Crystal Structures of Low- and High-spin Iron(III) Complexes with Quadridentate Schiff Bases ‡

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The crystal structures of three iron(III) complexes, $[Fe(acen)(Him)_2]BPh_4$ (**1**), $[Fe(salen)(Him)_2]ClO_4{\cdot}H_2O$ (**2**), and $[Fe(salphen)(Him)_2]BPh_4$ (**3**), were determined by the *X*-ray diffraction method [H_2acen = *NN'*-ethylenebis(acetylacetonylideneimine), H_2salen = *NN'*-ethylenebis(salicylideneimine), $H_2salphen$ = *o*-phenylenebis(salicylideneimine), and Him = imidazole. The low-spin complex (**1**) crystallizes in monoclinic space group $P2_1/n$ with a = 32.939(7), b = 12.705(2), c = 8.991(1) Å, β = 93.63(2)°, and Z = 4. The high-spin complex (**2**) crystallizes in monoclinic space group $P2_1/a$ with a = 16.146(8), b = 15.205(3), c = 10.042(3) Å, β = 92.73(3)°, and Z = 4. The high-spin complex (**3**) crystallizes in orthorhombic space group $Pna2_1$ with a = 26.966(8), b = 16.969(7), c = 8.977(3) Å, and Z = 4. The complex cation contains a quadridentate Schiff base in the equatorial plane and two imidazole molecules at the axial positions. The mean Fe–N (Schiff base), Fe–O, and Fe–N (imidazole) bond distances are 1.899, 1.920, and 1.990 Å for (**1**), respectively, 2.108, 1.917, and 2.143 Å for (**2**), and 2.125, 1.896, and 2.165 Å for (**3**), indicating that the metal to imine nitrogen bond distances are sensitive to the spin state of iron, whereas the changes in the Fe–O bond distances are very little affected. The cause of this trend, which was also found for other iron(III) complexes, is discussed in terms of the feasibility of π bonding. No relation between the relative orientation of axial imidazole rings and spin state was detected.

Six-co-ordinate iron(III) porphyrin and quadridentate Schiff-base complexes with general formula $[FeLB_2]Y$ (H_2L = porphyrin or Schiff-base ligand; B = imidazole or pyridine; Y = ClO_4, PF_6, or BPh_4, *etc.*) display interesting structural and electronic effects.[1–12] Variation of in-plane chelate and axial bases often leads to a change in spin state of iron(III), *i.e.* high-spin ($S = \frac{5}{2}$), low-spin ($S = \frac{1}{2}$), or spin-crossover state. Both ourselves and others[4–12] have been investigating such behaviour in both Schiff-base and porphyrin systems in an attempt systematically to delineate the important factors that lead to crossover behaviour. A primary determining factor of the spin state is the nature and number of the axial ligands, and the nature of the quadridentate ligand also plays a part.[1,9]

In this paper we report the crystal structures of $[Fe(acen)(Him)_2]BPh_4$ (1) (low spin), $[Fe(salen)(Him)_2]ClO_4{\cdot}H_2O$ (2) (high spin), and $[Fe(salphen)(Him)_2]BPh_4$ (3) (high spin) in order to elucidate the correlation between the in-plane co-ordination bonds and the spin state of six-co-ordinate iron(III) complexes with quadridentate Schiff bases [H_2acen = *NN'*-ethylenebis(acetylacetonylideneimine), H_2salen = *NN'*-ethylenebis(salicylideneimine), $H_2salphen$ = *o*-phenylenebis(salicylideneimine), and Him = imidazole]. The electronic properties of the low-spin complex (1) and spin-crossover complexes have previously been investigated[1–3] by e.s.r. and Mössbauer spectroscopy.

Experimental

Materials.—The compounds (1)—(3) were prepared according to the literature method.[1]

X-*Ray Data Collection.*—The crystals were mounted on a Rigaku AFC-5 automatic diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Automatic centring and least-squares routines were carried out on 25 reflections for each complex to obtain the cell constants given in Table 1. The ω–2θ scan technique was employed to record the intensities for a unique set of reflections for which $3 < 2\theta < 55°$. Three check reflections were measured every 100 reflections; they exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarization effects.

