for certain $[\mathrm{Ni(S_2C_2R_2)_2}]^{1-,2-}$ couples are even more negative,[20] but these dithiolene monoanions are extensively delocalized. Manifestations of this include a pronounced dependence of potential on substituent R and a relatively small g anisotropy (e.g., $g_x = 2.160$, $g_y = 2.042$, $g_z = 1.998$ in $[\mathrm{Ni(mnt)_2}]^-$[16]). The existence of a dithiolene structure in the enzymes is implausible given the highly anisotropic, nearly invariant Ni(III) EPR spectra ($g \approx 2.3, 2.2, 2.0$) of the "as prepared" state of most hydrogenases.[2] The present complexes when oxidized resemble this state in terms of g anisotropy but are not considered as site models owing to the lack of precedence of deprotonated amide as a physiological ligand. Rather, they do emphasize the role of anionic polarizable ligands, including thiolate, and the attendant net negative charge of the reduced species in markedly lowering redox potentials. Thiolate ligands at biological nickel sites doubtless modulate potentials by virtue of these properties. Indeed, Co(III) has recently been stabilized in a classical tetrathiolate environment[21,22] and in one case reversibly linked to Co(II) at a potential of -1.16 V vs SCE.[21b]

Future reports will deal with the redox processes of Ni(II) thiolate complexes and further investigations of anionic N_2S_2 ligand complexes of nickel and other metals.[11] As will be shown, ligand structural variation can afford even lower Ni(III)/Ni(II) potentials than that reported here.

Acknowledgment. This research was supported by National Science Foundation Grant CHE 85-21365.

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Pincer Porphyrin: X-ray Crystal Structure of a Binuclear Zinc/Copper Complex[1]

Sir:

Binucleating porphyrins are receiving considerable current attention as active-site models for multimetal proteins and for exploiting chemistry that is distinctive to binuclear complexes.[2-9] A critical aspect of such systems is achieving a well-defined geometric arrangement of the metal sites. For this reason relatively rigid urea[3] or arene[6,7] links between cofacial porphyrins have been favored as have multiple links in face-to-face porphyrins[5] and ligating superstructures.[2,4,8] The merits of these approaches are borne out in the few x-ray crystal structures that have successfully been determined on binuclear systems,[3,5,6] but even so, it is clear that "rigid" systems have important and subtle flexibility. Also, although large molecules that are rigid and symmetrical often crystallize well this can lead to unworkable solubility. Binucleating porphyrins with relatively flexible superstructures are synthetically accessible[8,10] and can be expected to have good solubility but in the absence of single-crystal x-ray data there will always remain uncertainty about the structures of their binuclear complexes. This leads us to communicate the first structural characterization of a binuclear complex of "pincer porphyrin", a binucleating porphyrin whose design is tailored to provide flexibility, solubility, and crystallizability.[9]

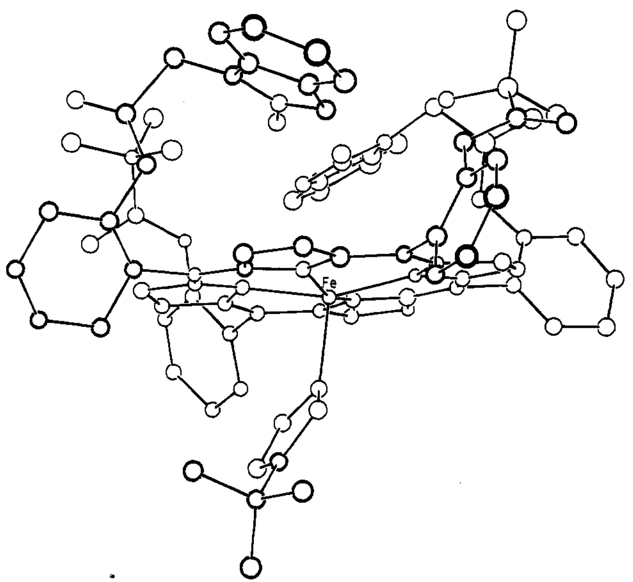
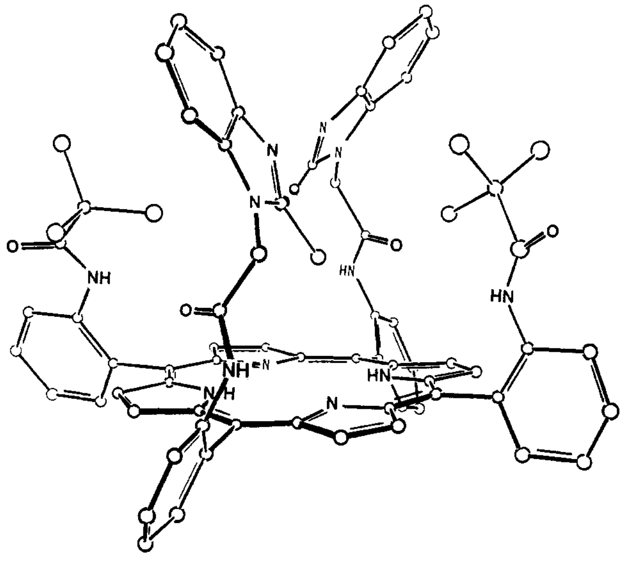


