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Molecular and Crystal Structure of a Binuclear *μ*-Acetato-Coupled ZnN_3−Zn Porphyrin, N_3 = Bis(2-picolyl)amine: Synthetic Approach To Model the Cytochrome *c* Oxidase Active Site

Nilkamal Bag,[†] Shuenn-Shing Chern,[‡]
Shie-Ming Peng,[‡] and C. K. Chang[*,†]

Departments of Chemistry, Michigan State University,
East Lansing, Michigan 48824,
and National Taiwan University, Taipei, Taiwan

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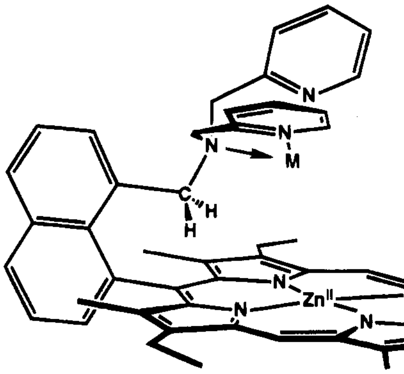
Introduction

The dioxygen binding site of mitochondrial cytochrome *c* oxidase comprises a heme group (a_3) and a nearby copper ion (Cu_B), and together they catalyze the four-electron reduction of dioxygen to water.[1,2] As this binuclear site exhibits unusual physical, spectroscopic, and ligand-binding properties, it has been one of the focal points of contemporary bioinorganic research.[3−5] Recently a number of oxo-bridged heme−copper models for the spin-coupled resting state were reported.[6,7] Holm's group successfully coupled Cu(II)−OH, Cu(II)−F, and Cu(II)−CN complexes with the iron(III) porphyrin perchlorate salt to obtain the bridged assemblies, while Karlin and co-workers relied upon oxidation by O_2 at low temperature to achieve the Fe(III)−O−Cu(II) moiety from the Fe(II)−porphyrin and Cu(I)−amine complex. Alternatively, such a bridged system could be assembled, presumably with greater flexibility, if a copper binding site could be covalently linked to a porphyrin heme.[3−5]

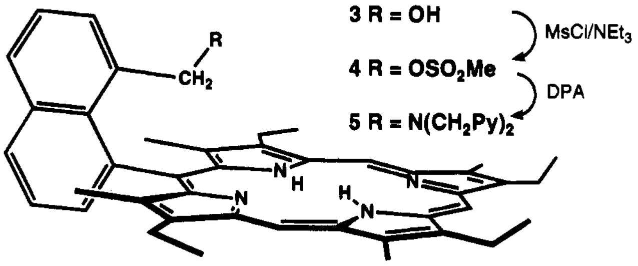
We wish to report the synthesis of a ditopic porphyrin, a molecule spatially designed to encapsulate two metals in a predetermined geometry. We present also the X-ray crystal structures and NMR characterizations of a *μ*-acetato-bridged dizinc(II) complex (**2**) and a monozinc(II) complex (**1**).



1 M = H-OCH$_3$
2 M = Zn^{2+}(Cl$^-$)(OAc$^-$)

Results and Discussion

The design of our superstructured porphyrin ligand is based on the premise that when a meso-carbon of a porphyrin ring is attached to the 1-naphthalene position, the 8-substituent on that naphthalene would have a very restricted conformation, similar to the strategy previously employed in our pillared diporphyrins.[8] Thus, if a bis(2-picolyl)amine (DPA) ligand is linked to a porphyrin via the 1-naphthalene−8-methylene connector, the pendant tripodal chelator would always provide one N-to-metal bond held nearly parallel to the porphyrin plane (see structure **2**). Our synthesis starts from the previously known[9] porphyrinylnaphthalenemethanol **3** which was coupled to DPA via the active mesylate **4** to give **5**, according to the reactions indicated.



The dizinc(II) complex **2**, $[Zn^{II}(DPA)(Cl^-)(OAc^-)Zn^{II}(Por)\cdot {}^2/_3CH_3CN\cdot {}^1/_3H_2O]$, was obtained from **5** and zinc acetate in the presence of sodium acetate in an acetonitrile/methanol mixture and isolated by precipitation with water and crystallization from CH_3CN/CH_2Cl_2. The monozinc(II) complex **1**, $[Zn^{II}(Por)(CH_3OH)]$, was derived from **2**, after **2** was chromatographed over silica gel. The zinc ion bound to the tripodal base above the porphyrin ring was demetalated during chromatography. Both compounds are air stable and have been characterized by ^1H NMR, mass, and UV−visible spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction.

