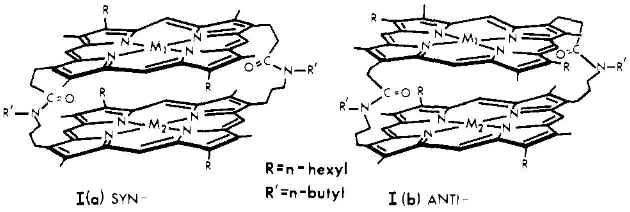
Crystal and Molecular Structure of Cofacial Dicopper Hexyldiporphyrin-7

Sir:

Dimeric porphyrins linked in a cofacial configuration have recently been synthesized.[1-4] The binuclear metal cofacial diporphyrins can form sandwiched complexes with various ligands and therefore are ideal systems for studying multielectron redox reactions.[1c,d,5] We have previously shown that the intramolecular separation of the two rings of diporphyrin plays an important role in ligand intercalation, but the metal-metal distances were estimated indirectly by using triplet EPR parameters.[1d] We now report the direct observation of distances and geometries of interest with the X-ray crystal structure determination of a cofacial dicopper hexyldiporphyrin-7 (Cu_2DP-7).[6]

The cofacial diporphyrin was prepared by coupling of the diacid chloride and the dibutylamine of 2,6-dihexyldeuteroporphyrin II, followed by copper insertion using copper acetate in a chloroform-methanol mixture.[1a] This procedure statistically yields two diasteric isomers designated as *syn*-**1a** and *anti*-**1b** and each compound should consist of an enantiomeric pair because of the asymmetry in the carboxyamide linkages. Since we have not been able to separate the mixture, we do not know whether the syn and anti forms are produced in equal amount. It is notable that of the several diporphyrin crystals we have examined, all are apparently in the syn configuration.



Small single crystals of Cu_2DP-7 were grown by the slow evaporation of a toluene-dimethyl sulfoxide solution. The crystal used for the X-ray diffraction work had a prismatic morphology; the maximum dimension of the crystal was 0.3 mm and the square cross section was about 0.07-0.08 mm on edge. The crystal was shown to be monoclinic, $P2_1/c$, $a = 15.36$ (1), $b = 9.34$ (1), $c = 31.05$ (2) Å, $\beta = 111.22$ (2)°, $d_0 = 1.19$ g cm^{-3}. The calculated density based upon two Cu_2DP-7 molecules per unit cell was 1.208 g cm^{-3}. This requires Cu_2DP-7 to lie at a center of symmetry in the crystal. Since Cu_2DP-7 is asymmetrical, the molecule must be disordered so that statistically it will appear to be centrosymmetrical. Prolonged exposure X-ray photographs gave no indication of a superstructure.

The problem of the relatively small size of the crystals of Cu_2DP-7 was further compounded by the fact that the crystals displayed an orientational-type twinning. However, since the positions of the reflections differed by about 0.65° in ω and 1.0-1.2° in χ, the diffraction patterns of the two crystals could be resolved with our diffractometer (Picker FACSI with crystal to detector distance of 650 mm).[7] Thus, since the intensities from the two crystals were about equal, we were effectively working with a crystal about half the morphological size described above ($V \sim 0.0007$ mm^3). A consequence was that the diffraction pattern extended only to about 1.2-Å spacings, and of approximately 2800 possible reflections to this limit, only 1380 (49%) were greater than 3 × $\sigma(I)$, where $\sigma(I)$ was based upon counting statistics. The intensities were measured by using Cu Kα radiation operating at 1040-W power, with balanced filters and employing a wandering ω-step-scan procedure.[8] Repeated attempts to grow larger or "untwinned" crystals of Cu_2DP-7 proved to be of no avail.

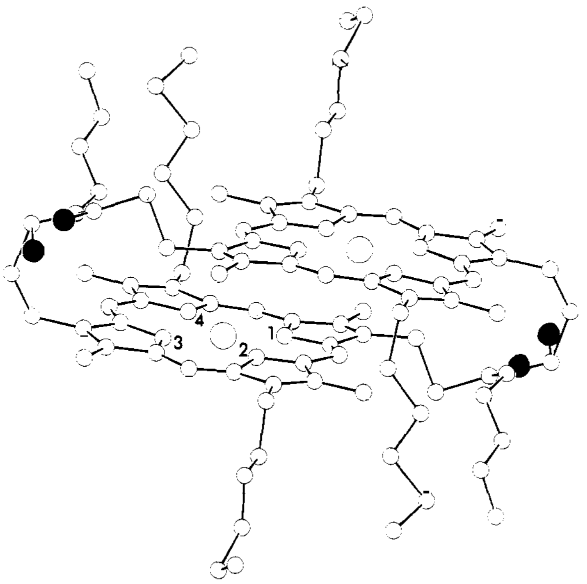


Figure 1. Perspective ORTEP drawing of Cu_2DP-7. Pyrrole nitrogen atoms numbered, disordered carbonyl oxygen atoms black.

