# *X*-Ray Structural Study of [Fe(saltrien)]X (X = Br·$2H_2O$, $BPh_4$, or $PF_6$).‡ Origin of Unusual Magnetic Behaviour of the Spin-crossover Complex [Fe(saltrien)]$PF_6$

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The crystal structures of three six-co-ordinate iron(III) complexes; [Fe(saltrien)]Br·$2H_2O$ (low-spin) (**1**), [Fe(saltrien)]$BPh_4$(spin-crossover) (**2**), and [Fe(saltrien)]$PF_6$(spin-crossover) (**3**) have been determined by *X*-ray analysis at 293 K, where $H_2$saltrien denotes the Schiff base derived from salicylaldehyde and triethylenetetra-amine. Crystals of (**1**) are monoclinic with $a$ = 24.601(3), $b$ = 10.024(2), $c$ = 12.084(2) Å, β = 131.934(9)°, space group $P2_1/c$, and $Z$ = 4. Crystals of (**2**) are monoclinic with $a$ = 25.99(1), $b$ = 10.825(7), $c$ = 28.418(9) Å, β = 102.75(3)°, space group $C2/c$, and $Z$ = 8. Crystals of (**3**) are monoclinic with $a$ = 9.526(2), $b$ = 27.646(4), $c$ = 17.724(2) Å, β = 92.78(1)°, space group $P2_1/c$, and $Z$ = 8. In all three complexes the geometry around the iron(III) ion is best described as a distorted octahedron, but substantial differences are observed for the bond distances and angles among these complexes; *e.g.* the Fe–N distances in (**2**) and (**3**) (2.1—2.2 Å) are much longer than those of (**1**) (1.94—2.00 Å), and the 12 angles subtended at the metal atom by adjacent atoms lie in the range 75—105° in (**2**) and (**3**), but 84—95° in (**1**). Crystals of (**3**) contain two slightly structurally different complex cations in an asymmetric unit, and the unusual variation of magnetic moment with temperature of this compound has been attributed to the presence of two crystallographically independent cations, one of which undergoes the high-spin ⟶ low-spin transformation in the temperature range 100—200 K, whereas for the other this occurs below 100 K.

Since Cambi and Szego[1] first observed 'magnetic isomerism' for the tris(dithiocarbamato)iron(III) complexes in 1931, a number of spin equilibrium systems of six-co-ordinate iron(III) complexes with Schiff bases[2—7] and porphyrins[8—11] have been prepared, and characterized in terms of the magnetic susceptibility, e.s.r., Mössbauer, and absorption spectra. The temperature dependences of magnetism of these complexes, however, have never been interpreted quantitatively by the theoretical expression.[12] This may be attributed to the fact that the energy gap between $^2T_{2g}$ and $^6A_{1g}$ is not constant over the temperature range studied.

In 1978, Wilson and co-workers[13] prepared a series of iron(III) complexes with $H_2$saltrien, the hexadentate Schiff base derived from salicylaldehyde and triethylenetetra-amine, and studied the temperature variation of the magnetic moments. As shown in Figure 1, the magnetic moment of [Fe(saltrien)]$BPh_4$ decreases monotonously with lowering of temperature. Such a behaviour is common for the majority of spin-crossover complex.[14,15] In contrast to this, the temperature variation of [Fe(saltrien)]$PF_6$ seems to be unusual. The magnetic moment is almost constant in the temperature range 300—200 K. With lowering of temperature, the transformation from a high-spin to a low-spin state gradually takes place, but is still incomplete even at 30 K, as shown in Figure 1.

In order to elucidate the origin of such unusual magnetic behaviour, in this study we have determined by *X*-ray analysis the crystal structures of three iron(III) complexes, [Fe(saltrien)]Br·$2H_2O$ (low-spin) (**1**), [Fe(saltrien)]$BPh_4$ (spin-crossover) (**2**), and [Fe(saltrien)]$PF_6$ (spin-crossover) (**3**).

