphycene) stereoisomers, a trend that also holds for the free bases. This reflects the significantly higher skeletal strain of the [3.0.1.0] isomers, especially the bond angle strain at the carbon atoms of the $(CH)_3$ inter-pyrrole linker.

Among the [2.0.2.0], [2.1.0.1], and [2.1.1.0] isomers, the relative stabilities of the metal complexes undergo interesting reversals with changing size of the coordinated metal ion (see Table 2). Thus, the small Ni(II) cation, which has an ionic radius of 0.63 Å for square planar four-coordination, forms a stable complex with the [2.0.2.0] porphyrin isomer and relatively higher-energy complexes with the [2.1.0.1] ligand. In contrast, the large Cd(II) cation, whose ionic radius for four-coordination is 0.92 Å,[12] forms relatively stable complexes with the [2.1.0.1] porphyrin isomer and relatively higher-energy complexes with the [2.0.2.0] ligand. This is clearly related to the fact that the [2.0.2.0] ligand has a significantly smaller central metal-binding cavity than the [2.1.0.1] ligand. Among all the porphyrin isomers considered, the relative energies of the [2.0.2.0] complexes (Table 2) exhibit a clean monotonically increasing variation with increasing radius of the coordinated metal ion. Table 1 also shows that the metal−nitrogen bonds are systematically shorter for the [2.0.2.0] complexes than for [2.1.0.1] complexes, the difference being the greatest for Ni(II): the Ni−N bond lengths in the [2.0.2.0] complex are 1.917 Å each, compared to 1.972 Å for the normal porphyrin complex and a mean length of 1.964 Å for the [2.1.0.1] complex. These results are reminiscent of what we found previously for [2.0.1] and [2.1.0] corrole complexes.[7] The relatively small Ga(III) ion forms a more stable complex with [2.0.1]corrole, which has a smaller central cavity, than with [2.1.0]corrole, which has a larger central cavity. For the larger In(III) cation, the trend is reversed, and the intermediate Sc(III) ion represents the crossover point.

The Zn(II) and Pd(II) ions have ionic radii of 0.74 and 0.78 Å,[12] respectively, which fall between those of Ni(II) and Cd(II). The Zn(II) and Pd(II) ions form roughly equally stable complexes with the [2.0.2.0] and [2.1.0.1] ligands. This is understandable: the relative compression of the metal−nitrogen bonds in the [2.0.2.0] complexes costs about as much energy as the relative elongation of these bonds in the [2.1.0.1] complexes.

The energetics of the [2.1.1.0] metal complexes deserves a comment (see Table 2). If the energies of metalloporphyrin isomers are averaged over all the metals considered, the [2.1.1.0] complexes have the lowest average energy, with the exception of ordinary porphyrin. This reflects not only the relatively low energy of the [2.1.1.0] skeleton, but also the rather high affinity of this ring system for metal ions of diverse sizes. The latter may be related to the low symmetry of this molecule, which may be associated with a flexible skeleton that better accommodates metal ions of diverse sizes.

***cis*- and *trans*-Isoporphycene.** The *cis*-[3.0.1.0] ligand clearly forms the most stable complexes with the small Ni(II) ion, all other complexes being significantly more unstable relative to the analogous porphyrin complexes. A factor contributing to the relative stability of the Ni(II) complex appears to be that the N−M−N bond angles are significantly more strained for the other complexes, the ideal bond angle being a right angle for approximately square planar complexes.

Irradiation of the Pd(II) complex of *cis*-[3.0.1.0] porphyrin leads to a mixture of cis and trans complexes in photochemical equilibrium,[2d] suggesting that the two stereoisomers are of comparable stability. Our calculations are in excellent agreement with this observation: the steroisomers of the Zn(II), Pd(II), and Cd(II) complexes are indeed of comparable stability, differing in energy by no more than 6 kcal/mol. The Cd(II) complex of the *trans*-[3.0.1.0] ligand is actually more stable than the analogous cis complex at the present level of theory and within the symmetry constraints used. Only for the smallest metal ion considered, Ni(II), is the cis complex strongly preferred over the trans complex.

The inward-pointing methine hydrogen of the *trans*-[3.0.1.0] complexes sterically interferes with the central metal ion, resulting in nonplanar molecular geometries, a model of the Cd(II) complex being shown in Figure 2. To evaluate the driving force leading to these nonplanar geometries, we also performed C_{2v}-constrained optimizations of the *trans*-[3.0.1.0] complexes for the four metal ions of interest. Relative to the nonplanar C_s structures, the planar C_{2v} structures are higher in energy by 2.54, 2.01, 1.81, and 5.67 kcal/mol for the Ni(II), Zn(II), Pd-

---

(11) Certain of the PM3 energies[10] shown in Table 2 are in excellent agreement with DFT results, but certain others are not and the magnesium results in ref 10 certainly seem to be very unreasonable.

(12) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr. B* **1969**, *25*, 925. (b) Shanon, R. D. *Acta Crystallogr. A* **1976**, *32*, 751.

