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Structure and g Tensor Orientation of the (Tetraphenylporphyrinato)iron(III) Bis(benzenethiolate) Anion

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Abstract: Single-crystal X-ray and ESR investigations of the potassium 18-crown-6 salt of (tetraphenylporphyrinato)iron(III) bis(benzenethiolate) have provided a detailed electronic characterization of a low-spin bis(thiolato)iron(III) porphyrin. The structural analysis at 115 K yielded Fe–N distances of 2.013 (4) and 2.003 (4) Å and an Fe–S distance of 2.336 (2) Å, characteristic of a low-spin Fe(III) complex. Principal g values of $|g_x| = 1.964$, $|g_y| = 2.213$, and $|g_z| = 2.337$ correspond closely to orientation of the magnetic field along the short Fe–N vector, the long Fe–N vector, and the normal to the porphyrin plane, respectively. Both the X-ray and ESR results are consistent with partial occupation of an iron d_{yz} orbital which interacts in a π fashion with filled sulfur p orbitals of the thiolate ligands.

While it has been recognized that the **g** tensor anisotropy of low-spin iron(III) complexes provides a detailed description of the electronic structure and while the anisotropy has been reported for a large number of porphyrin complexes and heme proteins,[1,2] in only a few instances has the orientation of the **g** tensor with respect to the molecular axes been experimentally established. A number of investigators[2] have determined the orientation of the **g** tensor in various low-spin forms of metmyoglobin and in oxidized cytochrome *c*. In all the heme proteins studied, the largest g value is within 15° of the normal to the heme plane. There appears, however, to be some experimental inconsistency regarding the orientation of the other two axes, and no generalization can be made concerning the influence of the porphyrin or imidazole ligands. To our knowledge no data of this kind have been reported for the P-type heme proteins or any low-spin sulfur coordinated ferric porphyrins. For these reasons, a series of X-ray and ESR measurements were undertaken to determine the orientation of the **g** tensor in the (tetraphenylporphyrinato)iron(III) bis(benzenethiolate) anion.

This particular complex (in the form of the potassium 18-crown-6 salt, **1**) was chosen and synthesized for this investigation because of its relationship to "(tetraphenylporphyrinato)iron(III) benzenethiolate benzenethiol" (**2**) and related materials which have been of long standing interest in this laboratory. A preliminary report[3] of the X-ray investigation of **2** at 115 K described the resolution of a disordered mixture of five-coordinate and six-coordinate forms. Further X-ray and neutron investigations of this material reveal a complex and dynamic structure. At least a portion of the six-coordinate species in this material may be present as the bisthiolate anion rather than the neutral thiolthiolate. The detailed examination of **1** reported herein will provide a basis to test this hypothesis. Parallel studies of **2** and materials isomorphous with it are in progress.

Experimental Section

Synthesis. All steps in the preparation of **1** were carried out under nitrogen. Potassium 18-crown-6 benzenethiolate was prepared by reaction of 2 mmol of pelletized 85% KOH, 2.5 mmol of 18-crown-6, and 2 mmol of benzenethiol in 75 mL of benzene freshly distiled from calcium hydride. The mixture was stirred overnight; water formed during the reaction was removed by distillation to half the original volume. The solution was filtered to remove excess KOH and added to the benzene layer of a 0.2-mmol preparation of **2** produced by the reaction of stoichiometric amounts of μ-oxo-iron(III) tetraphenylporphyrin and benzenethiol in 50 mL of benzene over 15% (v/v) aqueous sulfuric acid. Slow evaporation of the solvent produced black triclinic crystals suitable for X-ray analysis. ESR spectra of a polycrystalline sample at room temperature showed a single signal characteristic of low-spin Fe(III).

Structural Analysis. Crystallographic data were obtained[4] at 115 K. Experimental and data handling techniques were analogous to those described previously.[5] Because of the small size of the crystal, no absorption correction was applied. Experimental parameters are summarized in Ref 6. Patterson, difference-Fourier, and least-squares refinement techniques were used in the solution of the structure. In the final full-matrix least-squares refinement, positions and anisotropic thermal parameters of all nonhydrogen atoms were refined along with the positions of the hydrogen atoms. Isotropic temperature factors of the hydrogen atoms were fixed at 3.0 Å^2.