Figure 1. ORTEP drawing of the [Fe(PincerP)(4-*t*-BuHIm)] molecule illustrating how the two attached benzimidazole groups block access to one face of the porphyrin. The two benzimidazole planes make dihedral angles of 26.7 and 23.0° with the porphinato core.



In the structures of the mononuclear [Fe(4-*t*-BuHIm)(PincerP)][11] and the dinuclear $[\mathrm{(DMF)ZnCu(PincerP)}]\mathrm{PF_6}$ we have the elements of a model for the heme/copper active site of cytochrome oxidase. The structures reveal interesting conformational aspects

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(1) This paper is dedicated to the memory of Steven (Rodj) J. Rodgers (1957-1986).

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(11) Abbreviations used in this paper: 4-*t*-BuHIm = 4-*tert*-butylimidazole; PincerP = dianion of 5α,15α-bis[(*N*-(2-methylbenzimidazolyl)acetamido)phenyl]-10α,20α-bis(pivalamidophenyl)porphine = trans-L of ref 9; DMF = *N,N'*-dimethylformamide; THF = tetrahydrofuran; PincerP' = 5,6-dimethylbenzimidazole analogue of PincerP.

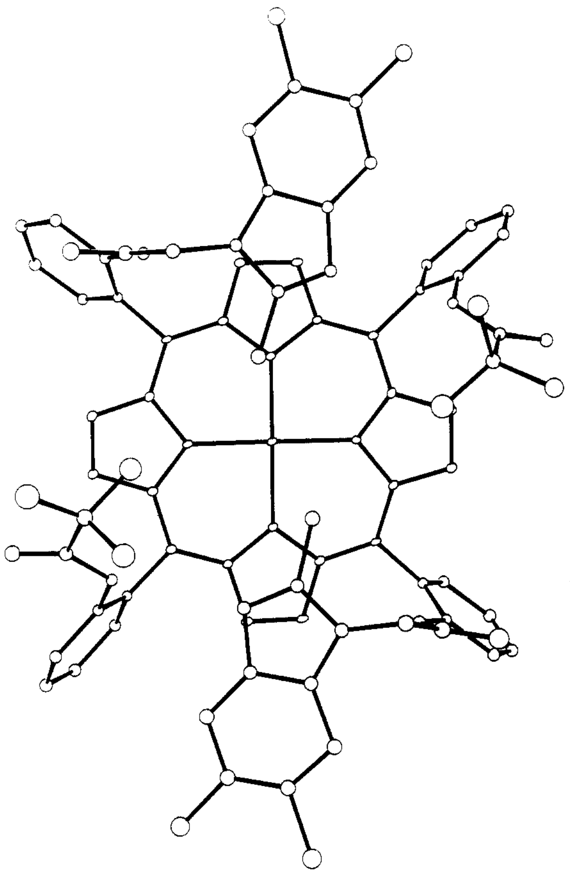

Figure 2. Computer-produced projection of the Cu(PincerP′) molecule. The porphinato plane is essentially parallel to the plane of the paper. The average Cu–N bond distance is 1.986 Å. The two benzimidazole planes make dihedral angles of 11.7 and 14.6° with the best plane of the 24-atom core.

of the ligating bis(benzimidazole) superstructure and its pivalamido pickets.