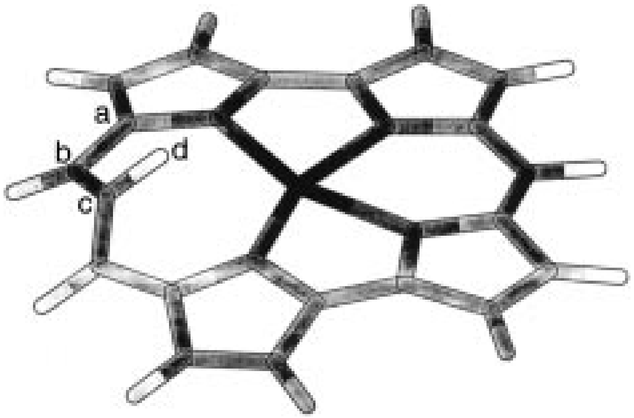

Figure 2. The a−b−c−d torsion angle gives a measure of the tilt of the inward-pointing C−H bond with respect to the major planar part of the molecule.

(II), and Cd(II) complexes, respectively.[13] For the C_s structures, the atoms in the trimethine interpyrrole linker lie approximately in a plane that is significantly tilted relative to the mean plane of the rest of the molecule. The a−b−c−d torsion angle shown in Figure 2 gives a measure of this tilt. This angle is 18.9, 20.6, 14.7, and 22.3° for the Ni(II), Zn(II), Pd(II), and Cd(II) complexes of the *trans*-[3.0.1.0] ligand. Thus, the inward-pointing methine hydrogen has the greatest out-of-plane displacement for the Cd(II) complex.

Ligand Preference of Metal Ions versus Metal Ion Preference of Ligands. For the most part, we have been concerned with the question, "Which porphyrin isomer gives the most stable complex for a particular metal ion?" This question is different from the question, "Which metal does a given porphyrin isomer prefer to bind?" Table 3 allows us to address the latter question, at least in a qualitative manner, with more rigorous calculations planned for a later date.

Based on Table 3, all ligands bind the smaller Ni(II) and Zn(II) ions more strongly than the larger Pd(II) and Cd(II) ions, respectively, which is presumably a simple consequence of the higher surface charge density of a smaller ion. However, the amount of energy by which a certain ligand prefers to bind Ni(II) over Pd(II) or Zn(II) over Cd(II) varies significantly with the ligand. Thus, the [2.0.2.0] ligand prefers Ni(II) over Pd(II) by a much larger margin than the [2.1.0.1] and [2.1.1.0] ligands. A similar trend holds for Zn(II) and Cd(II).

All the ligands bind the d^8 metal ions, Ni(II) and Pd(II), more strongly than the d^{10} ions, Zn(II) and Cd(II), which presumably reflects the large ligand field stabilization energies of square planar d^8 complexes. However, caution should be exercised in comparing affinities for non-isoelectronic metal ions, owing to possible artifacts in the methods used to calculate energies of transition metal atoms that enter the evaluation of the total bonding energies, E_b.

Another source of error in Table 3 is that we have not taken basis set superposition errors into account. However, experience leads us to believe that this error, relatively small at the nonlocal DFT level, should cancel out effectively when we compare different molecules.

Conclusions

The principal conclusions may be enumerated as follows. Ordinary porphyrin forms the most stable dianions and metal complexes compared to the other isomeric ligands, a finding of potential relevance to the question of why Nature chose porphyrin over its isomers. The relative energies of the various dianionic ligands may be ranked as follows: [1.1.1.1] < [2.1.1.0] < [2.0.2.0] < [2.1.0.1] < *trans*-[3.0.1.0] < *cis*-[3.0.1.0]. This order is different from that of the free-base forms of the porphyrin isomers. An interesting result reminescent of a study of corrole isomers is that the order of stabilities of the isomeric metalloporphyrins is metal-dependent and undergoes reversals with changing size of the coordinated metal ion. Thus, the small Ni(II) ion forms the most stable complex with the [2.0.2.0] porphyrin isomer (not counting normal porphyrin among the isomers) and relatively high-energy complexes with the [2.1.0.1] ligand. In contrast, the Cd(II) ion forms relatively stable complexes with the [2.1.0.1] porphyrin isomer and relatively unstable complexes with the [2.0.2.0] ligand. Similarly, the *trans*-[3.0.1.0] ligand forms increasingly more stable complexes relative to the cis stereoisomeric ligand with increasing size of the coordinated metal ion. Overall, we have clarified certain basic issues of the coordination chemistry of porphyrin isomers and hope that this study can serve as a platform from which investigations can be launched into other, more detailed aspects of transition metal complexes of these ligands.

Acknowledgment. We acknowledge support from the Norwegian Research Council, the VISTA program of Statoil (Norway), and a Senior Fellowship (AG) of the San Diego Supercomputer Center. Our co-workers Knut Jynge and Henning Nilsen are thanked for assistance with manuscript preparation. A.G. thanks Prof. Peter Taylor for his hospitality during a sabbatical period spent with his group.

IC9807994

---

(13) These numbers suggest that the errors in energy due to the use of the symmetry constraints shown in Table 2 should be quite modest and, presumably, on the order of a couple of kcal/mol.