

d-d bands due to the Ni²⁺ chromophore are consistent with a tetrahedral or distorted tetrahedral geometry,¹² as is generally observed for metal ions bound to the native zinc site of this protein.¹ Addition of azide to either of these derivatives causes no change in their spectra, consistent with the absence of a ligand-binding site on the Ni²⁺ ion when it is bound to the native zinc site. This behavior also is similar to that observed when other metal ions are bound to that site.

The ¹H NMR spectra of Ag₂Ni₂SOD (Figure 2E) and of reduced Cu₂Ni₂SOD (Figure 2D) are also extremely similar. There are 15 detectable paramagnetically shifted proton NMR signals which we assign to the three histidyl and one aspartyl residues, which are presumably coordinated to Ni²⁺. By considering the line width (which is contributed by the distance-dependent hyperfine interactions and chemical exchanges) of the isotropic shifts, the sharper signals can be tentatively assigned to C_δ-H or N-H protons and the broad signals to C_ε-H protons.³ We assign resonances, b, h, and j to N-H protons since they are not observed in D₂O. The upfield-shifted signals are tentatively assigned as C_β-H₂ protons of coordinated histidyl and aspartyl residues by comparison with paramagnetically shifted resonances of other proteins.³ Several other Ni²⁺-substituted derivatives of SOD have also been prepared in our laboratory. Their characterization and a fuller assignment of the NMR spectra of the above-described nickel derivatives are now in progress.

Acknowledgment. Financial support from the USPHS (GM 28222) is gratefully acknowledged. We also thank Dr. James A. Roe for many helpful discussions.

(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 789.

21-Thiatetra-*p*-tolylporphyrin and Its Copper(II) Bicarbonate Complex. Structural Effects of Copper-Thiophene Binding

Lechosław Latos-Grażyński* and Jerzy Lisowski

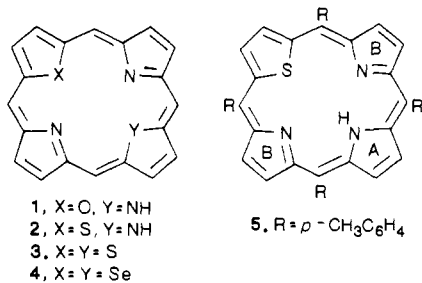
*Institute of Chemistry, University of Wrocław
50383 Wrocław, Poland*

Marilyn M. Olmstead and Alan L. Balch*

*Department of Chemistry, University of California
Davis, California 95616*

Received December 9, 1986

Replacement of the nitrogen atoms of porphyrins with other potential donors produces macrocycles with differing central cavity sizes whose complexing abilities remain unknown. Limited data regarding the oxa- and thiaporphyrins **1** and **2** are available,¹ while the dithia- and diselenaporphyrins **3** and **4** have received somewhat more attention.² Here we report the preparation and structural



(1) Johnson, A. W. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 729.

characterization of 21-thiatetra-*p*-tolylporphyrin (**5**, STTPH) and its copper(II) complex. This represents the first thorough structural characterization of a heteroporphyrin system. The structure of the copper complex is of particular interest because of the limited coordinating ability of the thiophene moiety,³ the geometric constraints imposed by the macrocycle, and the multiplicity of possibilities (S-bound, C-bound, η⁵-bound) available for metal/thiophene coordination.⁴

The condensation of 2,5-bis(*p*-tolylhydroxymethyl)thiophene⁵ with 2 mol of *p*-tolylaldehyde and 3 mol of pyrrole in boiling propionic acid conducted over 1 h, followed by cooling, produces a mixture from which STTPH, TTPH₂ (tetra-*p*-tolylporphyrin), and traces of S₂TTP (**3**) crystallize on standing for 24 h. The solid material was dissolved in carbon tetrachloride and subjected to chromatography on basic alumina. Two major bands eluted to give TTPH₂ and STTPH successively. The fraction containing STTPH was evaporated, and the product recrystallized from dichloromethane/ethanol to give STTPH in 5% yield (electronic spectrum which is porphyrin-like: UV-vis λ_{max} 428 (Soret), 514, 550, 618, 680 nm; ¹H NMR spectrum (360 MHz, CDCl₃, 25 °C) δ 9.785 (s, thiophene), 8.924 (d, *J* = 2.16 Hz, pyrrole A), 8.673, 8.599 (q, *J* = 4.5 Hz, pyrrole B), 8.129, 8.066 (s, ortho phenyl), 7.612, 7.535 (meta phenyl), 2.697 (s, *p*-methyl), -2.661 (t, *J* = 2.16 Hz, NH)). The NMR spectrum unambiguously locates the N-H group on pyrrole ring A as indicated by the long-range coupling to the adjacent C-H groups and the characteristic downfield shift.