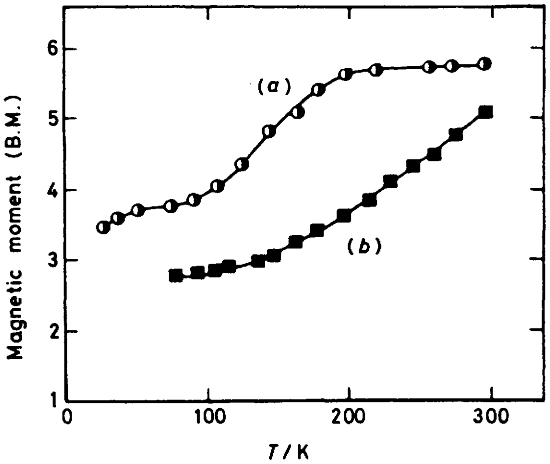

**Figure 1.** Variation with temperature of the molar susceptibility of (*a*) [Fe(saltrien)]$PF_6$ (**3**) and (*b*) [Fe(saltrien)]$BPh_4$ (**2**).[13] B.M. = 9.27 × $10^{-24}$ A $m^2$

## Experimental

*Preparations.*—The iron(III) complexes (**1**)—(**3**) were prepared by the published method.[13]

*Collection and Reduction of X-Ray Data.*—The crystals were mounted on a Rigakudenki AFC-5 automatic diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.710 69 Å) at 293 K. Automatic centring and least-squares routines were carried out on 25 high-angle reflections for each complex to obtain the cell constants given in Table 1. The θ—2θ scan technique was used to collect the intensities for a unique set of reflections for which $3 < 2\theta < 55°$. Scan widths were calculated as $A + B\tan\theta$, where $A$ is estimated from the mosaicity of the

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‡ *NN'*-3,6-Diazaoctane-1,8-diylbis(salicylideneiminato)iron(III) bromide dihydrate, tetraphenylborate, and hexafluorophosphate respectively.

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

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

| | (**1**) | (**2**) | (**3**) |
|---|---|---|---|
| Formula | $C_{20}H_{24}BrFeN_4O_2{\cdot}2H_2O$ | $C_{44}H_{44}BFeN_4O_2$ | $C_{20}H_{24}F_6FeN_4O_2P$ |
| $M$ | 524.2 | 727.5 | 553.3 |
| Space group | $P2_1/c$ | $C2/c$ | $P2_1/c$ |
| $a$/Å | 24.601(3) | 25.99(1) | 9.526(2) |
| $b$/Å | 10.024(2) | 10.825(7) | 27.646(4) |
| $c$/Å | 12.084(2) | 28.418(9) | 17.724(2) |
| β/° | 131.934(9) | 102.75(3) | 92.78(1) |
| $U$/Å$^3$ | 2 216 | 7 798 | 4 662 |
| $Z$ | 4 | 8 | 8[a] |
| $F$(000) | 1 076 | 3 064 | 2 264[a] |
| $D_c$/g cm$^{-3}$ | 1.58 | 1.24 | 1.58 |
| Crystal dimensions/mm | 0.3 × 0.3 × 0.2 | 0.05 × 0.2 × 0.3 | 0.05 × 0.3 × 0.3 |
| Scan rate/° min$^{-1}$ | 6 | 6 | 6 |
| Scan range (2θ)/° | 3—55 | 3—55 | 3—55 |
| μ(Mo-$K_\alpha$)/cm$^{-1}$ | 16.8 | 3.6 | 10.4 |
| Reflections collected | 5 080 | 5 140 | 5 551 |
| Independent reflections [$F_o > 3\sigma(F_o)$] | 3 475 | 3 352 | 3 298 |
| $R( = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$ | 0.062 | 0.091 | 0.087 |
| $R'\{ = [\Sigma w(\|\|F_o\| - \|F_c\|\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}\}$[b] | 0.074 | 0.124 | 0.098 |

[a] There are two crystallographically independent complexes in an asymmetric unit. [b] $w = 1/\sigma^2(F_o)$.

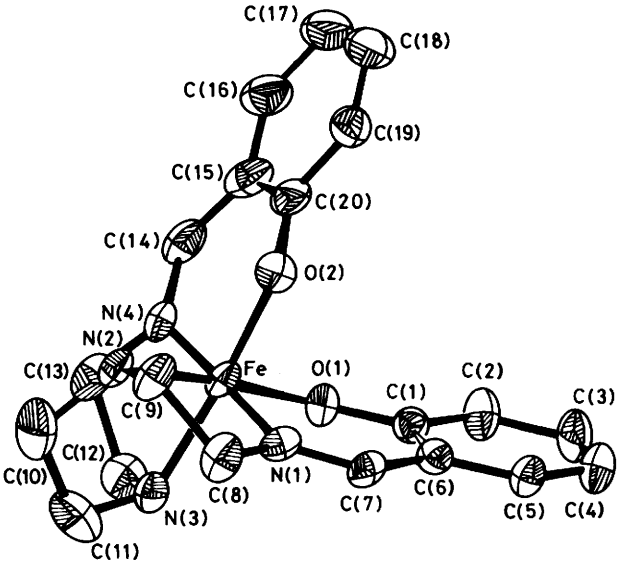

**Figure 2.** ORTEP drawing of [Fe(saltrien)]Br·2$H_2O$ (**1**)

crystal and $B$ allows for the increase in peak width due to $K_{\alpha_1}$–$K_{\alpha_2}$ splitting. The values of $A$ and $B$ were 1.5 and 0.5°, respectively.