ESR Measurements. Single-crystal ESR data were obtained at room temperature from three crystals mounted along orthogonal molecular axes (Fe–N(2), Fe–N(1) and the normal to the porphyrin plane as determined from a room-temperature structural analysis). One face on each crystal was identified and used to orient the crystal in the ESR spectrometer. Rotation about each axis provided three components of the $\mathbf{g}^2$ tensor. The estimated uncertainty in the orientation of the crystal in the magnetic field based on the reproducibility of both X-ray and ESR measurments is on the order of 2°. The precision of the measured g values (from an ESR spectrometer composed of a variety of commerical components) is about 0.001; the accuracy of the measured g values, calibrated with DPPH, is no better than 0.002. In the determination of the elements of the $\mathbf{g}^2$ matrix, diagonal elements were obtained as the average of the values available from two independent measurements. Deviations from the mean for the three averages corresponded to Δg = 0.000, 0.001, and 0.003.

Results and Discussion

Structural Analysis. Both the anion (Figure 1), and the cation (Figure 2), are located on crystallographic inversion centers. Final atomic parameters are given in Tables I and II; interatomic distances and angles can be found in Tables III through VI. Agreement between chemically analogous bond lengths of the porphyrinato ligand is within the experimental precision. With Ca and Cb to denote the α and β pyrrole carbon atoms, Cm the methine carbon atoms, and Cp the phenyl carbon atom α to Cm, averaged bond distances[7] are Ca–Cb = 1.433 (6) Å, Cb–Cb = 1.344 (6) Å, Cm–Ca = 1.388 (6) Å, Ca–N = 1.377 (7) Å, and Cm–Cp = 1.500 (6) Å. The averaged values for bond angles are Ca–N–Ca = 105.9 (4)°, N–Ca–Cb = 109.9 (4)°, N–Ca–Cm = 125.6 (4)°, Ca–Cb–Cb = 107.4 (4)°, and Ca–Cm–Ca = 124.6 (4)°. Average bond distances in the cation are K–O = 2.772 (3) Å, C–O = 1.420 (6) Å, and C-C = 1.488 (8) Å; bond angles at

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[6] Crystal Data: space group $P\bar{1}$, $Z = 1$, $a = 11.517$ (4) Å, $b = 11.554$ (4) Å, $c = 11.956$ (5) Å, $\alpha = 107.87$ (3)°, $\beta = 85.33$ (3)°, $\gamma = 72.07$ (3)°, $V = 1413.2$ (9) Å^3, Mo radiation ($\lambda = 0.71070$), crystal dimensions 0.08 × 0.12 × 0.16 mm, θ–2θ scan, background time = scan time, 2θ maximum = 50°, 3089 reflections ($I > 3\sigma(I)$), $R = 0.049$, $R_w = 0.056$, error of fit = 1.42.

[7] Values in parentheses are estimated standard deviations of the least significant digit for individual observations.

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Table I. Atomic Parameters for $Fe^{III}TPP(SC_6H_5)_2K$-18-crown-6 at 115 K