Structure Solution and Refinement.—In each case the positional parameters of the iron atom were determined by direct methods.[13] The remaining non-hydrogen atoms were located by subsequent Fourier maps and least-squares refinement. The refinement (H atoms were not included) was effected by the block-diagonal least-squares technique using anisotropic thermal parameters. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where w = 1. In the last stage of refinement, the Fourier difference map showed no significant peaks and all the parameter shifts were less than 0.3σ. The crystal data and the final R values are listed in Table 1. Programs used for the structure solution and anisotropic refinement were supplied by the local version[14] of the UNICS system.[15] Atomic scattering factors were taken from ref. 16, and the effects of anomalous dispersion for non-hydrogen atoms were corrected for in the structure factor calculations. All calculations were performed on a Facom M-200 computer at the Computer Centre of Kyushu University.

Results and Discussion

Molecular Structure of Complex (1).—Figure 1 shows the molecular structure of (1) and the atomic numbering scheme employed for all non-hydrogen atoms of the molecule. The atomic co-ordinates and the selected bond distances and angles are listed in Tables 2 and 3, respectively. The lattice of this molecule consists of a cationic complex and a tetraphenylborate anion, and the complex cation contains a quadridentate Schiff base in the equatorial plane with two imidazole molecules at the

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Crystal data for complexes (**1**)—(**3**)*

Complex	(1)	(2)	(3)
Formula	$C_{42}H_{44}BFeN_6O_2$	$C_{22}H_{22}ClFeN_6O_7$	$C_{50}H_{40}BFeN_6O_2$
M	731.5	573.8	823.6
Space group	$P2_1/n$	$P2_1/a$	$Pna2_1$
a/Å	32.939(7)	16.146(8)	26.966(8)
b/Å	12.705(2)	15.205(3)	16.969(7)
c/Å	8.991(1)	10.042(3)	8.977(3)
β/°	93.63(2)	92.73(3)	
U/Å^3	3 755	2 462	4 108
D_c/g cm^{-3}	1.29	1.55	1.33
F(000)	1 540	1 180	1 716
Crystal dimensions/mm	0.3 × 0.3 × 0.4	0.2 × 0.3 × 0.4	0.3 × 0.3 × 0.4
Reflections collected	5 225	4 778	5 522
Independent reflections ($F_o > 3\sigma\|F_o\|$)	3 718	3 337	3 673
μ(Mo-K_α)/cm^{-1}	4.6	8.0	4.3
$R\ (=\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$	0.075	0.063	0.058
$R'\ [=(\Sigma\|\|F_o\| - \|F_c\|\|^2/\Sigma\|F_o\|^2)^{\frac{1}{2}}]$	0.082	0.065	0.063

* Details common to all three complexes: $Z = 4$; scan rate 6° min^{-1}; scan range (2θ) 3.0—55.0°.

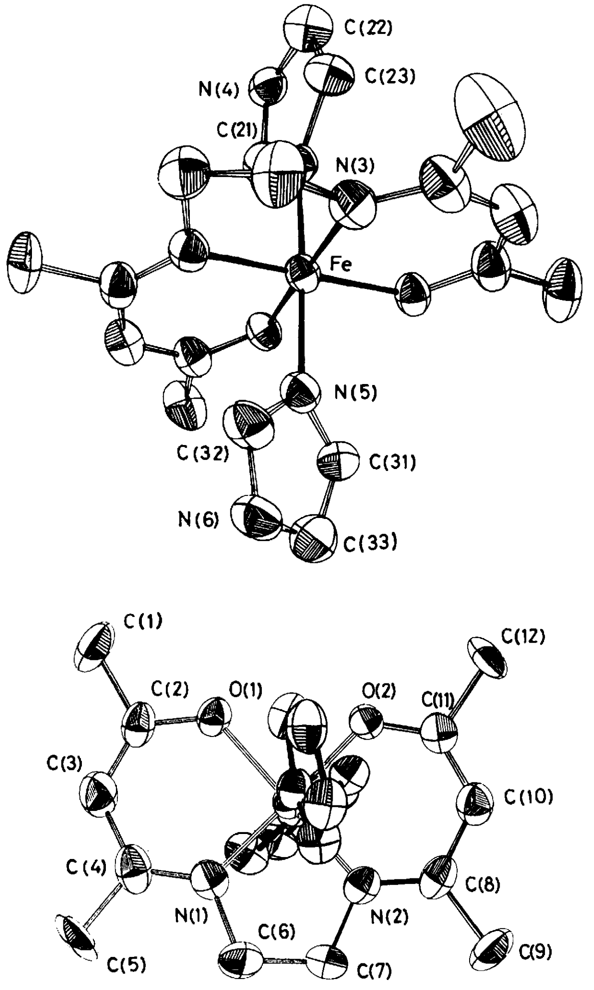

Figure 1. Molecular structures showing the cation of compound (1)