The absorption maximum $\lambda_{max}(CH_2Cl_2)$ of the Soret band of the free base porphyrin **5** is 408 nm. Introduction of one zinc(II) into the porphyrin macrocycle caused the Soret band to red-shift by 8 nm. It is interesting that the Soret band of the dizinc complex **2** shifts further to the red by 3 nm.

^1H NMR data for the two complexes **1** and **2** are compared with those for the free base ligands in Table 1. A striking effect has been noticed on the picolyl CH_2 protons: δ for bis(2-picolyl)amine (DPA) is 3.92 ppm which shifts to 2.58 ppm upon attaching to the porphyrin. Metal complexations produce further upfield shifts of the methylene protons: 2.05 ppm for **1** and

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[*] To whom correspondence should be addressed.

[†] Michigan State University.

[‡] National Taiwan University.

(1) (a) Scott, R. A. *Annu. Rev. Biophys. Biophys. Chem.* **1989**, *18*, 137. (b) Chan, S. I.; Li, P. M. *Biochemistry* **1990**, *29*, 1. (c) Babcock, G. T.; Wikström, M. *Nature* **1992**, *356*, 301. (d) Malmström, B. G. *Acc. Chem. Res.* **1993**, *26*, 332.

(2) (a) Hosler, J. P.; Ferguson-Miller, S.; Calhoun, M. W.; Thomas, J. W.; Hill, J.; Lemieux, L.; Ma, J.; Georgiou, C.; Fetter, J.; Shapleigh, J.; Tecklenburg, M. M. J.; Babcock, G. T.; Gennis, R. B. *J. Bioenerg. Biomembr.* **1993**, *25*, 121. (b) Fee, J. A.; Antholine, W. E.; Fan, C.; Gurbiel, R. J.; Surerus, K.; Werst, M.; Hoffman, B. M. In *Bioinorganic Chemistry of Copper*; Karlin, K. D., Tyeklár, Z., Eds.; Chapman & Hall: New York, 1993; p 485.

(3) (a) Gunter, M. J.; Mander, L. N.; Murray, K. S.; Clark, P. E. *J. Am. Chem. Soc.* **1981**, *103*, 6784. (b) Chang, C. K.; Koo, M. S.; Ward, B. *J. Chem. Soc., Chem. Commun.* **1982**, 716.

(4) Rodgers, S. J.; Koch, C. A.; Tate, J. R.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 3647.

(5) Collman, J. P.; Herrmann, P. C.; Boitrel, B.; Zhang, X.; Eberspacher, T. A.; Fu, L. *J. Am. Chem. Soc.* **1994**, *116*, 9783.

(6) (a) Lee, S. C.; Holm, R. H. *Inorg. Chem.* **1993**, *32*, 4745. (b) Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 5833. (c) Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 11789. (d) Lee, S. C.; Scott, M. J.; Kauffmann, K.; Münck, E.; Holm, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 401.

(7) (a) Nanthakumar, A.; Fox, S.; Murthy, N. N.; Karlin, K. D.; Ravi, N.; Huynh, B. H.; Orosz, R. D.; Day, E. P.; Hagen, K. S.; Blackburn, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 8513. (b) Karlin, K. D.; Nanthakumar, A.; Fox, S.; Murthy, N. N.; Ravi, N.; Huynh, B. H.; Orosz, R. D.; Day, E. P. *J. Am. Chem. Soc.* **1994**, *116*, 4753.

(8) (a) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388. (b) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417.

(9) Chang, C. K.; Kondylis, M. P. *J. Chem. Soc., Chem. Commun.* **1986**, 316.