Single crystals of Fe(4-*t*-BuHIm)(PincerP)·$(CH_3)_2CO$ were grown by heptane layering of an anaerobic acetone solution of Fe(THF)(PincerP)[9] with a slight excess of 4-tert-butylimidazole. Although limited in accuracy, X-ray data[12] define several important aspects of the structure. The geometry around iron(II) (average $Fe–N_p$ = 2.06, Fe···Ct = 0.33, $Fe–N_{Im}$ = 2.13 Å) is that expected of a five-coordinate high-spin iron(II) porphyrin.[13] The realization of five- rather than six-coordination is apparently the result of the superstructure blocking one face of the heme (Figure 1). The conformation of each benzimidazole arm is determined by weak H-bonding between its nitrogen atom lone pair and the amido N–H of an adjacent pivalamido picket. The N···N distances are 3.13 and 3.15 Å, suggesting a somewhat looser but overall similar structure compared to that recently described and illustrated more fully for Cu(PincerP).[9] The distortion of the amide planes from their phenyl planes can be rationalized by the interappendage H bonding, and the recurrence of this phenomenon is beginning to give us information about the energetics of superstructure conformations. A third crystal structure of a monomeric complex, that of Cu(PincerP′)·$3CHCl_3$ (where PincerP′ is the same ligand as PincerP except with 5,6-dimethyl substitution on the benzimidazole) again shows these structural features (Figure 2; N···N = 3.03, 3.06 Å).[14] The H bonding and benzimidazole orientations found in these complexes are consistent with ring-current shifts observed in the ^1H NMR spectrum of the free-base ligand.[9] The consistency of these observations allows us to be confident about the structures of other four- and five-coordinate species that do not yield single crystals. The absence of intramolecular and intermolecular ligation is notable and was an important part of the ligand design.

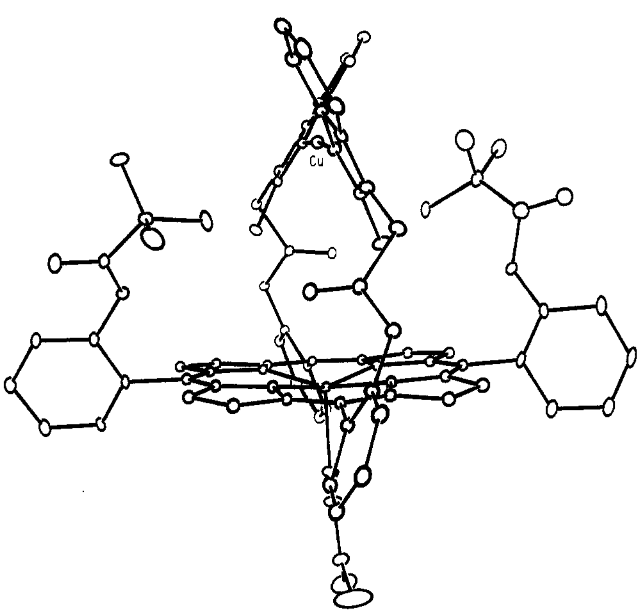

Figure 3. ORTEP diagram of the [(DMF)ZnCu(PincerP)]PF_6 molecule illustrating the extension of the two benzimidazole arms to form the "upstairs" metal binding site. The Zn and Cu ions are separated by 6.04 Å. The zinc ion is displaced 0.28 Å out-of-plane away from the copper ion side of the plane. The average Zn–N bond distance is 2.061 (9) Å, and the axial Zn–O distance is 2.117 (12) Å.