axial positions. The first co-ordination sphere around the iron atom is approximately octahedral with a N_4O_2 donor set. The angles O(1)–Fe–N(2), N(1)–Fe–O(2), and N(3)–Fe–N(5) (see Table 3) are all close to 180° [179.3(2), 178.6(2), and 173.7(2)°, respectively].

The iron atom is in the plane (within 0.005 Å) defined by the four ligand atoms N(1), N(2), O(1), and O(2) described by the equation $0.383\,83X + 0.844\,27Y + 0.397\,58Z = 2.491\,95$. The atoms C(6) and C(7) associated with the ethylenediamine link (in the *gauche* conformation) are at distances of −0.15 and +0.38 Å below and above the plane [Fe, O(1), O(2), N(1), and N(2)], respectively. The dihedral angle between the two imidazole molecules is 66°.

Molecular Structures of Complexes (**2**) *and* (**3**).—An ORTEP drawing of compound (**2**) is given in Figure 2 with the atomic numbering scheme, positional parameters and selected bond lengths and angles in Tables 4 and 3, respectively. The whole structure of this molecule is very similar to that of (**1**) in that the iron is of approximately octahedral co-ordination, being in the plane (within 0.004 Å) defined by the four ligand atoms N(1), N(2), O(1), and O(2). However, remarkable deviations from the ideal octahedral case were observed for some angles, *e.g.* O(1)–Fe–N(2) and N(1)–Fe–N(2) are 163.9(2) and 76.6(2)°, respectively.

Figure 3 shows the ORTEP drawing of compound (**3**). Its atomic co-ordinates and selected bond distances and angles are summarized in Tables 5 and 3, respectively. The structure of (**3**) is very similar to that of (**2**) in that the iron is exactly in the N(1), N(2), O(1), and O(2) plane (within 0.001 Å), and some bond angles deviate from those of the ideal octahedron, *e.g.* O(1)–Fe–N(2), N(1)–Fe–O(2), and N(1)–Fe–N(2) are 168.3(2), 167.5(2), and 77.9(2)°, respectively.

Correlation between Structure and Spin State.—The selected bond distances and angles which are potentially relevant to the spin state of the iron atom are summarized in Table 3. The most remarkable difference between the high-spin [(**2**) and (**3**)] and low-spin [(**1**)], complexes lies in the co-ordination bond distances. The mean length of co-ordination bonds [Fe–O(1), -O(2), -N(1), -N(2), -N(3), and -N(5)] is 1.936 Å for (**1**), whereas those of (**2**) and (**3**) are 2.059 and 2.062 Å, respectively.

It should be noted here that no significant difference was observed for the average Fe–O distances: 1.920, 1.917, and 1.896 Å for (**1**), (**2**), and (**3**), respectively. The present results are consistent with those of previous studies on similar iron(III) complexes with sexi- and tri-dentate Schiff bases, in that metal to imine nitrogen bond distances are in the range 2.06—2.10 and 1.90—1.96 Å for high- and low-spin states, respectively, whereas Fe–O distances are almost constant for both high- and low-spin complexes.[17–22] No reasonable explanation for these results has