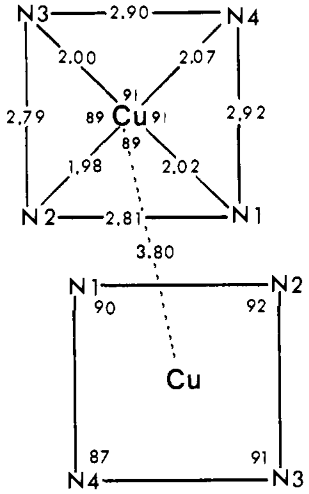


Figure 2. Projection of central core of one porphyrin of Cu_2DP-7 onto that of other. Distances in Å, angles in degrees; slip distance of 3.80 Å shown; N_1-N_2 component of slip is 0.63 Å; geometry of Cu environment also shown.

The structure of Cu_2DP-7 was solved by locating the Cu position and the positions of the coordinating nitrogen atoms from a Patterson function, including these into a Karle recycle of MULTAN, followed by a recycle including 18 additional atoms. The structure was then refined by Fourier methods and several cycles of least-squares refinement including isotropic thermal parameters to an R factor ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.16. When the positions of two disordered half oxygen atoms were included, the R value decreased to 0.15. Two more cycles of refinement constraining the hexyl side-chain distances to 1.54 ± 0.05 Å gave an R of 0.137. The refinement became stationary at this stage, and from the least-squares standard deviations in coordinates, the standard deviations were about ±0.1 Å in bond distances and

---

(1) (a) C. K. Chang, M. S. Kuo, and C. B. Wang, *J. Heterocycl. Chem.*, **14**, 943, (1977); (b) C. K. Chang, *J. Heterocycl. Chem.*, **14**, 1285 (1977); (c) C. K. Chang, *J. Chem. Soc., Chem. Commun.*, 800 (1977); (d) C. K. Chang, *Adv. Chem. Ser.*, No. **173**, 162 (1979).

(2) J. P. Collman, C. M. Elliott, T. R. Halbert, and S. B. Tovrog, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 18 (1977).

(3) H. Ogoshi, H. Sugimoto, and Z. Yoshida, *Tetrahedron Lett.*, 169 (1977).

(4) N. E. Kagan, D. Mauzerall, and R. B. Merrifield, *J. Am. Chem. Soc.*, **99**, 5484 (1977).

(5) J. P. Collman, M. Marrocco, P. Denisevich, C. Koval, and F. C. Anson, *J. Electroanal. Chem.*, **101**, 117 (1979).

(6) A preliminary report appears in "Program and Abstracts", American Crystallography Association Meeting, Calgary, Aug. 1980, PB6.

(7) A. Mavridis, A. Tulinsky, and M. N. Liebman, *Biochemistry*, **13**, 3661 (1974).

(8) R. L. Vandlen and A. Tulinsky, *Acta Crystallogr., Sect. B*, **B27**, 437 (1971); A. Mavridis and A. Tulinsky, *Inorg. Chem.*, **15**, 2723 (1976).

0002-7863/80/1502-7115$01.00/0

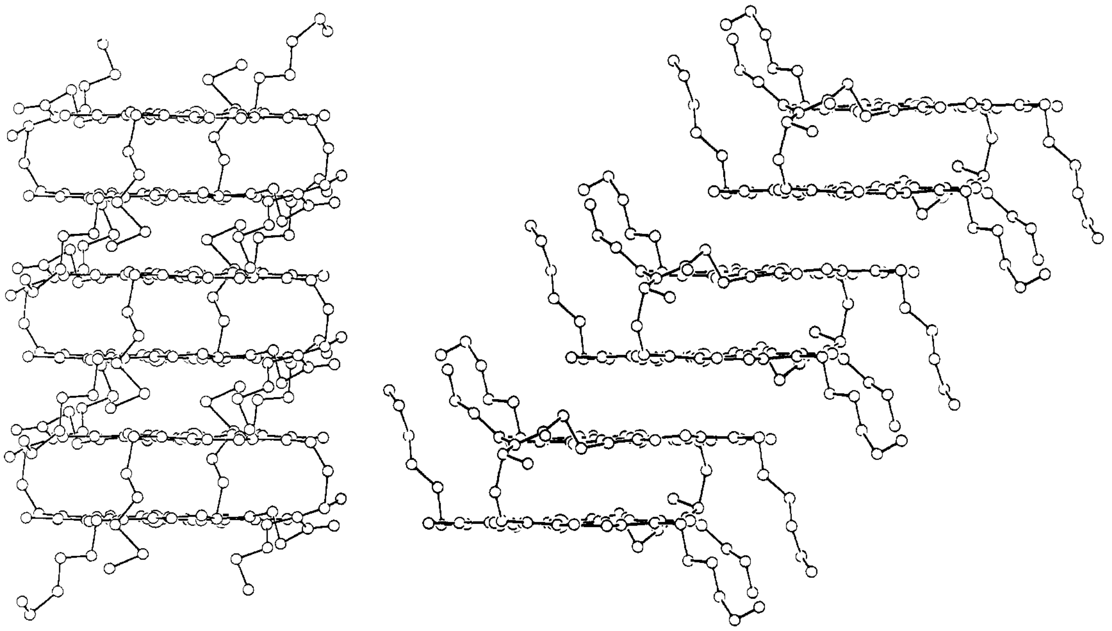


Figure 3. Stacking of Cu_2DP-7 along *b* axis. Views along ring directions and mutually perpendicular.