0020-1669/95/1334-0753$09.00/0

Table 1. ^{1}H NMR Chemical Shifts (ppm) in $CDCl_3$ at 25 °C

	3	**5**	**1**	**2**
meso	10.15 (s, 2H)	10.10 (s, 2H)	10.03 (s, 2H)	9.94 (s, 1H)
	9.96 (s, 1H)	9.95 (s, 1H)	9.98 (s, 1H)	9.79 (s, 1H)
naphthyl	8.34 (d, 1H)	8.26 (dd, 1H)	8.25 (dd, 1H)	8.17 (t, 2H)
	8.16 (t, 1H)	8.17 (d, 1H)	8.02 (d, 1H)	7.70 (d, 2H)
	8.00 (d, 1H)	8.08 (d, 1H)	7.93 (d, 1H)	7.66 (d, 2H)
	7.78 (t, 1H)	7.76 (dd, 1H)	7.75 (d, 1H)	
	7.62 (d, 1H)	7.64 (t, 1H)	7.68 (t, 1H)	
	7.60 (d, 1H)	7.62 (t, 1H)	7.56 (t, 1H)	
naph-CH_2	3.09 (s, 2H)	2.56 (s, 2H)	2.34 (s, 2H)	2.55 (s, 2H)
ethyl-CH_2	4.08 (q, 4H)	4.09 (q, 4H)	4.09 (q, 4H)	4.09 (q, 4H)
	3.99 (q, 2H)	3.88 (q, 4H)	3.95 (q, 2H)	3.87 (q, 2H)
	3.93 (q, 2H)		3.74 (q, 2H)	3.22 (q, 2H)
ethyl-CH_3	1.87 (t, 6H)	1.90 (t, 6H)	1.88 (t, 6H)	1.89 (t, 6H)
	1.70 (t, 6H)	1.64 (t, 6H)	1.64 (t, 6H)	1.56 (t, 6H)
Me	3.64 (s, 6H)	3.66 (s, 6H)	3.63 (s, 6H)	3.65 (s, 6H)
	2.12 (s, 6H)	2.09 (s, 6H)	1.95 (s, 6H)	1.57 (s, 6H)
NH	−2.98, −3.17	−3.07 (br, 2H)		

	DPA	**5**	**1**	**2**
picolyl	8.50 (d, 2H)	7.54 (m, 2H)	6.65 (t, 2H)	7.54 (t, 2H)
	7.58 (t, 2H)	5.95 (br, 2H)	6.39 (br, 2H)	6.91 (d, 2H)
	7.30 (d, 2H)	5.86 (t, 2H)	6.23 (t, 2H)	7.30 (d, 2H)
	7.10 (t, 2H)	5.68 (d, 2H)	6.09 (d, 2H)	7.10 (t, 2H)
picol-CH_2	3.92 (s, 4H)	2.58 (s, 4H)	2.05 (s, 4H)	1.25 (s, 4H)

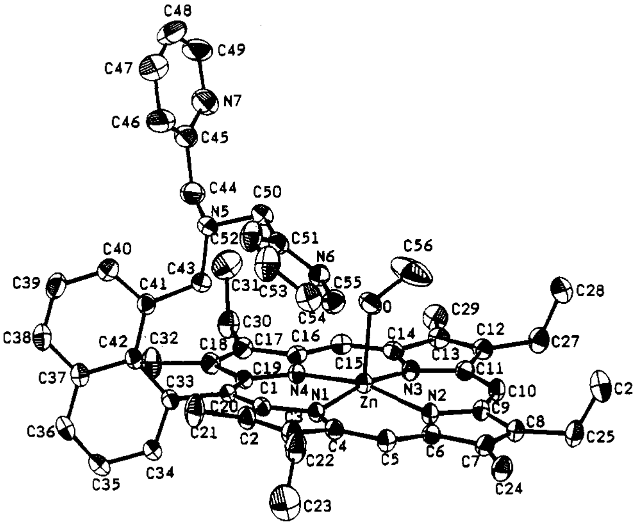

Figure 1. ORTEP plot and labeling scheme for **1**.

1.25 ppm for **2**. Since the upfield shift is caused by the diamagnetic ring current of the porphyrin macrocycle, the dizinc complex **2** must have a conformation where the pendant picolyl groups are brought much closer to the center of the ring than those in the metal-free **5** or monozinc **1**. The evidence of an acetate group on the Zn porphyrin of **2** is seen by the unique singlet at −2.06 ppm which integrates to 3 protons. The large shift of more than 4 ppm from normal acetates is possible only when acetate is serving as an axial ligand on the zinc porphyrin.

The crystal structures of **1** and **2** are shown by the ORTEP drawings in Figures 1 and 2, respectively. Crystal data and refinement parameters are given in Table 2. Table 3 lists the atomic coordinates of non-hydrogen atoms. A listing of selected bond distances and angles for both compounds is given in Table 4. For both compounds, structural features of the porphyrin macrocycle are essentially unchanged by the superstructure. There is a slight bending of the perpendicular naphthyl group away from the porphyrin plane at the C20−C33 junction, caused by steric interactions between the ring and the C43 methylene protons. The porphyrin Zn−N bonds average 2.064(3) Å in **1** and 2.065(6) Å in **2** and are consistent with literature values that vary from 2.051(3) to 2.076(9) Å in pentacoordinate Zn porphyrins.[10] Crystals of **1** contain methanol as a coordinating solvent molecule. The ligated MeOH nestles in the cavity made from the three "up" ethyl groups of the ring; the methoxy group orientation is dictated by the H-bonding to pyridyl N6. The axial Zn−O bond is somewhat skewed, presumably to make room for the H-bonding to happen, and tilts away from the

