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Synthesis and Structure of a Dimercapto — Iron(III) Porphyrin Derivative: $|Fe(SC_6HF_4)_2TPP||Na \subset 18C6|, C_6H_6$*

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A low-spin di-mercapto-iron(III)-*meso*-tetraphenylporphyrin complex, $|Fe(SC_6HF_4)_2TPP||Na \subset 18C6|$, C_6H_6 has been synthesized. This compound presents in the solid state a d type hyper-spectrum with a split Soret band at 383 and 461 nm. The crystals belong to the triclinic system space group $P\bar{1}$ with $a = 12.628(4)$, $b = 21.594(8)$, $c = 12.881(4)$ Å, $\alpha = 104.02(2)$, $\beta = 98.26(2)$, $\gamma = 76.40(2)^\circ$, $V = 3298$ Å^3, $Z = 2$. Pertinent structural parameters include relatively long equatorial Fe—Np bond distances of 1.998(3) Å and relatively short axial Fe—S bond distances of 2.312(1) Å. The structures of the two centrosymmetric crystallographically independent $|Fe(SC_6HF_4)_2TPP|^-$ anions are essentially identical.

Oxygenation of a five-coordinate high-spin mercapto-iron(II) porphyrin obtained with alkali-metal 2.3.5.6. fluoro-phenylthiolate, M^+, $^-SC_6HF_4$ ($\mathbf{O}$ = 222, 221, 18C6) and iron(II) picket-fence porphyrin $|Fe(II)TP_{piv}P|$ leads at ambient temperature in solution and in the solid state to dioxygen adducts which present spectroscopic properties very similar to those known for the oxy state of cytochromes P 450[1,2,15]. Under similar conditions, but using iron(II) meso-tetraphenyl porphyrin, $|FeTPP|$, the same reaction leads to a complex presenting a d type hyperspectrum.[3] The spectrum of this complex is very similar to that obtained by CHANG and DOLPHIN[4] by direct oxygenation of solutions containing $|Fe(II)\,PPIX\,DME|$ and an excess of potassium n butyl thiolate in DMSO at —45° C. It has later been shown by Ruf and Wende[5] using spectroscopic methods that the species responsible for this d type hyper-spectrum corresponds most probably to a dimercaptoiron(III) porphyrin derivative. We have now isolated a complex containing a low-spin di-mercapto-iron(III) porphyrin anion, $|Fe(SC_6HF_4)_2\,TPP|^-$ and present here its spectroscopic properties and structure. The X-ray structure and EPR spectral properties of a six-coordinate diphenylthiolato-iron(III) *meso*-tetraphenylporphyrin complex has already been described[6] and the structures and EPR properties of several thiol/thiolato iron(III) porphyrins have recently been determined[7].

EXPERIMENTAL

All experiments were done under an inert atmosphere by either Schlenk techniques or in a Vacuum Atmospheres dry-box unless otherwise stated. Solvents

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

were rigourously purified and dried under argon. The free tetraphenyl porphyrin and its iron(III) chloro complex were prepared by published methods[8-9]. The 2.3.5.6. fluorophenylthiol and the 18C6 polyether were obtained from ALDRICH Chem. Co. The sodium salt was prepared by reacting the thiol in dry doubly distilled THF and precipitated with pentane. UV-visible spectra were measured on a Cary 210 spectrometer. Solid state spectra were obtained on samples deposited as thin films. X band EPR spectra were taken at 100K with a Bruker spectrometer. Magnetic field measurements were made by using a NMR proton probe.

Synthesis and Crystallization of $|Fe(SC_6HF_4)_2TPP||Na \subset 18C6|$, C_6H_6 *1*

$|Fe(III)TPP\,Cl|$ (20 mg) was dissolved in 50 ml of benzene. An excess of 18C6 cryptated sodium 2.3.5.6. fluorophenylthiolate (72 mg) in 20 ml of benzene was added. Microcrystalline powders and single crystals suitable for X-ray studies of $|Fe(III)(SC_6HF_4)_2TPP||Na \subset 18C6|$, C_6H_6 were obtained by slow addition of pentane in the dark at 6 °C.