Three check reflections were measured every 100 reflections; they showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz and polarization effects, but not for absorption.

*Structure Determination.*—In each case the positional parameter of the iron atom was determined by a direct method,[16] which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier synthesis. Disorders were observed for the ethylene bridge [C(12) and C(13)] and fluorine atoms of the $PF_6^-$ anion in compound (**3**). The occupancy factors of these atoms were given as 0.5. Block-diagonal least-squares refinements minimized the function $\Sigma w(||F_o| - |F_c||)^2$ where $w = 1/\sigma^2(F_o)$. In the last stage of refinement, including anisotropic thermal parameters, the difference Fourier map showed no significant peaks and all the parameter shifts were less than 0.4σ. The final $R$ values, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, are summarized in Table 1. Programs used for the structure solution and anisotropic refinement were supplied by the local version[17] of the UNICS system.[18] Atomic scattering factors were taken from ref. 19, and anomalous dispersion corrections were applied to all non-hydrogen atoms. All calculations were performed on a Facom M-200 computer at the Computer Center of Kyushu University.

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

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Fe | 7 271(0.4) | 395(1) | 6 537(1) |
| O(1) | 8 153(2) | −386(3) | 7 303(4) |
| C(1) | 8 623(3) | −965(5) | 8 604(5) |
| C(2) | 9 338(3) | −1 234(5) | 9 163(6) |
| C(3) | 9 853(3) | −1 835(6) | 10 507(7) |
| C(4) | 9 697(4) | −2 237(6) | 11 377(7) |
| C(5) | 9 005(4) | −2 027(6) | 10 843(6) |
| C(6) | 8 474(3) | −1 380(5) | 9 494(5) |
| C(7) | 7 754(3) | −1 220(5) | 9 002(5) |
| N(1) | 7 219(2) | −621(4) | 7 828(4) |
| C(8) | 6 516(3) | −549(6) | 7 439(6) |
| C(9) | 6 183(3) | 797(5) | 6 710(6) |
| N(2) | 6 276(2) | 1 016(4) | 5 634(5) |
| C(10) | 5 701(3) | 432(7) | 4 139(6) |
| C(11) | 5 940(3) | −952(6) | 4 080(6) |
| N(3) | 5 720(2) | −934(4) | 4 879(4) |
| C(12) | 6 898(3) | −677(5) | 3 931(6) |
| C(13) | 6 873(3) | 838(5) | 3 717(5) |
| N(4) | 7 285(2) | 1 414(4) | 5 206(4) |
| C(14) | 7 658(3) | 2 482(5) | 5 537(5) |
| C(15) | 8 117(2) | 3 119(5) | 6 975(5) |
| C(16) | 8 554(3) | 4 190(5) | 7 200(6) |
| C(17) | 8 999(3) | 4 861(6) | 8 529(7) |
| C(18) | 9 016(3) | 4 477(5) | 9 659(6) |
| C(19) | 8 600(3) | 3 427(6) | 9 465(6) |
| C(20) | 8 133(2) | 2 729(5) | 8 119(5) |
| O(2) | 7 731(2) | 1 759(3) | 7 988(3) |
| Br | 5 986(0.3) | 4 291(1) | 4 680(1) |
| O(3) | 7 293(3) | 6 489(4) | 6 380(6) |
| O(4) | 4 787(3) | 3 134(5) | 4 958(7) |

## Results

*Molecular Structures of Complexes*.—The ORTEP drawing of compound (**1**) is shown in Figure 2, and the final positional parameters for the atoms are given in Table 2. Table 3 contains the important bond lengths and angles. The crystal structure of (**1**) is very similar to that of the low-spin complex [Fe(saltrien)]Cl·2$H_2O$,[13] which contains cations, anions, and water molecules linked by hydrogen bonds.

