December, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *55*, *3891—3895 (1982)* 3891

The Crystal and Molecular Structure of Six-coordinate Intermediate-spin Porphinatoiron(III) Complex. (Octaethylporphinato)bis(tetrahydrofuran)iron(III) Perchlorate

Hideki Masuda,* Tooru Taga, Kenji Osaki, Hiroshi Sugimoto,†
Zen-ichi Yoshida,†† and Hisanobu Ogoshi*,†††
Faculty of Pharmaceutical Sciences, Kyoto University, Shimoadachi-cho, Yoshida, Sakyo-ku, Kyoto 606
†*Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558*
††*Department of Synthetic Chemistry, Kyoto University, Honmachi, Yoshida, Sakyo-ku, Kyoto 606*
†††*Department of Materials Science and Technology, Technological University of Nagaoka, Kamitomioka, Nagaoka 949-54*

(Received January 9, 1982)

The crystal structure of (octaethylporphinato)bis(tetrahydrofuran)iron(III) perchlorate was determined by the X-ray method. The complex crystallizes in the monoclinic space group C2/m, $a=13.916(3)$ Å, $b=16.509(3)$ Å, $c=10.659(5)$ Å, $\beta=118.18(1)°$, and $Z=2$. The structure was solved by the direct method and refined by the full-matrix least-squares method. The final R value was 0.079 for 597 reflections. The complex has a crystallographically imposed twofold axis and a mirror of symmetry. The porphinato core is planar within 0.06 Å. The iron(III) ion lies at the center of the octahedron formed by the four porphinato nitrogen atoms and the two tetrahydrofuran oxygen atoms. The axial Fe–O distance, 2.187(11) Å, is considerably longer than the reported distances for high-spin porphinatoiron(III) complexes, while the equatorial Fe–N distance, 1.978(12) Å, is comparable to those for low-spin and intermediate-spin porphinatoiron(III) complexes. The Fe–O and Fe–N bond distances are well explained in terms of an intermediate-spin state of the iron(III) ion.

The existence of an intermediate-spin state ($S=3/2$) with the outer electron configuration $(d_{xy})^2(d_{yz})(d_{xz})(d_{z^2})$ in iron(III) porphyrins has been progressively recognized, since Maltempo *et al.*1) suggested a possibility of the quantum-mechanically mixed spin state of iron(III) ($S=3/2$ and $5/2$) to explain anomalous magnetic properties of ferricytochrome c′. Since Dolphin *et al.*2) assigned octaethylporphinatoiron(III) perchlorate, [Fe(III)(oep)]ClO_4, as an intermediate-spin complex, several synthetic intermediate-spin porphinatoiron(III) complexes were reported3) on the basis of magnetic susceptibility, ESR spectra, and Mössbauer spectra. So far six structures of the intermediate-spin or probably its admixed spin state complexes have been studied by the X-ray method.3a,3b,3d,4,5) Through these studies, the structures of the intermediate-spin complexes were characterized by the short Fe–N distance resembling those of low-spin derivatives and the long Fe–O distance rather than those of low- and high-spin derivatives. In an X-ray study of diaquatetraphenylporphinatoiron(III) cation, $[Fe(III)(tpp)(H_2O)_2]^+$,3a,6a) Scheidt *et al.*3d) claimed that if the axial Fe–O bond distances were increased to some values greater than 2.09 Å, the complex would become an intermediate-spin complex. The critical Fe–ligand distance to distinguish the intermediate-spin state from others is, however, still not clear. The title (octaethylporphinato)bis(tetrahydrofuran)iron(III) perchlorate, $[Fe(III)(oep)(thf)_2]ClO_4$, has recently been prepared by Ogoshi *et al.*,3c) and from their magnetic and spectroscopic studies the single intermediate-spin state was certainly assigned for this complex. Then, the Fe(III)–O(thf) distance in this complex was anticipated to give a typical Fe(III)–O distance for a pure $S=3/2$ iron(III), so that we took up this complex for the present X-ray study.