The above superstructure conformation is readily overcome by coordination of copper(I) to the benzimidazoles. Single crystals suitable for an X-ray structure determination[15] have been obtained for the Cu^IPF_6 salt in the case where zinc is the "downstairs" metal.[16] The structure of the [(DMF)ZnCu(PincerP)]$^+$ cation is shown in Figure 3. The zinc porphyrin is five-coordinate with an O-bound DMF axial ligand (derived from the crystallizing solvent) on the open face. The coordinate dimensions are not unlike those of Zn(H_2O)(TPP).[17] The "upstairs" metal coordination by the benzimidazole moieties gives two-coordinate copper(I) with a nearly linear N–Cu–N bond (174.7°). The

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(12) Crystal data for $FeO_5N_{14}C_{84}H_{79}$: triclinic, a = 13.511 (4) Å, b = 25.795 (8) Å, c = 11.478 (4) Å, α = 103.12 (3)°, β = 109.37 (3)°, γ = 89.27 (2)°, V = 3367 (2) Å^3, Z = 2, space group $P\bar{1}$, ρ_{calcd} = 1.25 g/cm^3, ρ_{obsd} = 1.24 g/cm^3, 4687 observed, measured data to 2θ = 105.1° (θ–2θ scans and graphite-monochromated Cu Kα radiation), all diffraction measurements at 99 ± 5 K. The structure was solved by direct methods and refined with full-matrix least-squares techniques to R = 17.8%. A reviewer has asked us to comment on the high R value and the refinement. The large R value and limited number of diffraction data reflect the very real problems of obtaining adequate diffraction-quality crystals of elaborate molecules. We attempted to maximize the number of data by the use of both low temperature and Cu radiation. With the limited number of data available we then chose to maintain a data/parameter ratio of 10 and hence not to use any anisotropic thermal parameters.

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(14) Crystal data for $CuCl_9O_4N_{12}C_{81}H_{75}$: monoclinic, a = 17.290 (4) Å, b = 22.649 (5) Å, c = 22.596 (5) Å, β = 111.92 (2)°, V = 8209 (5) Å^3, Z = 4, space group $P2_1/n$, ρ_{calcd} = 1.35 g/cm^3, ρ_{obsd} = 1.34 g/cm^3, 6533 observed data (average of two forms) to 2θ = 48.32° (θ–2θ scans and graphite-monochromated Mo Kα radiation), all measurements at 294 ± 1 K. The structure was solved by direct methods (MULTAN78) and refined with full-matrix least-squares methods to R = 9.1%.

(15) Crystal data for $ZnCuPF_6O_8N_{16}C_{86}H_{92}$: triclinic, a = 14.812 (2) Å, b = 17.578 (2) Å, c = 19.053 (2) Å, α = 88.26 (1)°, β = 82.94 (1)°, γ = 69.25 (1)°, V = 4603 (1) Å^3, Z = 2, space group $P\bar{1}$, ρ_{calcd} = 1.26 g/cm^3, 7033 observed data (average of two forms) to 2θ = 48.2° (graphite-monochromated Mo Kα radiation at 294 K). The structure was solved by direct methods (MULTAN78) and refined with full-matrix least-squares techniques to a current R = 9.8%. We expect to perform additional, specialized refinements in an attempt to better resolve disorder in one of the pickets and in at least one of the DMF solvate molecules.

(16) Zinc was inserted into the porphyrin by treatment with zinc acetate. Copper(I) was ligated "upstairs" by treatment of Zn(PincerP) with 1 equiv of $[Cu(CH_3CN)_4]PF_6$ in 2:3 benzene/methanol. Single crystals were grown by recrystallization from DMF with toluene vapor diffusion.

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average Cu–N bond length of 1.864 (7) Å is close to those in $[Cu_2(EDTB)]^{2+}$ (1.87 Å), which also has bis(benzimidazole) coordination to copper(I).[18] The conformation of the superstructure is significantly altered from that seen in mononuclear species. Instead of lying over the porphyrin ring the benzimidazoles stand in a relatively upright position such that the copper atom is 5.77 Å above the mean plane of the porphyrin. The planes of the benzimidazole rings intersect at an angle of 60°, which must be dictated at least in part by the minimization of steric interactions at copper. We note the presence of nonplanar phenyl amides in both the chelating arms and the pivalamido pickets even in the absence of obvious intramolecular interactions. Packing effects appear to be more energetically demanding than any π-delocalization stability that might occur if each *o*-amide was coplanar with its phenyl ring.