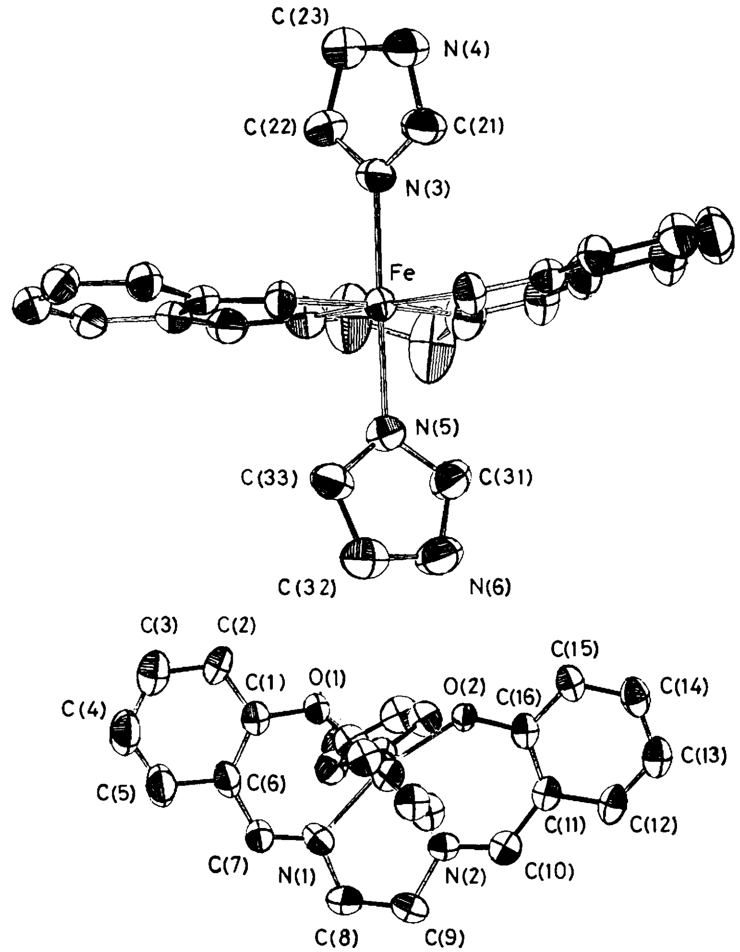

Figure 2. ORTEP views of the cation of compound (**2**)

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for (**1**)

Atom	x	y	z
Fe	839(0.4)	3 322(1)	−45(1)
O(1)	646(2)	3 763(4)	−2 017(5)
C(1)	622(3)	4 590(8)	−4 384(8)
C(2)	853(3)	4 335(6)	−2 903(8)
C(3)	1 245(3)	4 709(7)	−2 594(9)
C(4)	1 490(3)	4 507(7)	−1 268(9)
C(5)	1 924(3)	4 965(9)	−1 210(12)
N(1)	1 358(2)	3 970(5)	−150(6)
C(6)	1 651(3)	3 743(7)	1 168(9)
C(7)	1 392(3)	3 491(7)	2 486(8)
N(2)	1 025(2)	2 904(5)	1 900(6)
C(8)	834(3)	2 235(6)	2 732(7)
C(9)	1 021(3)	1 938(8)	4 288(8)
C(10)	463(3)	1 735(7)	2 253(8)
C(11)	226(2)	1 991(6)	990(8)
C(12)	−181(3)	1 442(7)	669(10)
O(2)	314(1)	2 685(4)	11(5)
N(5)	609(2)	4 622(4)	826(6)
C(31)	798(3)	5 607(6)	1 035(9)
C(32)	244(2)	4 680(6)	1 383(7)
N(6)	176 (2)	5 655(5)	1 915(6)
C(33)	525(3)	6 246(6)	1 718(9)
N(3)	1 015(2)	1 947(5)	−824(6)
N(4)	1 270(2)	355(5)	−975(8)
C(21)	1 285(3)	1 266(7)	−196(9)
C(22)	972(3)	431(7)	−2 122(9)
C(23)	807(3)	1 428(6)	−2 018(8)
B	3 387(3)	3 436(7)	1 759(8)
C(41)	3 215(2)	4 607(6)	1 201(7)
C(42)	3 252(2)	4 882(6)	−303(7)
C(43)	3 089(3)	5 820(7)	−914(9)
C(44)	2 892(3)	6 524(7)	−7(10)
C(45)	2 854(3)	6 280(7)	1 487(10)
C(46)	3 021(2)	5 327(6)	2 095(8)
C(51)	3 365(2)	3 261(5)	3 565(7)
C(52)	2 994(2)	3 370(6)	4 265(8)
C(53)	2 962(3)	3 194(7)	5 798(8)
C(54)	3 304(3)	2 859(6)	6 660(8)
C(55)	3 676(2)	2 726(6)	6 018(8)
C(56)	3 707(3)	2 946(6)	4 489(7)
C(61)	3 848(2)	3 330(6)	1 211(7)
C(62)	3 967(3)	2 608(7)	129(7)
C(63)	4 361(3)	2 575(8)	−361(9)
C(64)	4 665(3)	3 255(8)	269(10)
C(65)	4 555(3)	3 980(7)	1 342(10)
C(66)	4 161(2)	4 013(6)	1 798(9)
C(71)	3 078(2)	2 524(6)	978(7)
C(72)	3 164(3)	1 444(6)	1 244(9)
C(73)	2 915(3)	653(7)	583(9)
C(74)	2 571(3)	914(7)	−349(8)
C(75)	2 477(3)	1 967(7)	−603(8)
C(76)	2 733(2)	2 761(7)	58(7)