Experimental

$[Fe(III)(oep)(thf)_2]ClO_4$ was prepared by adding thf to [Fe(III)(oep)]ClO_4 in CH_2Cl_2.3c) Dark-violet, plate-like single crystals were obtained by recrystallization from a thf solution. A preliminary X-ray photographic examination established a monoclinic unit cell containing two chemical units of $[Fe(III)(oep)(thf)_2]ClO_4$. The systematic absences of hkl for $h+k=2n+1$ led to three possible space groups C2/m, Cm, and C2. The unit cell dimensions, $a=13.916(3)$ Å, $b=16.509(3)$ Å, $c=10.659(5)$ Å, and $\beta=118.18(1)°$, were determined by the least-aquares refinement of setting angles of 47 reflections on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\bar{\lambda}=0.71073$ Å). $D_x=1.28$ g/cm^3 and $D_m=1.24$ g/cm^3 (by flotation in aqueous calcium chloride solution).

Intensity data of 2212 reflections in the range $2\theta<50°$ were collected in the ω-2θ scan mode with a scan rate of 5° min^{-1} by the use of a crystal with dimensions of $0.2\times0.2\times0.1$ mm^3. The crystal was gradually damaged by X-ray exposure, so that the intensities were corrected by standard measurements of three reflections every 60 reflections. The intensity decline of the standard reflections throughout the measurements was about 20%. In view of a large systematic error caused by the crystal damage, 597 reliable data ($|F_o|>5\sigma(|F_o|)$) were used for the analysis. No absorption correction was applied ($\mu=4.59$ cm^{-1} for Mo $K\alpha$).

The structure was solved by the heavy atom method. The space group C2/m was tentatively assumed and successive Fourier syntheses revealed the approximate structure. The block-diagonal least-squares refinements to examine the three possible space groups, C2/m, C2, and Cm, resulted in rejection of the space groups C2 and Cm because these space groups gave several wrong positional shifts from the normal bond lengths and angles and non-positive temperature factors for some light atoms. Several cycles of refinement including the anisotropic thermal parameters were carried out to convergence with the weighting scheme of $w=1/\sigma(F_o)^2$. The hydrogen atoms were included as a fixed contribution in the last cycle: their positions were assumed to be in accord with the idealized geometry (C–H=1.00 Å), and their temperature factors were assumed

TABLE 1. POSITIONAL AND THERMAL PARAMETERS FOR THE ATOMS OF $[\mathrm{Fe^{III}(oep)(thf)_2}]\mathrm{ClO_4}$

Atom	$x^{a)}$	$y^{a)}$	$z^{a)}$	$B_{eq}^{b)}/\text{Å}^2$
Fe	0.0	0.0	0.0	3.26
N	−0.0610(8)	0.0844(6)	0.0739(10)	3.08
C(1)	−0.0525(10)	0.1673(8)	0.0670(12)	3.69
C(2)	−0.1086(10)	0.2084(10)	0.1355(14)	4.05
C(3)	−0.1536(10)	0.1503(9)	0.1788(14)	4.21
C(4)	−0.1245(10)	0.0768(9)	0.1401(14)	4.15
C(5)	−0.1518(15)	0.0	0.1658(20)	4.13
C(6)	0.0	0.2030(10)	0.0	4.05
C(7)	−0.1076(10)	0.2983(9)	0.1537(14)	3.94
C(8)	−0.2250(10)	0.1630(8)	0.2492(14)	4.41
C(9)	−0.0047(11)	0.3283(8)	0.2843(14)	5.82
C(10)	−0.1623(12)	0.1642(10)	0.4054(17)	9.26
O(T)	0.1507(11)	0.0	0.2025(15)	5.74
C(11)	0.2513(29)	0.0317(28)	0.2336(34)	8.95
C(12)	0.3281(24)	0.0311(25)	0.3781(37)	7.97
C(13)	0.2796(30)	−0.0336(20)	0.4375(32)	7.83
C(14)	0.1670(25)	−0.0395(28)	0.3274(37)	11.46
Cl	0.0326(19)	0.5000	0.0187(19)	9.62
O(1)	0.0855(29)	0.5000	0.1663(38)	11.75
O(2)	0.0876(28)	0.5000	−0.0697(46)	11.73
O(3)	−0.0280(25)	0.5667(13)	−0.0309(33)	8.72

a) Estimated standard deviations in the least significant figure(s) are given in parentheses. b) B_{eq} is the equivalent isotropic temperature factor defined by Hamilton.[11]