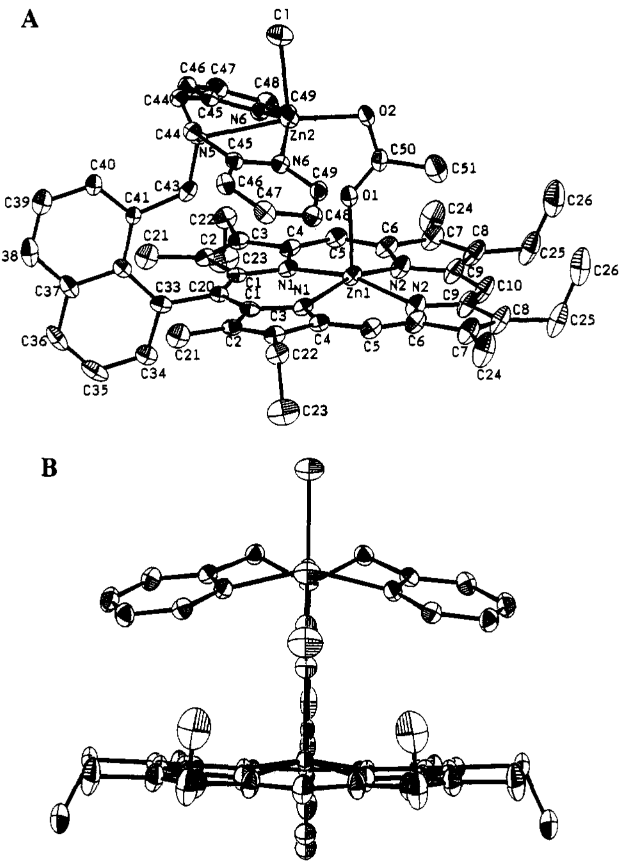

Figure 2. (A) ORTEP plot and labeling scheme for **2**. (B) View along the axis of the acetyl group.

Table 2. Crystallographic Data

	1	**2**
formula	$C_{56}H_{58}N_7OZn$	$C_{57}H_{58}N_7O_2ClZn_2\cdot{}^2/_3CH_3CN\cdot{}^1/_3H_2O$
fw	910.5	1072.7
cryst syst	triclinic	hexagonal
space group	$P\bar{1}$	$P6_3/m$
a, Å	10.735(6)	24.472(4)
b, Å	13.478(6)	24.472
c, Å	18.204(3)	15.913(3)
α, deg	72.59(3)	90.0
β, deg	88.63(3)	90.0
γ, deg	71.94(4)	120.0
V, Å^3	2382.5(17)	8253.2(21)
Z	2	6
ϱ(calc), g cm^{-3}	1.269	1.294
μ, cm^{-1}	5.720	9.887
transm coeff	0.964−1.000	0.951−1.000
scan speed, deg min^{-1}	2.06−8.24	2.06−8.24
scan width, deg	2(0.60 + 0.35 tan θ)	2(0.65 + 0.35 tan θ)
no. of measd reflns	8476	5401
no. of obsd reflns	6225 ($I > 2\sigma(I)$)	2199 ($I > 2\sigma(I)$)
no. of refined params	587	347
R, R_w	0.046, 0.047	0.053, 0.059
S	2.56	1.01

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[10] (a) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 982. (b) Song, H.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1989**, *111*, 6867. (c) Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 8851.

Table 3. All Refined and Calculated Atomic Coordinates and B_{eq} Values (Å^2) for **1** and **2**, Where Esd's Refer to the Last Digit Printed