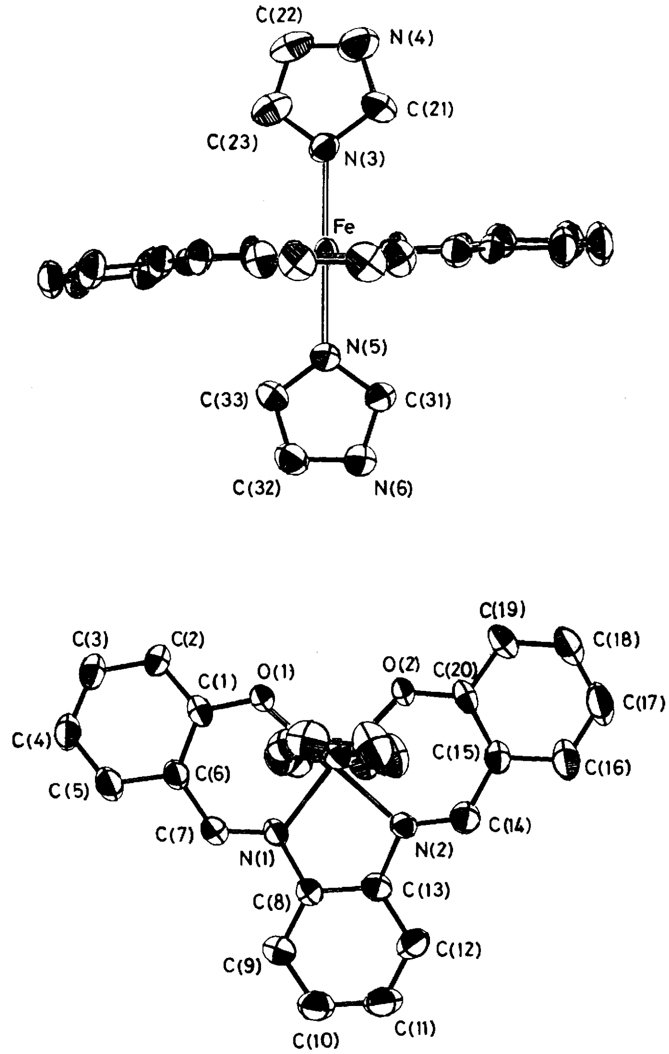

Figure 3. ORTEP drawings of the cation of compound (**3**)

yet been given. The following discussion gives some indication of the reasons.

It is well known that each *d* orbital in high-spin iron(III) complexes has one unpaired electron. In the case of low-spin iron(III) complexes, we have already shown, by the use of e.s.r. and Mössbauer spectra, that the ground-state configuration is $(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^1$ for complexes with quadridentate Schiff bases such as (**1**) (see below for the definition of the *x*, *y*, and *z* axes).[1] Therefore, as the spin state changes from high- to low-spin: (*a*) all the σ co-ordinations are facilitated because of the vacancy of iron d_σ orbitals, (*b*) π back donation from the iron d_{xz} and d_{yz} orbitals to the azomethine π* orbitals stabilizes the Fe–N bonds, and (*c*) the electronic repulsion between fully occupied iron d_{xz} and d_{yz} and oxygen p_π orbitals destabilizes the

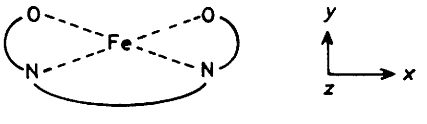

Table 3. Selected bond distances (Å) and angles (°) for the compounds (**1**)—(**3**)