UV-visible (25 °C solid) 383, 461, 587, 633 nm (Figure 1)

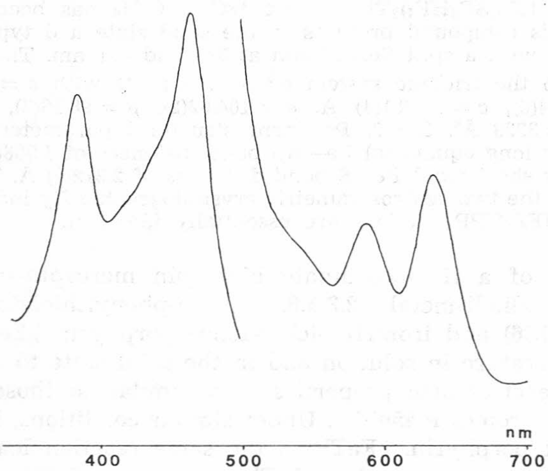

Figure 1. UV-visible spectrum at 25 °C of $|FeTPP(SC_6HF_4)_2||Na \subset 18C6|$, C_6H_6 solid.

E.S.R. (100 °K, solid) g : 1.945; 2.271; 2.370 (Figure 2).

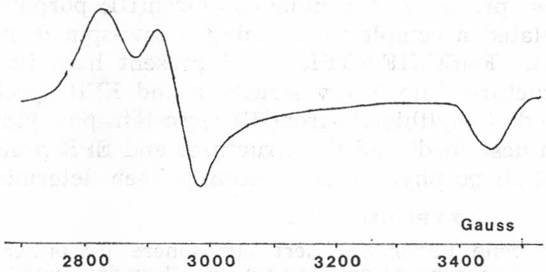

Figure 2. X band ESR spectrum at 100 K (9.385 GHz) of $|Fe(SC_6HF_4)_2TPP|$ $|Na \subset 18C6|$, C_6H_6 solid.

X-Ray Experimental Section

A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of *1* belong to the triclinic system.

The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with CuK_α radiation ($\lambda = 1.5418$ Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{74}H_{60}N_4O_6F_8NaS_2Fe$, mol wt.: 1396, $a = 12.628(4)$ Å, $b = 21.594(8)$ Å, $c = 12.881(4)$ Å, $\alpha = 104.02(2)$, $\beta = 98.26(2)$, $\gamma = 76.40(2)$, $V = 3298.3$ Å^3, $Z = 2$, dcalc $= 1.406$ gcm^{-3}, $\mu = 31.50$ cm^{-1}, $F_{000} = 1442$, space group $P\bar{1}$.

A prismatic crystal of $0.30 \times 0.26 \times 0.32$ mm was sealed in a Lindemann glass capillary and mounted on a rotation free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four circle automatic diffractometer, controlled by a P852 computer, using graphite monochromated radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\Theta/2\Theta$ flying step-scan used was $\Delta\omega = 0.9 + (CuK_{\alpha1,\alpha2}$ splitting$)^\circ$ with a step width of 0.04 deg. and a scan speed of 0.016 deg. sec^{-1}. 9186 reflections were recorded ($4 < \Theta < 57$). The resulting data-set was transfered to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used[10], with the exception of a local data-reduction program.

Three standard reflections measured every hour during the entire data-collection period showed no significant trend.

The raw step-scan data were converted to intensities using the Lehmann-Larsen method[11] and then corrected for Lorentz, polarization and absorption factors, the latter computed by the numerical integration method of BUSING and LEVY[12] (transmission factors between 0.389 and 0.533). A unique data set of 5674 reflections having $I > 3\sigma$ (I) was used for determining and refining the structure.