In conclusion, a binucleating porphyrin containing a certain degree of flexibility has been shown to form binuclear complexes whose structures can be definitively characterized by X-ray crystallography. The prospects appear good for the evolution of this approach into well-defined models for heterobinuclear sites of metalloproteins. Such models are essential for corroborating various structural proposals for binuclear active sites, particularly those based upon EXAFS data.

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Supplementary Material Available: Tables SI–SIV, giving atomic coordinates, bond distances and angles, and least-squares plane calculations for [Fe(PincerP)(4-*t*-BuHIm)], Tables SV–SX, listing atomic coordinates and anisotropic thermal parameters, calculated hydrogen atom positions, bond distances and angles, and least-squares plane calculations for Cu(PincerP′), and Tables SXI–SXV, giving atomic coordinates and anisotropic temperature factors, bond distances and angles, and least-squares plane calculations for $[(DMF)ZnCu(PincerP)]PF_6$ (36 pages). Ordering information is given on any current masthead page.

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Oxygen Content and Site Distribution in High-T_c Superconducting $YBa_2Cu_3O_y$ Ceramics

Sir:

Since the initial report of Wu, et al.[1] on high-temperature superconductivity (T_c = 90–95 K) in a $YBa_2Cu_3O_y$ ceramic, a number of studies on the structural properties of this material have appeared. While the basic triple perovskite motif ($a \simeq b \simeq c/3$, orthorhombic, space group *Pmmm*) is now unquestioned, two fundamental queries remain for a particular preparative (annealing) scheme: (1) the total oxygen content (y); (2) the distribution of oxygen atoms between two sites, O(4)[0, $^1/_2$, 0] and O(5)[$^1/_2$, 0, 0] as in Figure 1.[2–16] In most preparations, it has been generally assumed that y is ca. 7, and models have been proposed in which there is a random distribution between sites O(4) and O(5) (Figure 1a) or O(4) is preferentially occupied [$P(0, {}^1/_2, 0) = 1$ in the limit, Figure 1b].

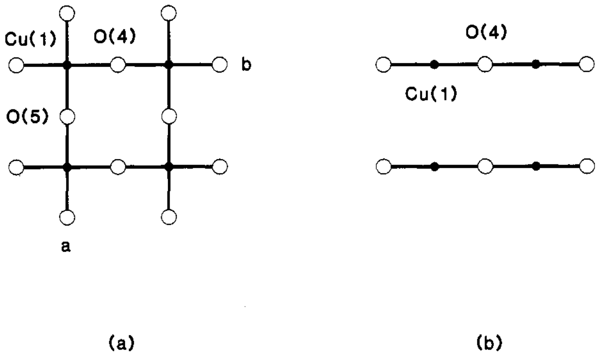

Figure 1. $z = 0$ section of the structure of $YBa_2Cu_3O_y$: (a) random occupation of sites O(4) and O(5); (b) preferential occupation of site O(4) to the exclusion of site O(5).

It is suggested here that accurate determination of the unit cell lengths for a given preparation can give a good estimate of the total oxygen content (y) and the distribution [$P(0, {}^1/_2, 0) = 1 - P({}^1/_2, 0, 0)$] of oxygen atoms in sites O(4) and O(5). As an added advantage, the metrical properties of a unit cell can be determined with equal accuracy by either X-ray or neutron diffraction; thus, the relatively poor X-ray scattering amplitude for oxygen would not necessitate utilization of the less readily available neutron diffraction technique.

In Table I, cell parameters for an extensive set of syntheses of $YBa_2Cu_3O_y$ ceramics are presented. Members of the set were generally selected on the basis of good-to-excellent precision in the reported cell constants. Two of these studies are singled out: (a) the X-ray determination of Siegrist et al.[14] for which $a \simeq b$, the minimum value for c is given, and, apparently, $P(0, {}^1/_2, 0) \simeq {}^1/_2$; (b) the neutron study of Greedan et al.,[7] for which a is sizably smaller than b, and there is a clear site preference [O(4)], although this site is only about 70% occupied [$y \simeq 6.7$].

Given the $z = 0$ section of the structure of $YBa_2Cu_3O_y$ (Figure 1), a strong preference [$P(0, {}^1/_2, 0) \simeq 1$] for the O(4) site is expected to yield a b-axis length that is significantly larger than the a-axis length. In contrast, absence of a strong site preference

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