	(**1**)	(**2**)	(**3**)
Fe–O(1)	1.928(4)	1.928(4)	1.883(5)
Fe–O(2)	1.912(5)	1.906(4)	1.910(5)
Fe–N(1)	1.906(7)	2.130(4)	2.108(6)
Fe–N(2)	1.892(5)	2.105(5)	2.143(6)
Fe–N(3)	1.983(6)	2.137(5)	2.172(6)
Fe–N(5)	1.997(6)	2.148(5)	2.158(6)
O(1)–Fe–O(2)	84.4(2)	107.8(2)	102.0(2)
O(1)–Fe–N(1)	94.2(2)	87.4(2)	90.4(2)
O(1)–Fe–N(2)	179.3(2)	163.9(2)	168.3(2)
O(1)–Fe–N(3)	91.1(2)	90.0(2)	92.6(2)
O(1)–Fe–N(5)	90.6(2)	89.3(2)	90.8(2)
N(1)–Fe–N(2)	85.8(3)	76.6(2)	77.9(2)
N(1)–Fe–O(2)	178.6(2)	164.8(2)	167.5(2)
N(1)–Fe–N(3)	94.5(3)	90.6(2)	88.8(2)
N(1)–Fe–N(5)	91.4(3)	91.4(2)	90.4(2)
N(2)–Fe–O(2)	95.6(2)	88.3(2)	89.7(2)
N(2)–Fe–N(3)	89.7(2)	91.7(2)	87.2(2)
N(2)–Fe–N(5)	88.7(2)	89.0(2)	89.3(2)
O(2)–Fe–N(3)	85.6(2)	88.8(2)	89.1(2)
O(2)–Fe–N(5)	88.6(2)	89.3(2)	91.0(2)
N(3)–Fe–N(5)	173.7(2)	177.9(2)	176.5(2)

Table 4. Atomic co-ordinates (× 10^4) with e.s.d.s for complex (**2**)

Atom	*x*	*y*	*z*
Fe	3 709(0.4)	3 443(1)	8 310(1)
O(1)	3 277(2)	3 487(3)	10 066(3)
O(2)	4 884(2)	3 552(3)	8 504(4)
N(1)	2 460(3)	3 317(3)	7 549(4)
N(2)	3 829(3)	3 326(4)	6 239(5)
C(1)	2 526(3)	3 502(3)	10 511(5)
C(2)	2 432(4)	3 696(4)	11 871(6)
C(3)	1 642(4)	3 683(4)	12 387(6)
C(4)	939(4)	3 462(4)	11 577(7)
C(5)	1 028(4)	3 293(4)	10 239(7)
C(6)	1 804(3)	3 329(3)	9 664(6)
C(7)	1 812(4)	3 235(4)	8 235(6)
C(8)	2 338(5)	3 313(7)	6 084(7)
C(9)	3 072(5)	3 021(7)	5 474(7)
C(10)	4 473(4)	3 505(5)	5 599(6)
C(11)	5 262(4)	3 735(4)	6 232(6)
C(12)	5 906(5)	3 952(6)	5 359(7)
C(13)	6 700(5)	4 160(6)	5 870(8)
C(14)	6 876(4)	4 153(5)	7 240(8)
C(15)	6 256(4)	3 943(4)	8 116(7)
C(16)	5 451(4)	3 734(4)	7 628(6)
N(3)	3 626(3)	4 842(3)	8 174(5)
C(21)	4 279(4)	5 376(4)	8 322(6)
C(22)	2 932(4)	5 368(4)	7 979(6)
N(5)	3 836(3)	2 040(3)	8 483(4)
C(31)	4 241(4)	1 531(4)	7 651(6)
N(6)	4 309(3)	708(3)	8 155(6)
C(32)	3 934(4)	687(4)	9 352(7)
C(33)	3 645(4)	1 521(4)	9 558(6)
N(4)	4 034(3)	6 227(3)	8 213(5)
C(23)	3 177(4)	6 234(4)	7 977(7)
O(20)	−574(3)	1 960(3)	12 147(5)
Cl	−877(1)	4 160(1)	13 873(2)
O(11)	−1 369(3)	4 508(4)	14 864(5)
O(12)	−1 328(4)	3 477(4)	13 178(7)
O(13)	−703(4)	4 813(4)	12 935(6)
O(14)	−136(4)	3 797(5)	14 446(6)