The structure was solved using the heavy atom method. After refinement of the non-hydrogen atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C—H=0.95 Å) and isotropic temperature factors of $1 + B_C$ Å^2 but not refined. Full least-squares refinement converged to $R(F) = 0.060$ and $Rw(F) = 0.080$ $(w = 1/|\sigma^2_{count} + (pI)^2|)$. The unitweight observation was 1.60 for $p = 0.08$. A final difference map revealed no significant maxima.

Table I lists the atomic positional parameters for all non-hydrogen atoms with the estimated standard deviations.

RESULTS AND DISCUSSION

The asymmetric unit of $|Fe(III)(SC_6HF_4)_2TPP||Na \subset 18C6|$, C_6H_6 *1* contains two half independent anionic porphyrinates, $|Fe(III)(SC_6HF_4)_2TPP|^-$ located on a crystallographic inversion center along with one sodium crown-ether cation, $|Na \subset 18C6|^+$ and one molecule of benzene located in general positions of space groups $P\bar{1}$. Figure 3. shows the structure of one anion, $|Fe(III)(SC_6HF_4)_2TPP|^-$ and Figure 4. displays the structure of $|Na \subset 18C6|^+$. Table 2 gives selected bond distances and angles.

In both anions, the metal and the four porphyrinato-nitrogens of the FeN_4S_2 octahedral coordination unit form square necessarily planar entities with $(Fe1 — Np)_{av} = (Fe2 — Np)_{av} = 1.998(3)$ Å and $(Np — Fe1 — Np)_{av} = (Np — Fe2 — Np)_{av} = 89.95(10)$ deg.

This $(Fe — Np)_{av}$ distance is not significantly different from those known for $|FeSC_6H_5)_2TPP|^-$ [6] and $|Fe(CN)_2TPP|^-$ [13] in which these mean values are

TABLE I

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Fe1	1.000	0.500	0.500	3.19(2)
N1	0.8402(3)	0.5282(2)	0.4568(3)	3.5(1)
C11	0.7568(4)	0.5522(2)	0.5232(4)	3.9(1)
C12	0.6564(4)	0.5713(3)	0.4598(4)	4.6(1)
C13	0.6780(4)	0.5584(3)	0.3569(4)	4.6(1)
C14	0.7930(4)	0.5314(2)	0.3553(4)	3.7(1)
N2	0.9673(3)	0.5211(2)	0.6530(3)	3.42(9)
C21	1.0418(4)	0.5116(2)	0.7402(4)	3.8(1)
C22	0.9859(4)	0.5316(3)	0.8372(4)	4.7(1)
C23	0.8799(4)	0.5513(3)	0.8082(4)	5.0(1)
C24	0.8665(4)	0.5455(2)	0.6934(4)	3.8(1)
C5	1.1529(4)	0.4877(2)	0.7379(4)	3.8(1)
C51	1.2215(4)	0.4804(3)	0.8406(4)	4.5(1)
C52	1.2297(5)	0.4262(3)	0.8832(5)	5.5(2)
C53	1.2981(6)	0.4179(3)	0.9750(5)	6.9(2)
C55	1.3513(5)	0.5174(4)	0.9837(6)	7.3(2)
C54	1.3571(6)	0.4629(4)	1.0229(5)	8.2(2)
C56	1.2834(5)	0.5262(3)	0.8922(5)	5.8(2)
C6	0.7667(4)	0.5605(2)	0.6343(4)	3.8(1)
C61	0.6649(4)	0.5904(3)	0.6919(4)	4.5(1)
C62	0.6564(5)	0.6498(3)	0.7627(5)	6.0(2)
C63	0.5599(6)	0.6794(3)	0.8131(5)	7.1(2)
C64	0.4736(5)	0.6486(4)	0.7906(5)	8.1(2)
C65	0.4811(5)	0.5896(4)	0.7197(5)	7.2(2)
C66	0.5762(4)	0.5605(3)	0.6703(5)	5.7(2)

Table I continued on the next page.