The first co-ordination sphere is approximately octahedral, with the terminal oxygen atoms located in *cis* positions. The configuration of the hexadentate ligand about the metal atom is similar to those of (**2**) and (**3**), but the deviation of the $FeN_4O_2$ unit from octahedral geometry is much smaller than those in (**2**) and (**3**). The angles O(1)–Fe–N(2), N(1)–Fe–N(4), and N(3)–Fe–O(2) are all close to 180° [173.2(2), 177.9(2), and 175.2(1)°, respectively]. The metal–ligand bond distances are uneven, and markedly less than those of high-spin species.[13]

**Table 3.** Important bond lengths (Å) and angles (°) for compounds (**1**)—(**3**)

| | (**1**) | (**2**) | (**3A**) | (**3B**) |
|---|---|---|---|---|
| Fe–O(1) | 1.869(4) | 1.894(9) | 1.908(10) | 1.898(9) |
| Fe–N(1) | 1.937(6) | 2.117(11) | 2.094(11) | 2.107(11) |
| Fe–N(2) | 2.000(5) | 2.200(12) | 2.231(14) | 2.208(13) |
| Fe–N(3) | 1.999(4) | 2.187(12) | 2.199(14) | 2.200(13) |
| Fe–N(4) | 1.925(5) | 2.133(11) | 2.096(12) | 2.110(12) |
| Fe–O(2) | 1.889(3) | 1.887(9) | 1.870(10) | 1.897(9) |
| Mean | 1.937 | 2.069 | 2.066 | 2.070 |
| O(1)–Fe–N(1) | 93.5(2) | 86.8(4) | 86.3(4) | 87.2(5) |
| O(1)–Fe–N(2) | 173.2(2) | 157.8(4) | 157.6(5) | 157.5(5) |
| O(1)–Fe–N(3) | 90.1(2) | 90.3(4) | 91.0(5) | 90.4(4) |
| O(1)–Fe–N(4) | 88.4(2) | 94.0(4) | 93.6(5) | 100.6(4) |
| O(1)–Fe–O(2) | 93.8(2) | 106.0(5) | 105.5(4) | 101.9(4) |
| N(1)–Fe–N(2) | 83.6(2) | 75.4(4) | 76.7(5) | 75.1(5) |
| N(1)–Fe–N(3) | 95.2(2) | 95.9(4) | 104.8(5) | 99.6(5) |
| N(1)–Fe–N(4) | 177.9(2) | 173.4(4) | 177.0(5) | 171.4(5) |
| N(1)–Fe–O(2) | 87.4(2) | 98.8(4) | 91.9(4) | 95.0(4) |
| N(2)–Fe–N(3) | 84.1(2) | 78.6(4) | 79.5(5) | 79.2(5) |
| N(2)–Fe–N(4) | 94.5(2) | 102.1(4) | 104.1(5) | 96.4(5) |
| N(2)–Fe–O(2) | 92.1(2) | 90.0(4) | 89.8(5) | 93.5(4) |
| N(3)–Fe–N(4) | 83.9(2) | 77.6(5) | 78.2(5) | 77.0(5) |
| N(3)–Fe–O(2) | 175.2(1) | 158.5(4) | 157.3(5) | 161.4(4) |
| N(4)–Fe–O(2) | 93.3(2) | 87.3(4) | 85.2(4) | 86.9(4) |

The ORTEP drawing of compound (**2**) is illustrated in Figure 3, and the atomic parameters and important bond distances and angles are listed in Tables 4 and 3, respectively. The lattice contains [Fe(saltrien)]$^+$ cations and tetraphenylborate anions. The co-ordination geometry is a distorted octahedron, with the two terminal oxygen atoms in *cis* positions. The angles O(1)–Fe–N(2), N(1)–Fe–N(4), and N(3)–Fe–O(2) all deviate markedly from 180° [157.8(4), 173.4(4), and 158.5(4)°, respectively]. The metal–ligand bond lengths are uneven; the two Fe–O bonds (1.89 Å average) are shorter than the Fe–N (imine nitrogen) (2.125 Å average). The 12 angles subtended at the metal atom by adjacent atoms substantially deviate from 90°, and range from 75.4 to 106.0° (*cf.* Table 3).