atom	x	y	z	atom	x	y	z
Fe	0.0000 (0)	0.0000 (0)	0.0000 (0)	H(47)	−0.1232 (47)	0.0451 (49)	0.4888 (47)
S	0.0414 (1)	0.1369 (1)	0.1686 (1)	H(48)	−0.2974 (48)	0.2338 (47)	0.5673 (46)
C(45)	−0.0693 (4)	0.1666 (4)	0.2956 (4)	H(49)	−0.3377 (49)	0.3722 (49)	0.4600 (45)
C(46)	−0.0525 (5)	0.0798 (5)	0.3569 (4)	H(50)	−0.1960 (47)	0.3333 (49)	0.2936 (46)
C(47)	−0.1384 (5)	0.1027 (5)	0.4543 (5)	H(2)	−0.2015 (47)	0.4057 (48)	−0.0937 (45)
C(48)	−0.2443 (5)	0.2118 (5)	0.4941 (5)	H(3)	−0.3770 (48)	0.3875 (47)	0.0254 (45)
C(49)	−0.2633 (5)	0.2995 (5)	0.4352 (5)	H(7)	−0.4214 (48)	0.0576 (47)	0.2328 (45)
C(50)	−0.1772 (5)	0.2766 (5)	0.3365 (5)	H(28)	−0.4499 (47)	0.4076 (47)	0.2539 (45)
N(1)	−0.1200 (3)	0.1592 (3)	−0.0173 (3)	H(29)	−0.6619 (49)	0.5125 (50)	0.2957 (46)
N(2)	−0.1408 (3)	−0.0219 (3)	0.0911 (3)	H(30)	−0.7937 (49)	0.4164 (48)	0.2006 (45)
C(1)	−0.0910 (4)	0.2355 (4)	−0.0760 (4)	H(31)	−0.7101 (49)	0.2081 (48)	0.0586 (46)
C(2)	−0.2019 (4)	0.3429 (4)	−0.0637 (4)	H(32)	−0.5044 (48)	0.1020 (48)	0.0138 (46)
C(3)	−0.2958 (4)	0.3317 (4)	0.0016 (4)	H(34)	−0.0971 (47)	−0.4216 (47)	0.0792 (47)
C(4)	−0.2451 (4)	0.2161 (4)	0.0294 (4)	H(35)	−0.0929 (48)	−0.5593 (50)	0.1781 (47)
C(5)	−0.3144 (4)	0.1681 (4)	0.0927 (4)	H(36)	−0.0379 (46)	−0.5379 (48)	0.3600 (45)
C(6)	−0.2642 (4)	0.0577 (4)	0.1222 (4)	H(37)	0.0255 (46)	−0.3580 (46)	0.4485 (46)
C(7)	−0.3343 (4)	0.0133 (4)	0.1947 (4)	H(38)	0.0293 (47)	−0.2222 (49)	0.3473 (46)
C(8)	−0.2536 (4)	−0.0923 (5)	0.2069 (4)	H(57A)	0.2166 (47)	0.1968 (47)	0.3183 (46)
C(9)	−0.1336 (4)	−0.1152 (4)	0.1423 (4)	H(57B)	0.1964 (48)	0.1595 (47)	0.4277 (46)
C(10)	−0.0255 (4)	−0.2143 (4)	0.1363 (4)	H(58A)	0.2406 (48)	0.3534 (50)	0.4610 (45)
C(27)	−0.4519 (4)	0.2390 (4)	0.1284 (4)	H(58B)	0.3756 (48)	0.2751 (47)	0.3839 (45)
C(28)	−0.5029 (5)	0.3639 (5)	0.2132 (4)	H(59A)	0.4577 (48)	0.3550 (46)	0.5571 (45)
C(29)	−0.6301 (5)	0.4312 (5)	0.2380 (5)	H(59B)	0.3204 (49)	0.4290 (49)	0.6307 (45)
C(30)	−0.7077 (5)	0.3731 (5)	0.1812 (5)	H(60A)	0.4459 (46)	0.3957 (49)	0.7750 (45)
C(31)	−0.6598 (5)	0.2489 (5)	0.0993 (5)	H(60B)	0.3445 (48)	0.3270 (47)	0.7706 (47)
C(32)	−0.5320 (5)	0.1830 (5)	0.0731 (4)	H(61A)	0.5692 (48)	0.2398 (50)	0.8327 (47)
C(33)	−0.0336 (4)	−0.3051 (4)	0.2012 (4)	H(61B)	0.4867 (49)	0.1663 (47)	0.8351 (46)
C(34)	−0.0728 (4)	−0.4085 (4)	0.1513 (4)	H(62B)	0.7370 (50)	0.0604 (47)	0.6916 (47)
C(35)	−0.0720 (5)	−0.4955 (5)	0.2098 (5)	H(62A)	0.6987 (48)	0.0361 (48)	0.8068 (48)
C(36)	−0.0343 (4)	−0.4799 (5)	0.3175 (5)	H(46)	0.0178 (48)	0.0015 (48)	0.3238 (45)
C(37)	0.0032 (4)	−0.3771 (5)	0.3688 (4)	H(8)	−0.2687 (47)	−0.1347 (48)	0.2550 (46)
C(38)	0.0042 (4)	−0.2905 (5)	0.3109 (4)				
K	0.5000 (0)	0.0000 (0)	0.5000 (0)				
O(1)	0.3643 (3)	0.0486 (3)	0.3288 (3)				
O(2)	0.3439 (3)	0.2521 (3)	0.5417 (3)				
O(3)	0.5153 (3)	0.2062 (3)	0.6858 (3)				
C(57)	0.2608 (5)	0.1680 (6)	0.3734 (5)				
C(58)	0.3052 (5)	0.2745 (5)	0.4372 (5)				
C(59)	0.3844 (5)	0.3505 (5)	0.6098 (5)				
C(60)	0.4160 (5)	0.3260 (5)	0.7204 (5)				
C(61)	0.5540 (5)	0.1740 (6)	0.7856 (5)				
C(62)	0.6675 (5)	0.0553 (6)	0.7437 (5)				

[a] Atoms labeled as in Figures 1 and 2. [b] Fractional coordinates (standard deviations).

oxygen average 112.5 (4)° and those at carbon average 108.6 (4)°.