Table I continued

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
S1	0.9751(1)	0.39738(6)	0.4998(1)	4.17(3)
CT1	0.9860(4)	0.3496(2)	0.3699(4)	4.3(1)
CT2	0.8955(5)	0.3467(3)	0.2949(5)	5.5(2)
CT3	0.9039(7)	0.3060(3)	0.1961(6)	7.7(2)
CT4	0.9986(7)	0.2675(3)	0.1636(5)	7.8(2)
CT5	1.0868(6)	0.2699(3)	0.2346(5)	6.9(2)
CT6	1.0827(5)	0.3107(3)	0.3357(5)	5.4(2)
F1	0.7970(3)	0.3833(2)	0.3196(3)	7.4(1)
F2	0.8111(5)	0.3050(2)	0.1281(4)	12.4(2)
F3	1.1869(4)	0.2322(2)	0.2091(4)	10.8(1)
F4	1.1757(3)	0.3108(2)	0.4012(3)	7.1(1)
Fe2	1.000	0.000	0.000	3.41(3)
N3	0.9574(3)	0.0528(2)	-0.1131(3)	3.8(1)
C31	1.0182(4)	0.0514(3)	-0.1942(4)	4.1(1)
C32	0.9603(5)	0.0969(3)	-0.2585(4)	5.1(1)
C33	0.8645(5)	0.1250(3)	-0.2162(5)	4.9(1)
C34	0.8624(4)	0.0981(2)	-0.1262(4)	4.0(1)
N4	0.8569(3)	0.0414(2)	0.0606(3)	3.6(1)
C41	0.7773(4)	0.0901(3)	0.0283(4)	4.1(1)
C42	0.6919(4)	0.1107(3)	0.0995(4)	4.6(1)
C43	0.7189(4)	0.0747(3)	0.1744(4)	4.6(1)
C44	0.8226(4)	0.0300(2)	0.1501(4)	3.9(1)
C7	0.7773(4)	0.1165(3)	-0.0593(4)	4.1(1)
C71	0.6805(4)	0.1677(3)	-0.0835(4)	4.4(1)
C72	0.5794(5)	0.1542(3)	-0.1141(6)	6.3(2)

Table I continued on the next page.

Table I continued

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C73	0.4880(5)	0.2016(4)	-0.1311(6)	8.4(2)
C74	0.4984(6)	0.2635(4)	-0.1184(6)	8.2(2)
C75	0.5968(7)	0.2792(3)	-0.0891(6)	8.3(2)
C76	0.6901(6)	0.2312(3)	-0.0707(6)	6.7(2)
C8	1.1219(4)	0.0123(2)	-0.2138(4)	4.0(1)
C81	1.1768(4)	0.0178(3)	-0.3052(4)	4.3(1)
C82	1.1427(5)	-0.0067(3)	-0.4105(5)	5.5(2)
C83	1.1967(5)	-0.0023(3)	-0.4942(5)	6.4(2)
C84	1.2854(5)	0.0253(3)	-0.4745(5)	6.2(2)
C85	1.3202(5)	0.0506(3)	-0.3710(5)	5.9(2)
C86	1.2661(5)	0.0471(3)	-0.2848(5)	5.5(2)
S2	1.0549(1)	0.08813(7)	0.1193(1)	4.43(3)
CT7	1.1958(4)	0.0748(3)	0.1195(4)	4.3(1)
CT8	1.2677(5)	0.0410(3)	0.1916(5)	6.3(2)
CT9	1.3784(6)	0.0327(4)	0.1906(7)	10.6(3)
CT10	1.4263(6)	0.0505(5)	0.1217(8)	15.1(3)
CT11	1.3573(6)	0.0847(4)	0.0521(6)	11.5(2)
CT12	1.2460(5)	0.0960(3)	0.0509(5)	6.4(2)
F5	1.2254(4)	0.0212(2)	0.2641(3)	9.6(1)
F6	1.4385(4)	-0.0014(3)	0.2663(5)	15.6(2)
F7	1.3995(4)	0.1061(3)	-0.0171(5)	18.7(2)
F8	1.1841(4)	0.1299(2)	-0.0180(3)	9.5(1)
Na	0.9448(2)	0.2399(1)	0.6104(3)	7.93(8)
O1C	0.9036(6)	0.1846(3)	0.4757(5)	12.5(2)
C2C	0.957(1)	0.1747(5)	0.3945(7)	15.4(3)

Table I continued on the next page.