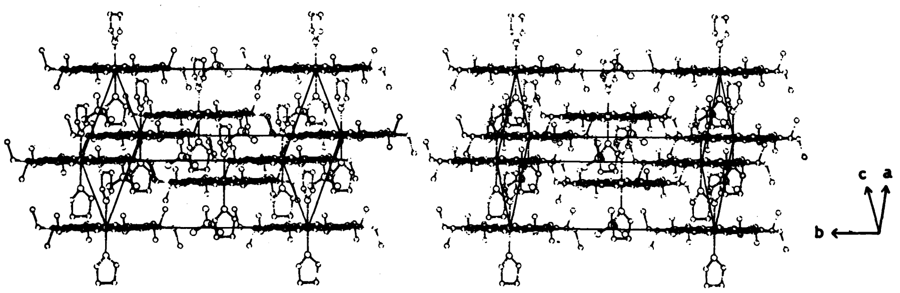

Fig. 1. Stereoscopic view of the crystal structure of $[\mathrm{F^{III}_e(oep)(thf)_2}]\mathrm{ClO_4}$.

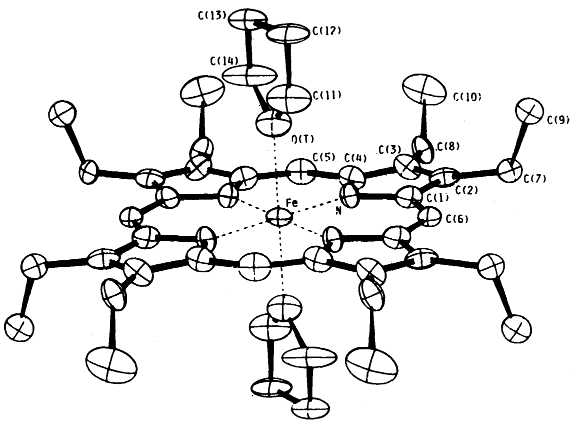

Fig. 2. Computer-drawn model in perspective of the $[\mathrm{Fe^{III}(oep)(thf)_2}]^+$ cation. The vibrational ellipsoids are drawn at the 30% probability level. The labeling scheme used for the atoms in the molecule is also shown.

to be isotropical (B=8.00 Å). The final R value was 0.079. The final difference Fourier map showed the high peak (*ca.* 0.6 electron/Å^3) to remain around the disordered perchlorate anion, but it was judged to be essentially featureless.

Atomic scattering factors[7a)] and anomalous terms[7b)] were taken from the International Tables for X-Ray Crystallography. All computations were performed on a FACOM M-200 computer at the Data Processing Center of Kyoto University by using the program system KPAX.

Results

The atomic parameters for all atoms except hydrogen atoms are listed in Table 1. Tables of anisotropic temperature factors for non-hydrogen atoms, positional parameters for hydrogen atoms, and observed and calculated structure factors are kept as a Document No. 8255 at the Chemical Society of Japan.

As shown in Fig. 1, the crystal structure consists of the discrete $[\mathrm{Fe(III)(oep)(thf)_2}]^+$ cations and perchlorate anions packed in layers parallel to the (001) plane. The layers are stacked with van der Waals contacts along the c axis. The plane normal to all the porphinato rings is in the approximate [101] direction.

A stereographic view of $[\mathrm{Fe(III)(oep)(thf)_2}]^+$ cation is provided in Fig. 2. The numbering scheme of the porphyrin is given in Figs. 2 and 3. The iron atom exists

TABLE 2. BOND DISTANCES AND ANGLES FOR $[\mathrm{Fe^{III}(oep)(thf)_2}]\mathrm{ClO_4}$[a]