The difference between the Fe–N(1) and Fe–N(2) distances (2.013 (4) and 2.003 (4) Å, respectively)[8] is consistent with the partial occupation of the d_{yz} orbital (vide infra), but this difference is only marginally significant. The Fe–S distance of 2.336 (2) Å is 0.03 Å longer than the corresponding distance in the low-spin ferric tris(diethyldithiocarbamate)[9] and 0.13 Å longer than the Fe-S distance in the low-spin $Fe(SC_6H_4CHNCH_2CH_2NH_2)_2$ cation[10] in which the thiolate is trans to an amine ligand. These observations support the contention[11] that in the low-spin form of cytochrome P450, where EXAFS measurements give an Fe–S distance of 2.19(3) Å, the sulfur donor is trans to a nitrogen rather than a sulfur donor. The Fe-S distance in **2** differs little from the values of 2.33 and 2.35 Å reported for the bis(pentamethylene sulfide)iron(III) tetraphenylporphyrin cation[8] and the value of 2.324 (2) Å found for five-coordinate high-spin iron(III) protoporphyrin IX dimethyl ester *p*-nitrobenzenethiolate[1] (**3**). The sulfur–phenyl carbon distance of 1.774 (5) Å is in good agreement with the value of 1.771 (2) Å found[12] for the benzenethiolate ligands of the $Fe_4S_4(SC_6H_5)_4$ dianion and not significantly longer than the 1.750 (7) Å observed in **3**. As one would expect, the Fe-S-C angle in this six-coordinate complex, 108.7°, is larger than that found in the five-coordinate **3**, 100.4°.

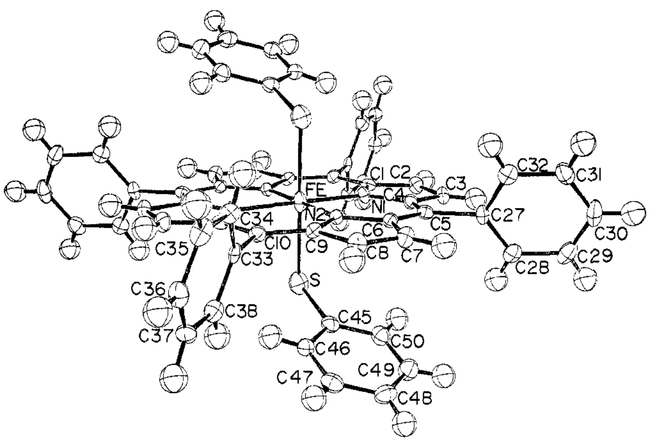

Figure 1. Structure and numbering system of the (tetraphenylprophyrinato)iron(III) bis(benzenethiolate) anion.

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[8] Fe–N distances of 1.991 (12) and 1.988 (8) Å observed in a parallel room temperature structure determination of **1** are not significantly different from those reported for the bis(imidazole)iron(III) tetraphenylporphyrin cation (Collins D. M.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2066–2072), or for the bis(pentamethylene sulfide)iron(III) tetraphenylporphyrin cation (Mashiko, T.; Marchon, J.; Musser, D. T.; Reed, C. A.; Kastner, M. E; Scheidt, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 3653–3655). The Fe–S distance observed at room temperature is 2.346 (4) Å.

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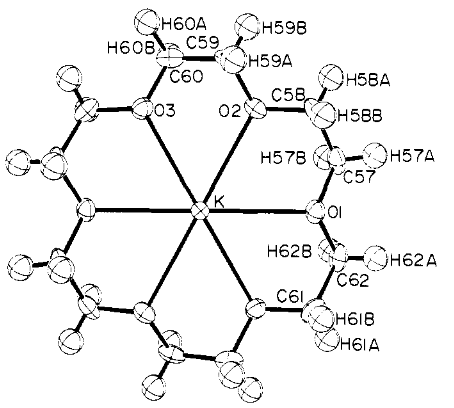

Figure 2. Structure and numbering system of the potassium 18-crown-6 cation.