Table I continued

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C3C	1.0809(9)	0.1624(5)	0.4385(8)	13.6(3)
O4C	1.0938(4)	0.2228(2)	0.5178(5)	9.0(2)
C5C	1.1990(7)	0.2160(5)	0.5635(8)	11.7(3)
C6C	1.2068(7)	0.2714(5)	0.6465(9)	11.5(3)
O7C	1.1252(5)	0.2864(3)	0.7240(5)	10.6(2)
C8C	1.1394(9)	0.2412(5)	0.7880(9)	13.1(4)
C9C	1.0662(9)	0.2698(6)	0.8689(9)	15.3(4)
O10C	0.9616(6)	0.2821(3)	0.8262(7)	15.0(3)
C11C	0.888(1)	0.3311(6)	0.876(1)	21.7(5)
C12C	0.876(1)	0.3827(7)	0.8471(8)	18.2(5)
O13C	0.8402(6)	0.3824(3)	0.7353(5)	13.7(2)
C14C	0.7403(9)	0.3915(6)	0.705(1)	18.5(5)
C15C	0.7045(7)	0.3778(5)	0.587(1)	13.3(4)
O16C	0.7523(6)	0.3084(4)	0.5567(7)	17.8(3)
C17C	0.741(1)	0.2874(6)	0.4533(7)	17.8(5)
C18C	0.7683(8)	0.2116(7)	0.432(1)	20.3(5)
CS1	0.4414(7)	0.2425(4)	0.4509(7)	9.8(3)
CS2	0.4802(7)	0.2532(4)	0.5562(8)	10.0(3)
CS3	0.5369(8)	0.2022(5)	0.5990(7)	10.3(3)
CS4	0.5524(8)	0.1422(4)	0.5389(8)	10.8(3)
CS5	0.5171(9)	0.1310(5)	0.4374(8)	11.9(3)
CS6	0.4593(8)	0.1796(5)	0.3874(8)	11.4(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

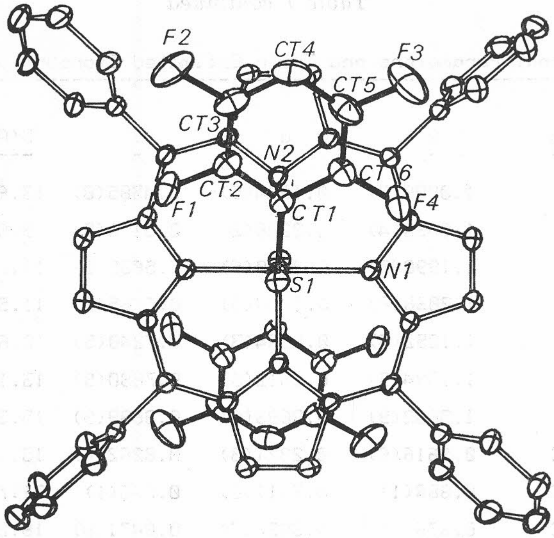

Figure 3. ORTEP plot of one porphyrin unit with part of the labeling scheme used. Ellipsoïds are scaled to enclose 40% of the electronic density. Hydrogen atoms are omitted.