Bond distance	l/Å	Bond distance	l/Å
Fe–N	1.978(12)	O(T)–C(11)	1.38(4)
Fe–O(T)	2.187(11)	O(T)–C(14)	1.40(4)
N–C(1)	1.38(2)	C(11)–C(12)	1.40(4)
N–C(4)	1.37(2)	C(13)–C(14)	1.45(4)
C(1)–C(2)	1.46(2)	C(12)–C(13)	1.55(6)
C(3)–C(4)	1.40(2)	Cl–O(1)	1.39(3)
C(2)–C(3)	1.34(2)	Cl–O(2)	1.47(5)
C(4)–C(5)	1.39(2)	Cl–O(3)	1.34(2)
C(1)–C(6)	1.37(2)		
C(2)–C(7)	1.50(2)		
C(3)–C(8)	1.52(3)		
C(7)–C(9)	1.53(2)		
C(8)–C(10)	1.47(2)		
Bond angle	ϕ/°	Bond angle	ϕ/°
N–Fe–N′	90.5(5)	O(T)–Fe–N	89.9(4)
N–Fe–N″	180.0(6)	O(T)–Fe–N′	90.1(4)
N–Fe–N‴	89.5(5)	Fe–O(T)–C(11)	128.9(18)
Fe–N–C(1)	127.9(11)	Fe–O(T)–C(14)	126.0(16)
Fe–N–C(4)	129.9(9)	C(11)–O(T)–C(14)	104.9(33)
C(1)–N–C(4)	102.2(12)	O(T)–C(11)–C(12)	115.0(36)
N–C(1)–C(2)	110.8(14)	O(T)–C(14)–C(13)	111.5(33)
N–C(4)–C(3)	114.7(13)	C(11)–C–(12)C(13)	101.6(29)
N–C(1)–C(6)	122.3(14)	C(12)–C(13)–C(14)	103.2(27)
N–C(4)–C(5)	119.2(15)	O(1)–Cl–O(2)	124.7(22)
C(1)–C(2)–C(3)	106.6(14)	O(1)–Cl–O(3)	110.3(17)
C(2)–C(3)–C(4)	105.7(15)	O(2)–Cl–O(3)	99.7(19)
C(2)–C(1)–C(6)	126.9(13)	O(3)–Cl–O(3)′	111.2(20)
C(3)–C(4)–C(5)	126.1(17)		
C(3)–C(2)C(7)	130.0(16)		
C(2)–C(3)–C(8)	126.4(14)		
C(1)–C(2)–C(7)	123.4(15)		
C(4)–C(3)–C(8)	127.8(14)		
C(2)–C(7)–C(9)	112.7(10)		
C(3)–C(8)–C(10)	112.7(12)		
C(1)–C(6)–C(4)′	117.6(11)		
C(4)–C(5)–C(1)‴	118.8(15)		

a) Estimated standard deviations are in parentheses. The one-primed atom notes the atom translated by mirror plane. The two-primed atom notes the atom translated by twofold axis. The three-primed atom notes the atom translated by twofold and mirror plane.

at the center of symmetry, and lies on the plane of the oep macrocycle. The four porphinato nitrogens and the two oxygen atoms of thf molecules complete a deformed octahedron. The porphinato core is planar within 0.06 Å. The C(5) atom lies on the mirror plane and the C(6) atom lies on a twofold axis. The orientation of the ethyl groups attached to the core is similar to that in $[\mathrm{Fe(III)(oep)}]\mathrm{ClO_4}$.[4a]

Bond distances and bond angles are given in Table 2. The axial Fe–O(thf) distance, 2.187(11) Å, is considerably longer than the sum of ionic radii for high-spin Fe(III) (0.65 Å) and O (1.40 Å),[10] and is also larger than those of typical high-spin six-coordinate porphinatoiron(III) complexes, $[\mathrm{Fe(III)(tpp)(tetrahydrothiophene\ 1\text{-}oxide)_2}]^+$ (average 2.078 Å)[6b] and $[\mathrm{Fe(III)(tpp)(H_2O)_2}]^+$ (average 2.095 Å).[3a,6a] It is rather close to those in the mixed ($S=5/2$, $3/2$) or high-spin $[\mathrm{Fe(III)(oep)(EtOH)_2}]^+$ (average 2.137 Å)[5a] and $[\mathrm{Fe(III)(tpp)(EtOH)_2}]^+$ (2.142 Å).[5b] The Fe–N bond distance, 1.978(12) Å, is significantly shorter than those of typical high-spin six-coordinate complexes, diaquatetraphenylporphinatoiron(III) cation ($[\mathrm{Fe(III)(tpp)(H_2O)_2}]^+$) (average 2.045 Å)[3a,6a] and $[\mathrm{Fe(III)(tpp)(tetrahydrothiophene\ 1\text{-}oxide)_2}]^+$ (average 2.045 Å).[6b] It is, however, in agreement with those observed in intermediate-spin $[\mathrm{Fe(III)(tpp)C(CN)_3}]$ (average 1.995 Å),[3d] and is also comparable with those of typical low-spin six-coordinate porphinatoiron(III) complexes, $[\mathrm{Fe(III)(tpp)(imidazole)_2}]^+$ (average 1.989 Å)[9a] and $[\mathrm{(protoporphyrin\ IX)iron(III)(1\text{-}methylimidazole)_2}]^+$ (average 1.991 Å),[9b] and $[\mathrm{Fe(III)(tpp)(CN)_2}]^-$ (average 2.000 Å).[9c]