±1-2° in bond angles. The atomic parameters of Cu_2DP-7 have been deposited as supplementary material.[9]

A perspective ORTEP drawing of the structure of Cu_2DP-7 is shown in Figure 1 where the black circles represent the disordered carbonyl oxygen atoms of the porphyrin bridges. A least-squares plane calculation of the porphyrin ring, including the Cu atom, showed that it is planar within ±0.1 Å. The two porphyrin rings are not stacked exactly over each other, and the manner in which the rings slip is depicted schematically in Figure 2. From Figure 2, which shows the projection of the central core of one porphyrin onto that of the other, it can be seen that the slip of 3.80 Å corresponds closely to the methine-methine direction, giving a Cu-Cu distance of 5.22 Å. This also gives a slip angle of 43.2°.[10] When viewed perpendicular to the porphyrin rings, the projection of N2 is such that it nearly coincides with the center of the pyrrole ring below it while centrosymmetrically related N2 projects near the center of the pyrrole above it. The interplanar distance between rings is 3.52 ± 0.08 Å, corresponding to a normal van der Waals contact. The geometry of the immediate environment of the Cu atom is also shown in Figure 2 from which it can be seen to be square planar within the errors of the determination.

The *n*-hexyl chains of a given ring assume approximately centrically related extended configurations perpendicular to the ring giving rise to a number of close van der Waals contacts with hexyl chains of the opposite ring (Figure 1). The *n*-butyl chain of the carboxyamide group also has an extended and perpendicular configuration with respect to the porphyrin ring (Figure 1). This aliphatic side-chain structure in combination with the crystal packing leads to hydrocarbon channels in the crystal within which porphyrin rings are stacked (Figure 3). In fact, the interplanar distance between dimer molecules (3.47 ± 0.08 Å) is also normal van der Waals and is the same as that within a dimer, but, somewhat unexpectedly, the intermolecular Cu-Cu distance is less (4.60 Å) than the intramolecular distance. The latter results because there is less intermolecular slip (3.17 Å) between adjacent rings of dimer molecules (slip angle = 46.4°).

The disorder displayed by Cu_2DP-7 is unusual in that the three-carbon-atom aliphatic portions of the seven-atom bridges between porphyrin rings and the carboxamide half of the bridges have different configurations in the same molecule (Figure 1). Since these configurations are, except for the carbonyl oxygen, *centrosymmetrically* related in the dimer, the crystal is composed of dl enantiomorphs which leads *only* to disordered carbonyl oxygen atoms in the overall structure (Figure 1). This is dramatically borne out by the order displayed in the hexyl groups and *n*-butyl groups of this cofacial diporphyrin.

The slipped configuration of this Cu_2DP-7 may be a general structural feature of other metallodiporphyrins and free base diporphyrins. Preliminary results of a free base H_2DP-7 also show that the two rings are stacked with similar geometry.[11] The slipped configuration is certainly of significance for ligand intercalation; for example, dioxygen adducts to Co_2DP and Fe_2DP could also assume a slipped "trans" geometry. While direct X-ray structure proof of these complexes is still lacking, we have observed changes in EPR spectra and electrocatalytic behavior of the dicobalt system as we shortened the amide linking chains between the rings which physically limit the degree of slippage and vary the metal-oxygen bond geometry.[12]

The details of the structure determination will appear elsewhere.

Acknowledgments are made by C.K.C. to the donors of the Petroleum Research Fund, administered by American Chemical Society, and National Science Foundation (CHE-7815285) for partial support of this research.

Supplementary Material Available: Table of atomic parameters of Cu_2DP-7 and figure describing numbering system (3 pages). Ordering information is given on any current masthead page.

Marcos H. Hatada, A. Tulinsky,* C. K. Chang
Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

Received June 2, 1980

---

[9] See paragraph at end of paper regarding supplementary material.

[10] Slip angle = $\sin^{-1}$ (magnitude of slip/Cu-Cu distance).

[11] Unpublished results of this laboratory.

[12] A preliminary account was presented by C. K. Chang and C.-B. Wang at the Airlie House Symposium on "Interaction Between Iron and Proteins in Oxygen and Electron Transport", Airlie House, VA, April 1980; manuscript in preparation.

Biomimetic Synthesis of Macroline[1]

Sir:

Much current interest in the later stages of indole alkaloid biogenesis[2] together with the search for simple and direct synthetic

---

[1] Dedicated to the memory of Robert C. Elderfield, 1904-1979.

0002-7863/80/1502-7116$01.00/0