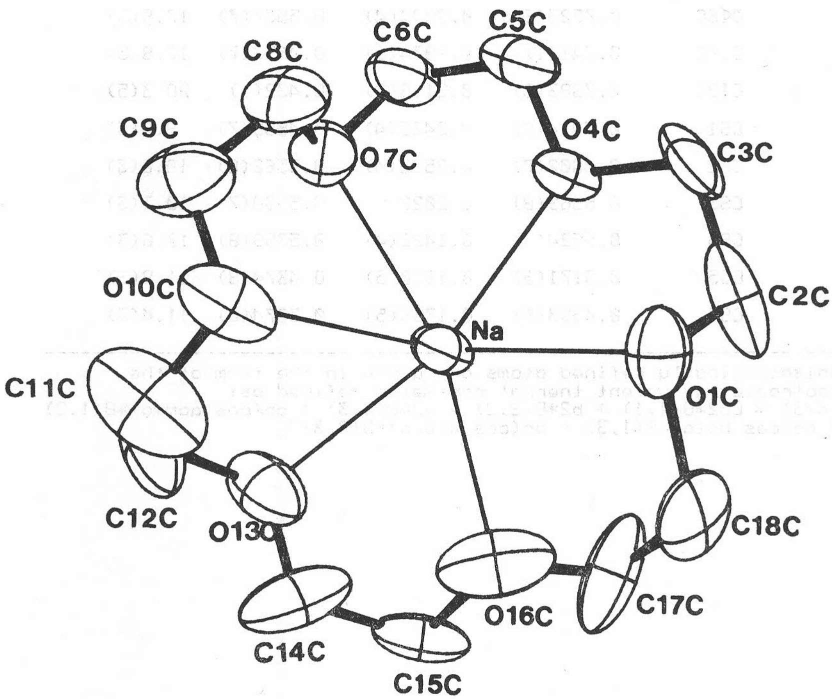

Figure 4. ORTEP plot of the $|Na \subset 18C6|^{+}$ crown. Ellipsoïds are scaled to enclose 40% of the electronic density. Hydrogen atoms are omitted.

1.989(10) and 2.000(6) Å respectively. As in these two low-spin iron III anionic porphyrinates, the average Fe—Np distance present in *1* is slightly longer than the 1.990 value obtained by averaging the Fe—Np distances in a number of analogous neutral or positively charged species[14]. The small increase is probably due to the overal negative charge of the dimercapto — complex[15].

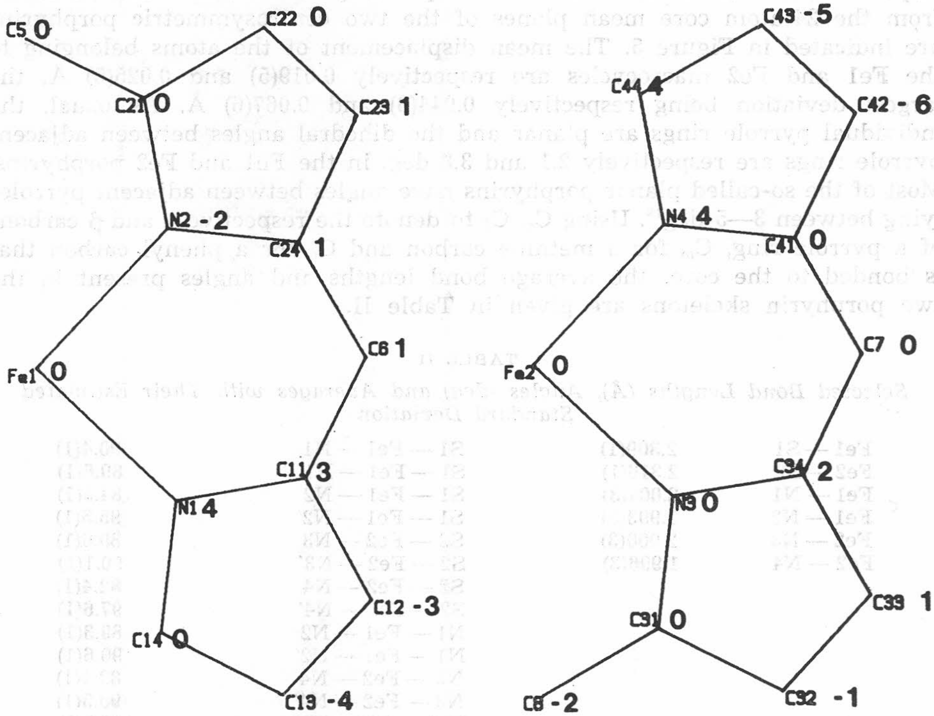

Figure 5. Stick model of the two half porphyrin cores. The dark numbers are the deviations in 0.01 Å units of the atoms from the porphyrin core mean planes.