atom	x	y	z	B_{eq}	atom	x	y	z	B_{eq}
				Compound **1**					
Zn	0.58450(4)	0.58452(3)	0.655139(22)	3.118(18)	C25	0.2144(4)	1.0077(3)	0.51686(22)	4.87(20)
O	0.48556(22)	0.55899(20)	0.75894(13)	4.66(14)	C26	0.1092(4)	1.0299(4)	0.5694(3)	8.0(3)
N1	0.74440(23)	0.61027(19)	0.69718(14)	2.93(13)	C27	0.1066(3)	0.6460(3)	0.49541(20)	4.47(20)
N2	0.49410(24)	0.75280(19)	0.61083(14)	3.11(13)	C28	0.0062(4)	0.6643(3)	0.55334(23)	5.85(25)
N3	0.44381(24)	0.56451(20)	0.59181(14)	3.00(13)	C29	0.2765(4)	0.3924(3)	0.53200(21)	4.97(22)
N4	0.70065(24)	0.42407(19)	0.67250(14)	2.99(13)	C30	0.7412(4)	0.1375(3)	0.67603(21)	4.75(21)
N5	0.7541(3)	0.28491(22)	0.96200(16)	4.10(15)	C31	0.6755(5)	0.0876(3)	0.7444(3)	7.2(3)
N6	0.5952(3)	0.56381(23)	0.88675(15)	4.16(15)	C32	0.9875(4)	0.1624(3)	0.74572(23)	5.43(22)
N7	0.5856(3)	0.0927(3)	1.04811(23)	7.22(23)	C33	1.0331(3)	0.3525(3)	0.77807(18)	3.37(17)
C1	0.8552(3)	0.5318(3)	0.73950(18)	3.06(16)	C34	1.1297(3)	0.3660(3)	0.72988(21)	5.12(21)
C2	0.9222(3)	0.5842(3)	0.77751(20)	3.87(19)	C35	1.2642(4)	0.3141(3)	0.75358(24)	6.21(24)
C3	0.8550(3)	0.6933(3)	0.75372(21)	4.16(20)	C36	1.2989(3)	0.2491(3)	0.82588(23)	5.43(22)
C4	0.7445(3)	0.7088(3)	0.70346(18)	3.34(17)	C37	1.2056(3)	0.2301(3)	0.87845(19)	3.85(18)
C5	0.6498(3)	0.8107(3)	0.66842(19)	3.50(18)	C38	1.2471(3)	0.1612(3)	0.95415(21)	4.74(20)
C6	0.5346(3)	0.83196(25)	0.62553(18)	3.26(17)	C39	1.1603(4)	0.1437(3)	1.00659(21)	5.22(21)
C7	0.4377(3)	0.9394(3)	0.59221(18)	3.56(17)	C40	1.0256(4)	0.1950(3)	0.98557(20)	4.66(20)
C8	0.3387(3)	0.9229(3)	0.55839(19)	3.66(17)	C41	0.9779(3)	0.2610(3)	0.91258(18)	3.44(18)
C9	0.3735(3)	0.8050(3)	0.57088(18)	3.38(16)	C42	1.0671(3)	0.28211(25)	0.85546(18)	3.16(17)
C10	0.2964(3)	0.7528(3)	0.54717(18)	3.55(17)	C43	0.8296(3)	0.3117(3)	0.89487(19)	3.98(18)
C11	0.3274(3)	0.6412(3)	0.55731(17)	3.22(17)	C44	0.7298(4)	0.1798(3)	0.97241(22)	5.32(23)
C12	0.2446(3)	0.5888(3)	0.53151(18)	3.53(18)	C45	0.6816(4)	0.1369(3)	1.04951(24)	5.69(23)
C13	0.3142(3)	0.4811(3)	0.54936(18)	3.53(18)	C46	0.7346(5)	0.1405(4)	1.11579(25)	8.0(3)
C14	0.4394(3)	0.4660(3)	0.58752(17)	3.21(17)	C47	0.6916(5)	0.0943(5)	1.1856(3)	9.8(4)
C15	0.5391(3)	0.3676(3)	0.61617(18)	3.38(17)	C48	0.5974(5)	0.0478(4)	1.1854(3)	10.6(4)
C16	0.6591(3)	0.34774(25)	0.65455(17)	3.14(17)	C49	0.5463(5)	0.0489(4)	1.1181(3)	9.5(3)
C17	0.7585(3)	0.2415(3)	0.68053(18)	3.55(18)	C50	0.6279(3)	0.3726(3)	0.95270(20)	4.51(20)
C18	0.8617(3)	0.2544(3)	0.71294(18)	3.67(18)	C51	0.6463(3)	0.4799(3)	0.94972(19)	3.99(19)