The thf molecule lies approximately on the mirror plane xoz. The O(T) atom exactly lies on the mirror plane, but the C(11), C(12), C(13), and C(14) atoms are disordered out of the mirror plane with 1/2 occupancy. The large thermal motion of the thf ligand presumably permits a number of possible conformations including the twisting form with an approximate C2 symmetry. The average C–O bond distance of 1.391 Å

Table 3. COMPARISON OF AVERAGE BOND PARAMETERS, MAGNETIC MOMENTS, AND MÖSSBAUER PARAMETERS OF SOME INTERMEDIATE-SPIN IRON(III) PORPHINATO COMPLEXES

Complex	Spin state	Bond parameters (l/Å)			ESR g-values	Magnetic moment	Mössbauer parameters b)			Ref.
		Fe–N	Fe–Ct a)	Fe–L		μ_B/BM	ε/mm s^{-1}	ΔE_Q/mm s^{-1}	T/K	
5-Coordinate complexes										
[Fe^{III}(tpp)]ClO$_4$·0.5 m-xylene	{3/2, 5/2}	2.001	0.28	2.029 L=ClO$_4$	$g_{//}$=2.03 $g_\perp$=4.75 at 10 K	4.5—5.3 at 298 K	0.38 0.38 0.34 0.30	3.50 3.48 3.17 2.79	4.2 77 195 295	3a
[Fe^{III}(tpp)]ClO$_4$·0.5 toluene	{3/2, 5/2}	1.997	0.27	2.025 L=ClO$_4$	—	4.1 at 40 K 5.0 at 297 K	0.39	3.4	4.2	3b
[Fe^{III}(oep)]ClO$_4$	3/2	1.994	0.26	2.067 L=ClO$_4$	$g_{//}$=1.48 $g_\perp$=5.83 at 77 K g=3.91 at 295 K	4.16 at 77 K 4.78 at 295 K	0.40 0.39 0.31	3.54 3.57 3.14	4.2 77 298	3c,4a
[Fe^{III}(oep)]ClO$_4$	3/2	—	—	—	—	4.5 at 295 K	0.37 0.37 0.29	3.57 3.52 3.16	4.2 115 295	2
6-Coordinate complexes										
[Fe^{III}(oep)(EtOH)$_2$]ClO$_4$	3/2	—	—	—	—	4.1 at 84 K 4.2 at 127 K 4.4 at 191 K 4.8 at 275 K	0.38 0.36 0.29	3.47 3.32 2.97	4.2 115 295	2
[Fe^{III}(oep)(EtOH)$_2$]ClO$_4$·EtOH	{3/2, 5/2} or 5/2	2.036	≈0	2.137 L=EtOH	—	—	—	—	—	5a
[Fe^{III}(tpp)(EtOH)$_2$]BF$_4$	5/2	2.027	≈0	2.142 L=EtOH	$g_{//}$=2 $g_\perp$=6 at 77 K	5.9 at 4—100 K	0.42	1.89	4.2	5b
[Fe^{III}(tpp)C(CN)$_3$]	3/2	1.995	≈0	2.217 L=C(CN)$_3$	$g_{//}$=2.00 $g_\perp$=5.26 at 78 K	5.4• at 78—298 K 5.1 at 78—298 K in CHCl$_3$	0.30 0.30	3.03 3.18	78 298	3d
[Fe^{III}(oep)(thf)$_2$]ClO$_4$	3/2	1.978	≈0	2.187 L=thf	g=4.61 at 77 K g=3.86 at 298 K $g_{//}$=2.00 $g_\perp$=4.68 at 77 K in CH$_2$Cl$_2$	4.21 at 77 K 4.73 at 275 K	0.42 0.31	3.34 3.04	77 298	This work

a) Relative to Fe metal. b) C_t notes the center of four nitrogen atoms.

and the average C–C bond distance of 1.467 Å are within the range of those for the metal coordinated thf molecules.8)

The perchlorate anion is disordered around the center of symmetry. The Cl, O(1), and O(2) atoms lie on the mirror plane, and the O(3) atom exists at a general position. The perchlorate anion is surrounded by the six [Fe(III)(oep)(thf)$_2$]$^+$ cations, and the short intermolecular distances are 3.295 Å between O(3) and C(5), and 3.417 Å between O(2) and C(11).