As shown by figure 3. the axial thiolato ligands eclipse in both anions almost two opposite Fe — Np bonds. The intersections of the Fe1—S—C and Fe2—S—C planes and the corresponding porphyrin mean-planes lie 3.8 and 8.2 deg. respectively away from two opposite Fe — Np bonds. Moreover, these Fe — S bonds are tipped in both anions by 5.3(Fe1) and 7.7(Fe2) deg. The mean-value of the Fe — S bond distances is 2.312(1) Å. This value is 0.012 Å shorter than the corresponding distance of 2.324(2) Å present in the high spin five-coordinate *p*-nitrophenylthiolate-iron(III) PPIXDME complex[16] and 0.058 Å shorter than in the high-spin, five coordinate 2.3.5.6. fluorophenylthiolate iron(II) picket fence porphyrin anion[17]. The standard deviation of the mean-value is given identical to that of the bonds. These differences are quite small when compared with the Fe — Nax distance changes observed in the correspon-ding *N*-ligated iron porphyrinato complexes, but at least they present the expected direction[14]. Except, for the six-coordinate thiol-thiolato, ‖ HS—3Me—1Bu ‖ S—3Me—1Bu | FeTPP | (Fe—S=2.293(2) Å) and ‖ HSBzl ‖ SBzl | FeTPP | (Fe — S = 2.316(1) Å) where only average Fe — S bond lengths for thiol and thiolate ligands have been obtained[7], so far, all the Fe—S bond distances found were in the range of 2.324—2.370 Å, despite the fact that the corresponding compounds differ in nature of the sulfur ligand (thiolate or thioether) oxidation state and coordination number of iron[14,17].

The two porphyrins present in *1* are almost planar. Table 3 gives the displacements from a number of least-squares planes. The deviations found from the 24-atom core mean planes of the two centrosymmetric porphyrins are indicated in Figure 5. The mean displacement of the atoms belonging to the Fe1 and Fe2 macrocycles are respectively 0.019(5) and 0.025(5) Å, the largest deviation being respectively 0.044(6) and 0.067(6) Å. As usual, the individual pyrrole rings are planar and the dihedral angles between adjacent pyrrole rings are respectively 2.1 and 3.8 deg. in the Fe1 and Fe2 porphyrins. Most of the so-called planar porphyrins have angles between adjacent pyrroles lying between 3—5 deg[18]. Using C_α, C_β to denote the respective α and β carbons of a pyrrole ring, C_m for a methine carbon and C_p for a phenyl carbon that is bonded to the core, the average bond lengths and angles present in the two porphyrin skeletons are given in Table II.

TABLE II

Selected Bond Lengths (Å), Angles (deg) and Averages with Their Estimated Standard Deviation