C19	0.8247(3)	0.37084(24)	0.70943(17)	2.92(16)	C52	0.7138(4)	0.4902(3)	1.00853(22)	5.80(24)
C20	0.8954(3)	0.42019(25)	0.74253(17)	2.96(16)	C53	0.7286(4)	0.5898(4)	1.0015(3)	6.9(3)
C21	1.0363(4)	0.5336(3)	0.83662(25)	6.04(25)	C54	0.6785(4)	0.6755(3)	0.93716(24)	6.0(3)
C22	0.8842(4)	0.7821(3)	0.7785(3)	5.91(25)	C55	0.6122(4)	0.6595(3)	0.88171(21)	5.00(22)
C23	0.9761(5)	0.8257(4)	0.7312(3)	9.6(4)	C56	0.3564(5)	0.5832(6)	0.7634(3)	12.8(6)
C24	0.4473(4)	1.0469(3)	0.59482(21)	4.67(21)					
				Compound **2**					
Zn1	0.20538(7)	0.43941(7)	$^1/_4$	4.13(9)	C26	0.4699(6)	0.5472(7)	0.0913(10)	11.7(11)
Zn2	0.13850(7)	0.22642(8)	$^1/_4$	4.26(9)	C33	−0.0286(6)	0.3340(6)	$^1/_4$	4.1(8)
Cl	0.13188(23)	0.12954(21)	$^1/_4$	7.7(3)	C34	−0.0496(7)	0.3774(7)	$^1/_4$	5.2(9)
N1	0.1361(3)	0.4120(3)	0.1601(4)	3.7(4)	C35	−0.1139(8)	0.3572(8)	$^1/_4$	6.7(13)
N2	0.2730(3)	0.4910(3)	0.1600(4)	5.0(5)	C36	−0.1577(7)	0.2954(8)	$^1/_4$	6.1(11)
N5	0.0263(4)	0.1827(4)	$^1/_4$	3.2(5)	C37	−0.1395(6)	0.2492(7)	$^1/_4$	4.7(9)
N6	0.1144(3)	0.2335(3)	0.1265(4)	4.0(4)	C38	−0.1849(6)	0.1851(8)	$^1/_4$	6.0(10)
O1	0.2062(4)	0.3523(4)	$^1/_4$	4.6(5)	C39	−0.1675(7)	0.1400(7)	$^1/_4$	5.6(9)
O2	0.2324(4)	0.2784(4)	$^1/_4$	5.5(6)	C40	−0.1037(6)	0.1581(6)	$^1/_4$	4.2(7)
C1	0.0721(4)	0.3790(4)	0.1708(5)	3.5(5)	C41	−0.0572(5)	0.2193(5)	$^1/_4$	3.1(6)
C2	0.0415(4)	0.3618(4)	0.0877(5)	3.9(5)	C42	−0.0731(6)	0.2679(6)	$^1/_4$	3.8(8)
C3	0.0885(4)	0.3839(4)	0.0304(5)	4.3(5)	C43	0.0104(6)	0.2324(6)	$^1/_4$	4.0(7)
C4	0.1470(4)	0.4157(4)	0.0754(5)	4.0(5)	C44	0.0127(4)	0.1485(4)	0.1706(5)	4.1(5)
C5	0.2066(4)	0.4482(4)	0.0386(5)	4.6(6)	C45	0.0561(4)	0.1904(4)	0.1032(5)	3.9(5)
C6	0.2642(5)	0.4835(4)	0.0761(5)	5.0(6)	C46	0.0366(4)	0.1854(4)	0.0205(6)	4.7(6)
C7	0.3241(5)	0.5185(5)	0.0329(6)	6.2(7)	C47	0.0778(5)	0.2261(5)	−0.0390(6)	5.4(7)
C8	0.3690(5)	0.5472(5)	0.0931(7)	6.7(7)	C48	0.1371(4)	0.2707(4)	−0.0153(6)	5.0(6)
C9	0.3364(5)	0.5293(4)	0.1726(6)	5.8(6)	C49	0.1538(4)	0.2728(4)	0.0683(6)	4.3(5)
C10	0.3646(7)	0.5483(7)	$^1/_4$	6.6(10)	C50	0.2459(6)	0.3357(6)	$^1/_4$	4.9(8)
C20	0.0421(6)	0.3645(5)	$^1/_4$	3.4(7)	C51	0.3138(8)	0.3846(10)	$^1/_4$	9.7(16)
C21	−0.0264(5)	0.3263(5)	0.0650(6)	6.1(7)	C52	0.33333	$^2/_3$	1.10426	17.4(13)
C22	0.0822(5)	0.3782(5)	−0.0651(5)	5.2(6)	C53	0.33333	$^2/_3$	1.00833	21.3(16)
C23	0.0817(7)	0.4334(6)	−0.1059(6)	8.5(10)	N7	0.33333	$^2/_3$	0.93580	38.2(27)
C24	0.3334(6)	0.5227(6)	−0.0600(7)	8.9(8)	O3	0	0	0	31.6(24)
C25	0.4381(5)	0.5853(6)	0.0824(7)	8.6(8)					