The structure of STTPH was investigated through an X-ray crystal structure.⁶ The molecule is planar, as can be seen in Figure 1. Because of the presence of sulfur, the core size of the macrocycle is restricted: the nonbonded S(1)⋯N(1') distance is 3.585 Å while the N(2)⋯N(2') distance is 4.383 Å (somewhat longer than the tetragonal form (4.108 Å)^{7a} or the triclinic form (4.06, 4.20 Å)^{7b} of tetraphenylporphyrin).

Insertion of copper(II) was achieved by boiling a mixture of STTPH in chloroform and an ethanolic solution of copper(II) chloride hydrate in the presence of triethyl orthoformate and solid sodium carbonate for 0.5 h. After evaporation of the solution, the residue was subjected to chromatography on neutral alumina with dichloromethane as eluent, and the product, Cu(STTPH)(C-O₃H) (**6**; yield 70%), was recrystallized from dichloromethane/toluene (λ_{max} 466 (Soret), 580, 630, 710 nm).

(2) Ulman, A.; Manassen, J. *J. Am. Chem. Soc.* **1975**, *97*, 6540. Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *J. Am. Chem. Soc.* **1979**, *101*, 7055. Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *Inorg. Chem.* **1981**, *20*, 1987. Hill, R. L.; Gouterman, M.; Ulman, A. *Inorg. Chem.* **1982**, *21*, 1450.

(3) (a) Giordano, T.; Rasmussen, P. G. *Inorg. Chem.* **1975**, *14*, 1628. (b) Giordano, T.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1987**, *17*, 1917. (c) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1983**, *248*, C9. (d) van Stein, G. C.; van Koten, G.; Spek, A. L.; Duisenberg, A. J. M.; Klop, E. A. *Inorg. Chim. Acta* **1983**, *78*, L61.

(4) (a) Singer, H. *J. Organomet. Chem.* **1967**, *9*, 135. (b) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1306. (c) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689. (d) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1986**, *61*, 128. (e) Bucknor, S. M.; Draganjac, M.; Rauffuss, T. B.; Ruffing, C. J.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5379. (f) Draganjac, M.; Ruffing, C. J.; Rauffuss, T. B. *Organometallics* **1985**, *4*, 1909. (g) Lesch, D. A.; Richardson, Jr., J. W.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (h) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569.

(5) Ulman, A.; Manassen, J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1066.

(6) Dark-blue parallelepipeds of STTPH (**5**) were grown by diffusion of ethyl ether into a dichloromethane solution of the macrocycle. They belong to the monoclinic space group *P2₁/n* (No. 14) with *a* = 9.484 (2) Å, *b* = 9.305 (2) Å, *c* = 21.370 (5) Å, β = 100.04 (2)°, and *Z* = 2 at 130 K. Refinement of 1699 reflections with *I* > 2σ*I* and 249 parameters gave *R* = 0.051. There is a center of symmetry at the center of the macrocycle; hence the sulfur atom is disordered. The major form involving S(1) with 0.38 occupancy is shown in Figure 1; its centrosymmetrically related form interchanges the approximate positions of S(1) and N(1'). The minor form with 0.12 occupancy for each of the centrosymmetrically related positions places the sulfur atom near N(2) (or N(2')).

(7) (a) Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 1938. (b) Silvers, S. J.; Tulinsky, A. *J. Am. Chem. Soc.* **1967**, *89*, 3331.

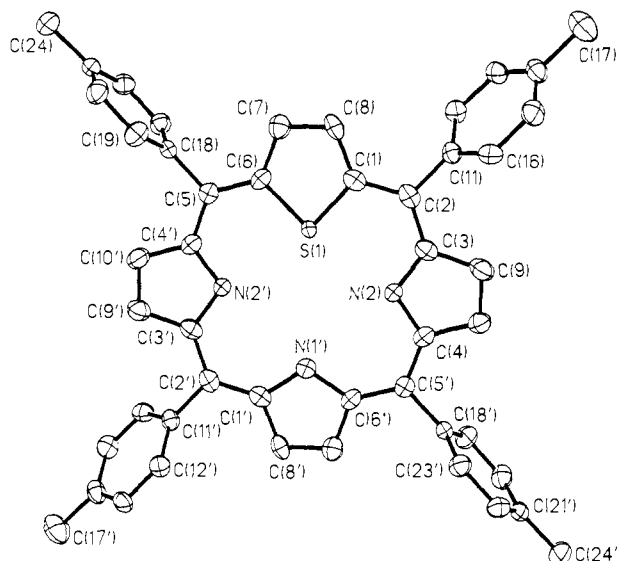


Figure 1. View of STTPH, **5**. The S(1)–C(1) and S(1)–C(6) distances are 1.713 (4) and 1.732 (4) Å. The porphyrin core is planar with the largest out-of-plane distances (Å): N(2'), –0.050; N(2), 0.049; N(1'), 0.048; S(1), –0.042; C(7), 0.040; with the remaining less than 0.031.