Fe1—S1	2.309(1)	S1—Fe1—N1	90.4(1)
Fe2—S2	2.316(1)	S1—Fe1—N1′	89.6(1)
Fe1—N1	2.004(3)	S1—Fe1—N2	84.5(1)
Fe1—N2	1.993(3)	S1—Fe1—N2′	95.5(1)
Fe2—N3	2.000(3)	S2—Fe2—N3	89.8(1)
Fe2—N4	1.996(3)	S2—Fe2—N3′	90.1(1)
		S2—Fe2—N4	82.4(1)
		S2—Fe2—N4′	97.6(1)
		N1—Fe1—N2	89.3(1)
		N1—Fe1—N2′	90.6(1)
		N3—Fe2—N4	89.4(1)
		N3—Fe2—N4′	90.5(1)
		Fe1—S1—CT1	108.5(1)
		Fe2—S2—CT2	106.7(1)
		Fe—N—C_α	127.0(1)
		Pyrrole Rings	
N—C_α	1.376(2)	C_α—N—C_α	105.9(2)
C_α—C_β	1.439(2)	N—C_α—C_β	109.7(2)
C_β—$C_{\beta'}$	1.339(3)	C_α—C_β—$C_{\beta'}$	107.3(2)
C_α—C_m	1.388(2)	N—C_α—C_m	126.3(2)
		C_α—C_m—$C_{\alpha'}$	123.3(2)
		C_α—C_m—C_p	118.3(2)
		Phenyl Rings	
C_m—C_p	1.496(2)		
C—C	1.375(2)	C—C—C	120.0(1)
		Thiolate Phenyl Rings	
S—C	1.739(5)	S—C_α—C_β	122.4(2)
C—C	1.367(3)	C_β—C_α—$C_{\beta'}$	115.1(5)
C—F	1.350(3)	C—CH—C	116.1(6)
		$\overset{F}{\overset{\vert}{-C}}-\overset{F}{\overset{\vert}{C}}-$	119.8(7) to 124(1)

Crown $|Na \subset 18C6|^+$

C — O	1.401(5)
C — C	1.446(7)
Na — O	2.364(5) to 2.80(1)

The phenyl rings have normal geometries with a $(C—C)_{av}$ bond distance of 1.357(2) Å and $(C—C—C)_{av}$ bond angle of 120.0(1) deg. Their dihedral angles with the porphyrin core mean plane are 81.0, 117.6 and 66.4, 107.9 deg. respectively in the Fe1 and Fe2 porphyrins.

The mean value of the S—C(C_6HF_4) bond distance is 1.739(5) Å and the average Fe—S—C bond angle is 107.6(1) deg. The C_6HF_4 rings are planar within experimental error. The C—C—C bond angles are slightly affected by the different substituents (see Table II). The negative charge of the porphyrin anion is balanced by a $|Na \subset 18C6|^+$ cation. Table II gives some bond lengths found within this cation. They are similar to those found elsewhere[19]. The $(C—C)_{av}$ bond distance in the C_6H_6 molecule of crystallization is 1.35(1) Å and $(C—C—C)_{av}$ bond angles is 119.9(3) deg. No unusual intermolecular contacts have been found.

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Supplementary Material Available

Listings of:

— the coordinates of the hydrogen atoms (Table 4, 3 pages)
— the temperature factors of all anisotropic atoms (Table 5, 4 pages)
— the observed and calculated structure factors (times 10) for all observed
— reflections (Table 6, 25 pages).

Ordering information is given on any current masthead page.

SAŽETAK

Sinteza i struktura jednog dimerkapto-željezo(III) porfirinskog derivata: $[Fe(SC_6HF_4)_2TPP]$ $[Na \subset 18C6] \cdot C_6H_6$

P. Doppelt, J. Fischer i R. Weiss

Sintetiziran je niskospinski dimerkaptoželjezo(III)-mezo-tetrafenilporfirinski kompleks, $[Fe(SC_6HF_4)_2TPP]$ $[Na \subset 18C6] \cdot C_6H_6$. Taj spoj pokazuje u čvrstom stanju hiperspektar d-tipa s rascijepljenom Soretovom vrpcom pri 383 i 461 nm. Kristali su triklinski, prostorna grupa *P1*, s a = 12,628(4), b = 21,594(8) c = 12,881(4) Å, α = 104,02(2), β = 98,26(2), γ = 76,40(2)°, V = 3298 Å^3, Z = 2. Nađene su relativno duge ekvatorijalne Fe-Np udaljenosti od 1,998(3) Å i relativno kratke aksijalne udaljenosti Fe—S od 2,312(1) Å. Utvrđeno je da su dva kristalografski neovisna $[Fe(SC_6HF_4)_2TPP]^-$ aniona u biti identična.