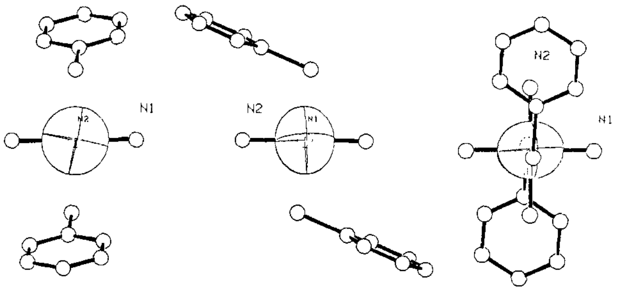

Figure 3. Ellipsoid representation of the **g** tensor viewed along three molecular axes.

ESR Measurements. In the right-handed coordinate system in which x corresponds to the N(2) to Fe direction and y corresponds to the Fe to N(1) direction, the experimentally determined elements of $\mathbf{g}^2$ are $\langle g^2\rangle_{11} = 3.865$, $\langle g^2\rangle_{22} = 4.918$, $\langle g^2\rangle_{33} = 5.432$, $\langle g_2\rangle_{12} = -0.074$, and $\langle g^2\rangle_{23} = 0.111$. Diagonalization of this tensor gives principle g values of 1.964, 2.213, and 2.337,[13] in reasonable agreement with values of 1.960, 2.216, and 2.335 obtained from a polycrystalline spectrum without correction for lineshape.

Figure 3 illustrates the orientation of the **g** tensor in the complex. As previously observed in the study of ferric heme proteins, the principle axis corresponding to the largest g is within 15° (in this case 12°) of the normal to the porphyrin plane. Perhaps more significant is the observation that the principle axis corresponding to the smallest g value is only 4° from the Fe–N(2) direction. Taylor[2] has demonstrated that, neglecting spin–orbit coupling and covalency,[14] the partially occupied d orbital in low-spin Fe(III) systems of this type lies in the plane defined by the two largest principle g values. This corresponds closely to the d_{yz} orbital in the molecular axis coordinate system defined above. The inference that the d_{yz} orbital is higher in energy than either d_{xz} or d_{xy} is easily rationalized as a consequence of its interaction with filled p orbitals on the ligand sulfur atoms. Since the α-carbon of the benzene thiolate is not far from the plane defined by Fe, N(2), and S, it is entirely reasonable that the axis corresponding to the smallest g value lies close to the Fe–N(2) direction. However, it must be pointed out that before any useful generalization can be constructed concerning the orientation of the **g** tensor in materials of this kind, it will be necessary to examine a material in which the axial ligand takes on a less symmetric orientation. It is conceivable that there is an indirect interaction between the iron ion and the thiolate ligand that involves the prophyrin ligand. If such an interaction is predominant, one would expect the **g** tensor to be aligned with the porphyrin rather than the thiolate ligand.

Because the displacements of the principle axes of the **g** tensor from the idealized molecular axes (Figure 3) are not large compared to the experimental uncertainties, it is difficult to ascribe these displacements to specific distortions of the complex. As more data on related complexes becomes available, however, it may be possible to relate these displacements to various types of structural asymmetry.

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Supplementary Material Available: Tables II–VI and a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(13) The ordering here is the "common" ordering with g_x smallest and g_z largest. See ref 12 or Bohan, T. L. *J. Magn. Reson.* **1977**, *26*, 109–118 for the "proper" choice of coordinate system and assignment of signs.

(14) Analysis[2] of the principle g values provides squared coefficients in the ground-state wave functions of 1.001, 0.007, and 0.003 for the three real d orbitals defined in the principle axis coordinate system. Since these coefficients are nearly normalized and since contributions from the second two atomic orbitals are small, neither covalency nor spin–orbit induced mixing appear to be significant.

Linear to Bent Geometry Changes in Gas- and Solution-Phase Photochemistry of Tricarbonylnitrosylcobalt

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Abstract: Photochemical reactions of $Co(CO)_3NO$ in both the gas and solution phases are reported and interpreted in terms of a bent cobalt–nitrosyl unit in the excited state. The molecular orbital reasons for expecting a bent excited state are discussed. In the gas phase, two types of photochemical reactions are observed: reactions at the coordinated nitrosyl and carbonyl exchange. The reaction with gaseous HCl produces the disproportionation products of HNO, N_2O, and H_2O. This reaction is interpreted in terms of an "NO^-" photointermediate. In both the gas and solution phases, associative carbonyl-exchange reactions with Lewis base entering ligands are observed. The solution-phase photoreactions are quantitatively treated by using kinetic theory and discussed in terms of a bent excited state.

The photochemistry of metal–nitrosyl complexes is of interest not only because of the potential for unusual photoreactions arising from excited-state geometry changes in the MNO group, the subject of this paper, but also because nitrosyl photochemistry

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