The structure of the paramagnetic copper(II) complex, **6**, was determined by X-ray crystallography.⁸ Figure 2 shows a perspective view of the molecule. The copper(II) possesses irregular, five-coordinate geometry. The unique Cu–N(2a) distance of 1.993 (10) Å is slightly shorter than the other two Cu–N distances, 2.042 (7) and 2.067 (8) Å. All of these are comparable to the Cu–N distances in copper(II) tetraphenylporphyrin (1.981 (7) Å)⁹ and copper(II) tetrapropylporphyrin (1.994, 2.005 Å).¹⁰ The Cu–O(1a) distance is quite long.

The most notable feature of **6** is the nonplanarity of the porphyrin and the nature of the thiophene–copper(II) interaction. While the thiophene ring is planar, it is sharply bent out of the plane of the porphyrin. The shape of the porphyrin resembles

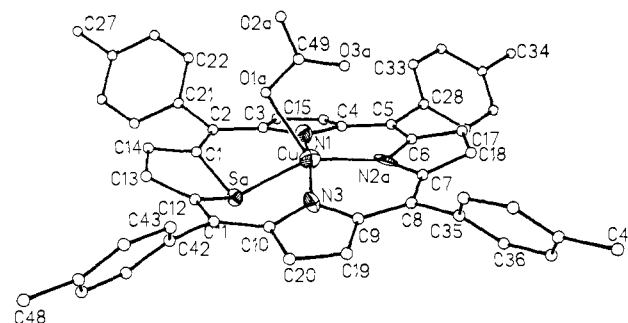


Figure 2. Perspective drawing of Cu(STTP)(CO₃H), **6**. Selected bond distances (Å): Cu–S, 2.277 (3); Cu–N(1), 2.067 (8); Cu–N(2a), 1.993 (10); Cu–N(3), 2.042 (7); Cu–O(1a), 2.246 (12); S–C(1), 1.729 (10); S–C(12), 1.750 (10). Selected bond angles (deg): S–Cu–N(1), 84.0 (2); S–Cu–N(2a), 148.0 (3); S–Cu–N(3), 86.1 (2); S–Cu–O(1a), 88.3 (3); N(1)–Cu–N(2a), 90.9 (4); N(1)–Cu–N(3), 166.4 (3); N(2a)–Cu–N(3), 92.7 (4); N(2a)–Cu–O(1a), 123.7 (4); N(1)–Cu–O(1a), 95.5 (4); N(3)–Cu–O(1a), 96.9 (7).

that seen in metal complexes of porphyrin *N*-oxides¹¹ and *N*-alkylporphyrins.¹² The dihedral angle between the thiophene plane and the CuN₃ plane is 27.5°. This bending opens up the center of the porphyrin to accommodate the copper and allows for the copper to interact with the thiophene sulfur in a side-on fashion. The angle between the thiophene plane and the Cu–S bond is 54.4°. Similar angles are found in the two ruthenium–thiophene complexes, which have been structurally characterized.^{4e,f} The Cu–S distance, 2.277 (3) Å, is clearly a bonding distance. It falls somewhat below the range (2.297–2.410 Å) previously noted for other Cu(II)–S distances.¹³ This slight compression, no doubt, results from the constraints of the macrocyclic ligand. Thus the thiophene is η¹-bonded to copper through sulfur which is pyramidal. This represents the first structural characterization of this bonding mode to a first-row transition metal.

Acknowledgment. We thank the Polish Academy of Sciences (MR-I-9) and the National Institutes of Health (GM26226) for financial support.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for **5** and **6** (11 pages). Ordering information is given on any current masthead page.

(8) Dark-green needles of Cu(STTP)(CO₃H)·1/2C₂H₆ were grown by diffusion of toluene into a chloroform solution of the complex. They belong to the space group C2/c (No. 15) with *a* = 30.221 (7) Å, *b* = 15.327 (4) Å, *c* = 17.795 (4) Å, β = 92.50 (2)°, and *Z* = 8 at 130 K. Refinement yielded *R* = 0.062 for 2469 reflections with *I* > 3σ*I* and 311 parameters. There is disorder in the location of the sulfur atom and the carbonate oxygens. The major form, with 0.75 occupancy, is shown in Figure 2, and its dimensions are the ones given. The minor form, with 0.12 occupancy, interchanges the positions of S and N(2) and places S(2) near N(2) (or near N(2') in the centrosymmetrically related partner). Only dimensions of the major form are discussed.

(9) Fleischer, E. B.; Miller, C. K.; Webb, L. E. *J. Am. Chem. Soc.* **1964**, *86*, 2342.

(10) Moustakali, I.; Tulinsky, A. *J. Am. Chem. Soc.* **1973**, *95*, 6811.

(11) Balch, A. L.; Chan, Y.-W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 6510.

(12) Anderson, O. A.; Kopelove, A. B.; Lavalley, D. K. *Inorg. Chem.* **1980**, *19*, 2101.

(13) Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Inorg. Chem.* **1981**, *20*, 151.