Discussion

The bond distances and bond angles observed in several intermediate-spin iron(III)-porphyrins are listed in Table 3. Data of ESR spectra, effective magnetic moments, and Mössbauer spectra are also included in Table 3. The ESR spectrum of [Fe(III)(oep)(thf)$_2$]ClO$_4$ shows one broad signal at g=4.16 in the solid state, and the anisotropic $g_{//}$ and $g_\perp$ values are quite different from those of the usual high-spin complex ($g_{//}$=2, $g_\perp$=6) and those of the low-spin complexes (g=2.2—2.8). The effective magnetic moments, μ_{eff}, of 4.21 μ_B at 77 K and 4.73 μ_B at 275 K3c) are close to 3.87 μ_B calculated for S=3/2 rather than to 5.92 or to 1.73 μ_B for S=5/2 or 1/2, respectively. The large quadrupole splitting in the Mössbauer spectrum eliminates both possibilities of a low-spin complex and a high-spin complex. Hence, these spectroscopic data suggest that the iron(III) complex has a pure S=3/2 ground state.

Generally, a low-spin six-coordinated iron(III)-porphyrin becomes a high-spin complex when the axial ligand is replaced by a more weakly interacting ligand.3b) In this case, both the axial and equatorial bond distances

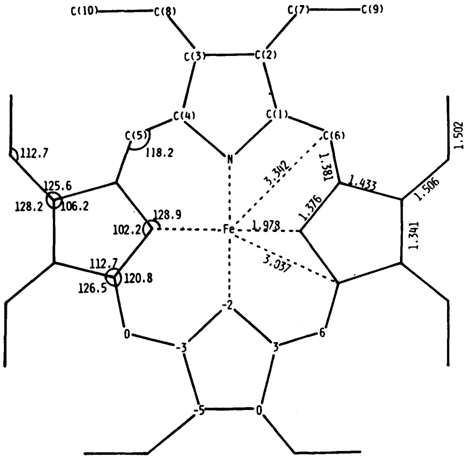

Fig. 3. Formal diagram of the porphinato skeleton in [Fe^{III}(oep)(thf)$_2$]ClO$_4$ molecule. On the top of the diagram, the numbering scheme for the atoms is displayed. On the right-hand side and left-hand side of the diagram, the chemically equivalent bond distances and angles. On the bottom of the diagram, the numbering symbol for each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core.

increase without change of the octahedral symmetry around the central metal ion. If the axial ligand becomes very weak, the axial bond distance is further increased, while the equatorial distance is decreased, and then the octahedral symmetry falls down to the lower D_{4h} symmetry. The intermediate-spin state may be arisen in this situation. Scheidt *et al.*[6a] gave 2.096 Å for the critical Fe–O distance in the transition from the high-spin to intermediate-spin state. The Fe–O distance of 2.137 Å has, however, been observed in the quantum mechanically $S=5/2$ and 3/2 mixed spin complex, [Fe(III)(oep)(EtOH)$_2$]$^+$,[5a] and the Fe–O distance of 2.142 Å was reported for a high-spin complex [Fe(III)-(tpp)(EtOH)$_2$]$^+$.[5b] The present Fe–O(thf) distance of 2.187 Å is longer than these Fe–O distances. The long axial Fe–O distance and short equatorial Fe–N distance strongly suggest that this complex has a pure intermediate-spin state, since in view of the stability of chemical bonds, the vacant $d_{x^2-y^2}$ and singly occupied d_{z^2} orbital levels in the intermediate-spin state are consistent with the long axial and short equatorial bond distances. Hence the Fe–O distance of 2.187 Å observed here may be a typical Fe–O distance for a pure $S=3/2$ state.