pyridine, as can be seen by the angles 98.08(10), 97.45(10), 93.98(10), and 97.96(10)° for O−Zn−N1, O−Zn−N2, O−Zn−N3, and O−Zn−N4, respectively. Crystals of **2** have four acetonitrile and two water solvate molecules per unit cell. The binuclear structure of **2** illustrates the presence of one bridging acetate ligand. As shown in Figure 2B, the geometry of the bridged dizinc complex is a highly symmetrical one. There is a crystallographic plane of symmetry in structure **2**. The Zn−Cl bond distance of 2.294(4) Å observed is longer than those of typical four-coordinated complexes.[11] The $Zn2-N_{py}$ distance of 2.085(7) Å in **2** is also larger than those in other four-coordinate Zn−pyridine complexes[11,12] but shorter than those in pyridine-ligated five-coordinate Zn porphyrins which fall within the range of 2.143(4)−2.200(3) Å.[10c,13] In comparison, the "harder" amine nitrogen N(5) binds more weakly to Zn2, with a distance Zn2−N5 of 2.398(9) Å.

The ditopic porphyrin **5** is capable of forming other metal and mixed-bimetal complexes, among which we have prepared Fe/Zn, Fe/Cu, Co/Co, and Co/Cu systems.[14] While efforts are

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(11) (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1977**, *16*, 1119. (b) Ida, K.; Sakiyama, H.; Okawa, H.; Matsumoto, N.; Aratake, Y.; Murase, I.; Kida, S. *Polyhedron* **1992**, *11*, 65.

Table 4. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for **1** and **2**

1		**2**	
		Distances	
Zn−N1	2.060(3)	Zn1−N1	2.058(6)
Zn−N2	2.077(3)	Zn1−N2	2.072(7)
Zn−N3	2.051(3)	Zn1−O1	2.142(9)
Zn−N4	2.066(3)	Zn2−N5	2.398(9)
Zn−O	2.135(2)	Zn2−N6	2.085(7)
C20−C33	1.514(4)	Zn2−O2	1.994(9)
		Zn2−Cl	2.294(4)
		C20−C33	1.503(18)
		Angles	
N1−Zn−N2	90.12(10)	N1−Zn1−N2	89.7(3)
N1−Zn−N3	167.93(10)	N1−Zn1−N2	162.9(3)
N1−Zn−N4	87.46(10)	N1−Zn1−N1	88.1(3)
N2−Zn−N3	88.09(10)	N2−Zn1−N2	87.5(3)
N2−Zn−N4	164.59(10)	N5−Zn2−N6	74.23(19)
N3−Zn−N4	91.10(10)	N6−Zn2−N6	141.1(3)
Zn−O−C56	126.0(3)	N5−Zn2−O2	169.2(3)
		N6−Zn2−O2	103.35(10)

being made to characterize these complexes, none has so far afforded crystals suitable for crystallographic analyses. The demonstration of the bridged dizinc structure **2** has certainly justified further research with this ligand. Perhaps also significant in terms of molecular design strategy, this work establishes the naphthylporphyrin to be a useful platform upon which rigid superstructure can be built without the use of strapping on both ends such as found in previous binuclear models[3] and many basket-handle porphyrins.[15]

Experimental Section

Materials. Reagents and solvents were used as received unless otherwise stated. CH_2Cl_2 and THF were distilled from CaH_2. Bis(2-picolyl)amine (DPA) was synthesized by the method of Gruenwedel.[16] UV−visible spectra were measured on a Cary 219 or a Shimadzu 160 spectrophotometer, with samples dissolved in CH_2Cl_2. ^1H NMR spectra were recorded on Varian Gemini-300 or VXR-500 spectrometer, in "100%" $CDCl_3$ (minimum 99.8 atom % D, Cambridge Isotope Laboratories) with the residual $CHCl_3$ as the internal standard set at 7.24 ppm. Mass spectra were obtained from on an HP 5890 mass spectrometer.