Table 5. Atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for complex (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	4 931(0.3)	3 244(1)	3 487(2)	N(5)	4 484(2)	2 321(4)	4 452(7)
O(1)	5 170(2)	3 528(3)	5 383(5)	C(31)	4 000(3)	2 202(5)	4 251(11)
C(1)	5 545(3)	3 288(5)	6 193(8)	N(6)	3 837(3)	1 652(5)	5 241(10)
C(2)	5 604(3)	3 584(5)	7 652(8)	C(32)	4 229(4)	1 404(7)	6 066(12)
C(3)	6 012(3)	3 364(5)	8 492(12)	C(33)	4 641(4)	1 812(6)	5 564(10)
C(4)	6 363(4)	2 833(6)	7 967(11)	B	2 011(3)	5 491(5)	4 817(9)
C(5)	6 313(3)	2 497(6)	6 568(10)	C(71)	2 303(3)	4 688(4)	5 411(8)
C(6)	5 899(3)	2 718(5)	5 644(8)	C(72)	2 146(3)	4 262(5)	6 663(9)
C(7)	5 871(3)	2 335(5)	4 200(9)	C(73)	2 433(3)	3 614(5)	7 194(10)
N(1)	5 526(2)	2 451(3)	3 217(6)	C(74)	2 877(3)	3 386(5)	6 505(11)
C(8)	5 535(3)	2 048(4)	1 831(8)	C(75)	3 028(3)	3 804(5)	5 243(10)
C(9)	5 907(3)	1 507(5)	1 406(10)	C(76)	2 751(3)	4 443(5)	4 726(9)
C(10)	5 890(4)	1 146(5)	22(11)	C(81)	2 106(3)	5 579(4)	2 987(8)
C(11)	5 498(3)	1 299(5)	−964(10)	C(82)	2 268(3)	6 283(5)	2 337(9)
C(12)	5 126(3)	1 836(5)	−557(9)	C(83)	2 351(3)	6 350(6)	790(9)
C(13)	5 143(3)	2 196(4)	830(8)	C(84)	2 264(3)	5 699(6)	−119(9)
N(2)	4 788(2)	2 765(3)	1 322(6)	C(85)	2 107(3)	4 985(6)	501(9)
C(14)	4 426(3)	2 972(5)	475(8)	C(86)	2 034(3)	4 933(5)	2 042(9)
C(15)	4 072(3)	3 589(5)	792(8)	C(61)	1 421(3)	5 408(4)	5 209(8)
C(16)	3 723(3)	3 755(6)	−349(9)	C(62)	1 076(3)	5 077(5)	4 194(9)
C(17)	3 386(3)	4 390(5)	−192(9)	C(65)	730(3)	5 491(5)	7 022(10)
C(18)	3 394(3)	4 832(5)	1 088(10)	C(64)	398(3)	5 156(5)	5 984(10)
C(19)	3 723(3)	4 684(4)	2 245(9)	C(63)	573(3)	4 942(6)	4 587(10)
C(20)	4 054(3)	4 045(4)	2 142(8)	C(66)	1 233(3)	5 595(5)	6 640(9)
O(2)	4 363(2)	3 908(3)	3 291(6)	C(91)	2 262(3)	6 264(4)	5 673(7)
N(3)	5 373(2)	4 142(4)	2 383(7)	C(92)	1 987(3)	6 959(5)	5 883(10)
C(21)	5 237(3)	4 599(5)	1 236(9)	C(93)	2 184(4)	7 634(6)	6 579(12)
N(4)	5 617(3)	5 065(4)	827(8)	C(94)	2 686(3)	7 620(6)	7 126(11)
C(22)	6 021(3)	4 895(5)	1 731(10)	C(95)	2 962(3)	6 932(5)	6 845(12)
C(23)	5 863(3)	4 325(5)	2 697(10)	C(96)	2 753(3)	6 274(5)	6 183(10)

Fe–O bonds. As a result, the Fe–N bonds should be much stabilized by both the effects of (*a*) and (*b*), whereas the effects of (*a*) and (*c*) may be counter-balanced in the Fe–O bonds to minimize the changes in bond length. Thus, the sensitive and insensitive variations in Fe–N and Fe–O bonds, respectively, are understandable.

Geiger *et al.*[23] pointed out that the relative orientation of imidazole rings is the controlling factor for the spin state of porphyrin complexes. In the present cases, however, no such relation was observed between the dihedral angles of the imidazole molecules and the spin state; *i.e.* dihedral angles formed by the two imidazole molecules are 66, 70, and 7°, for complexes (**1**), (**2**) and (**3**), respectively.

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