For cytochrome c′ it has been believed that its protein ligation to heme occurs at the fifth coordination site through the histidine residue,[12] and that the π-bonding mode of the ligation is definitely related to the function of hemoproteins. In the synthetic intermediate-spin complexes as a model heme for cytochrome c′, however, the weak σ-characterisities of the axial ligands seems to play an important role in the intermediate-spin complex formation, and the weakness of the ligand field strength may be necessary for the occurrence of the intermediate-spin states. Therefore, the coordination aspect in the cytochrome c′ may be speculated by the electronically weak bonding of histidine as in the manner of a long Fe–imidazole N distance and/or of a large tilting angle of histidine with respect to the porphinato core of heme.

The authors wish to thank Professor Nobuo Morimoto and Dr. Katsutoshi Tomita, Faculty of Science, Kyoto University, for the use of the Rigaku AFC-5 diffractometer.

References

1) M. M. Maltempo, *J. Chem. Phys.*, **61**, 2540 (1974); M. M. Maltempo, T. H. Moss, and M. A. Cusanovich, *Biochim. Biophys. Acta*, **342**, 290 (1974); M. M. Maltempo, *ibid.*, **379**, 97 (1975).

2) D. H. Dolphin, J. R. Sams, and T. B. Tsin, *Inorg. Chem.*, **16**, 711 (1977).

3) a) M. E. Kastner, W. R. Scheidt, T. Mashiko, and C. A. Reed, *J. Am. Chem. Soc.*, **100**, 666 (1978); b) C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kastner, W. R. Scheidt, K. Spartalian, and G. Lang, *ibid.*, **101**, 2948 (1979); c) H. Ogoshi H. Sugimoto, and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, **54**, 3414, (1981); d) D. A. Summerville, I. A. Cohen, K. Hatano, and W. R. Scheidt, *Inorg. Chem.*, **17**, 2906 (1978).

4) H. Masuda, T. Taga, K. Osaki, H. Sugimoto, Z. Yoshida, and H. Ogoshi, *In org. Chem.*, **19**, 950 (1980).

5) a) F. W. B. Einstein and A. C. Willis, *Inorg. Chem.*, **17**, 3040 (1978); b) P. Gans, G. Buisson, E. Duie, J. R. Regnard, and J. C. Marchon, *J. Chem. Soc., Chem. Commun.*, **1979**, 393.

6) a) W. R. Scheidt, I. A. Cohen, and M. E. Kastner, *Biochemistry*, **18**, 3546 (1979); b) T. Mashiko, M. E. Kastner, K. Spartalian, W. R. Scheidt, and C. A. Reed, *J. Am. Chem. Soc.*, **100**, 6354 (1978).

7) a) "International Tables for X-Ray Crystallography," ed by J. A. Ibers and W. C. Hamilton, Kynoch, Birmingham, England (1974), Vol. IV, p. 99; b) *ibid.*, p. 148.

8) D. J. Brauer and C. Kruger, *Inorg. Chem.*, **14**, 3053 (1975); K. O. Hodgson and K. N. Raymond, *ibid.*, **11**, 171 (1972); D. J. Brauer and G. D. Stucky, *J. Organomet. Chem.*, **37**, 217 (1972); D. J. Brauer and C. Kruger, *ibid.*, **42**, 129 (1972); J. L. Atwood and K. D. Smith, *J. Chem. Soc., Dalton Trans.*, **1974**, 921; J. J. Daly and R. P. A. Sneeden, *J. Chem. Soc., A*, **1967**, 736; C. A. Reed, T. Mashiko, W. R. Scheidt, K. Spartalian, and G. Lang, *J. Am. Chem. Soc.*, **102**, 2302 (1980).

9) a) D. M. Collins, R. Counterman, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2066 (1972); b) R. G. Little, K. R. Dymoch, and J. A. Ibers, *ibid.*, **97**, 4532 (1975); c) W. R. Scheidt, K. J. Haller, and K. Hatano, *ibid.*, **102**, 3017 (1980).

10) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York (1975), p. 259.

11) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

12) P. C. Weber, R. G. Bartsch, M. A. Cusanovich, R. C. Hamilton, A. Howard, S. R. Jordan, M. D. Kaman, T. E. Meyer, D. W. Weatherford, Ng. H. Xuong, and F. R. Salemme *Nature* (*London*), **286**, 302 (1980).