Synthesis of 5-[8-((Bis(2-picolyl)amino)methyl)-1-naphthyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (5). The hydroxymethyl naphthalene porphyrin **3**[9] was treated with methanesulfonyl chloride in the presence of a trace amount of triethylamine to give the mesylate derivative **4**, to which, dissolved in a minimum volume of CH_2Cl_2, was added a 10-fold excess of bis(2-picolyl)amine (DPA). Over an oil bath, temperature was slowly increased to distill CH_2Cl_2 from the mixture, and heating was continued for 2 h at 90 °C. After cooling, the crude product was dissolved in CH_2Cl_2, and the solution was extracted several times with 1% aqueous HCl to remove the excess amine. The dried product was column-chromatographed on silica gel. A purple band containing the desired porphyrin was eluted with 4% methanol in CH_2Cl_2 containing a few drops of triethylamine. The overall yield was 78%. UV−vis: λ_{max} (rel intens) 408.5 nm (1.00), 504.5 (0.08), 538.5 (0.04), 573.5 (0.03), 627 (0.01). MS: *m/e* 815 (M^+), 723 ($M^+ - CH_2Py$), 618 ($MH^+ - N(CH_2Py)_2$). NMR: see Table 1.

Synthesis of the Dizinc Complex 2. To zinc acetate (65 mg, 0.3 mmol) and anhydrous sodium acetate (70 mg) dissolved in methanol (5 mL) was added a CH_3CN solution (50 mL) of **5** (100 mg, 0.12 mmol). After being stirred and refluxed for 1 h, the mixture was cooled. The solvent was removed under reduced pressure, and the solid mass thus obtained was washed with water to remove excess zinc acetate and sodium acetate. The solid was then dissolved in CH_2Cl_2, and the mixture was filtered and dried to give a pink solid in quantitative yield. UV−vis: λ_{max} (rel intens) 419.5 nm (1.00), 547.5 (0.06), 582.0 (0.03). NMR: see Table 1.

Synthesis of the Monozinc Complex 1. Compound **2** was dissolved in CH_2Cl_2, and the solution was subjected to column chromatography over silica gel. On elution with 0.5% methanol in CH_2Cl_2, a pink band moved out very fast and was collected. It formed a crystalline mass after solvent was evaporated. UV−vis: λ_{max} (rel intens) 416.5 nm (1.00), 544.5 (0.06), 579 (0.03). MS: *m/e* 877 and 879 (M^+). NMR: see Table 1.

Crystal Structure Determination. Crystals of **1** suitable for single-crystal X-ray diffractometry were grown by slow diffusion of methanol into the sample solution in CH_2Cl_2 followed by slow evaporation. Crystals of **2** were obtained by slow evaporation of the sample dissolved in CH_3CN/CH_2Cl_2. Data collection was performed on a Nonius diffractometer at 25 °C using graphite-monochromated Mo Kα radiation. Crystal data and data collection parameters are listed in Table 2. The crystals used for analysis were of approximate dimensions $0.50 \times 0.50 \times 0.50$ mm. The unit cell parameters were determined by a least-squares fit of 25 machine-centered reflections having 2θ values in the ranges 19.6−25.3° for **1** and 17.5−31.06° for **2**. Data collection was performed using the $\theta/2\theta$ scan method to $2\theta < 50°$. The intensity data were reduced and corrected for Lorentz and polarization factors using the applied programs. Semiempirical absorption corrections were applied. The crystal structures were solved by direct methods using the NRCVAX program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions with fixed isotropic thermal parameters. The highest difference Fourier peaks were 0.39 and 0.72 e Å^{-3}, respectively, for **1** and **2** near the metal atoms.

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Supplementary Material Available: Additional ORTEP drawings and tables of complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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(12) (a) Horrocks, W. D., Jr.; Ishley, J. N.; Whittle, R. R. *Inorg. Chem.* **1982**, *21*, 3265. (b) *Inorg. Chem.* **1982**, *21*, 3270.

(13) Scheidt, W. R.; Lee, Y. H. *Struct. Bonding* (*Berlin*) **1987**, *64*, 1.

(14) The mixed binuclear complexes were prepared by metalation of the free base porphyrin **5** followed by washing the product in CH_2Cl_2 with 6 N HCl to demetalate and protonate the DPA ligand. The second metal ion was then re-inserted into the DPA moiety. Attempts to prepare a μ-oxo-bridged Fe/Cu system by various methods (e.g. basic alumina) resulted in a 1:1 Fe−Cu complex exhibiting an IR peak at 882 cm^{-1} which may be attributed to the asymmetric Fe−O−Cu stretching.

(15) Momenteau, M.; Reed, C. A. *Chem. Rev.* **1994**, *94*, 659.

(16) Gruenwedel, D. W. *Inorg. Chem.* **1968**, *7*, 495.