From the crystallographic requirement (unit-cell volume and

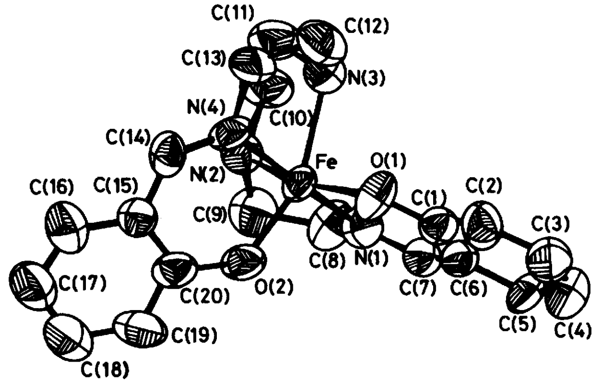

**Figure 3.** ORTEP drawing of [Fe(saltrien)]$BPh_4$ (**2**)

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

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Fe | 6 019(1) | 4 929(2) | 1 137(1) | B | 2 808(6) | 4 796(13) | 1 231(5) |
| O(1) | 5 370(4) | 4 062(10) | 1 022(3) | C(51) | 3 353(5) | 5 602(11) | 1 260(4) |
| C(1) | 5 150(6) | 3 287(14) | 673(5) | C(52) | 3 347(6) | 6 930(13) | 1 240(5) |
| C(2) | 4 787(6) | 2 367(17) | 768(6) | C(53) | 3 810(6) | 7 637(14) | 1 264(5) |
| C(3) | 4 553(9) | 1 561(19) | 389(7) | C(54) | 4 295(6) | 7 063(15) | 1 304(5) |
| C(4) | 4 666(8) | 1 628(19) | −67(7) | C(55) | 4 327(6) | 5 759(16) | 1 326(5) |
| C(5) | 5 012(7) | 2 500(17) | −169(6) | C(56) | 3 857(5) | 5 064(15) | 1 301(5) |
| C(6) | 5 270(6) | 3 348(13) | 203(5) | C(61) | 2 622(5) | 4 865(11) | 1 751(4) |
| C(7) | 5 648(6) | 4 197(13) | 71(5) | C(62) | 2 769(6) | 5 839(12) | 2 089(5) |
| N(1) | 5 945(4) | 4 931(11) | 378(4) | C(63) | 2 540(7) | 5 949(12) | 2 501(6) |
| C(8) | 6 320(7) | 5 722(17) | 171(6) | C(64) | 2 171(6) | 5 061(14) | 2 584(5) |
| C(9) | 6 723(7) | 6 314(16) | 609(6) | C(65) | 2 024(6) | 4 077(13) | 2 260(5) |
| N(2) | 6 814(5) | 5 467(11) | 1 042(4) | C(66) | 2 251(5) | 3 999(12) | 1 855(5) |
| C(10) | 7 122(7) | 4 310(15) | 973(7) | C(71) | 2 318(5) | 5 335(10) | 808(4) |
| C(11) | 7 041(6) | 3 386(15) | 1 357(7) | C(72) | 1 779(5) | 5 288(13) | 840(5) |
| N(3) | 6 456(5) | 3 163(11) | 1 267(4) | C(73) | 1 363(6) | 5 781(13) | 483(5) |
| C(12) | 6 295(7) | 2 558(15) | 1 698(6) | C(74) | 1 483(6) | 6 317(12) | 62(5) |
| C(13) | 6 371(7) | 3 503(16) | 2 116(6) | C(75) | 2 010(6) | 6 377(12) | 20(5) |
| N(4) | 6 146(5) | 4 720(11) | 1 899(4) | C(76) | 2 422(6) | 5 890(12) | 376(5) |
| C(14) | 6 014(6) | 5 337(15) | 2 191(6) | C(81) | 2 951(6) | 3 364(11) | 1 104(5) |
| C(15) | 5 847(6) | 6 781(15) | 2 068(5) | C(82) | 2 929(5) | 2 996(12) | 620(5) |
| C(16) | 5 757(7) | 7 554(18) | 2 446(5) | C(83) | 3 139(6) | 1 858(13) | 516(5) |
| C(17) | 5 619(8) | 8 785(18) | 2 360(7) | C(84) | 3 369(6) | 1 044(12) | 896(5) |
| C(18) | 5 563(7) | 9 303(16) | 1 893(7) | C(85) | 3 385(6) | 1 363(13) | 1 366(5) |
| C(19) | 5 652(6) | 8 572(14) | 1 508(6) | C(86) | 3 169(6) | 2 518(13) | 1 475(5) |
| C(20) | 5 786(6) | 7 303(14) | 1 597(5) | | | | |
| O(2) | 5 852(4) | 6 609(9) | 1 226(3) | | | | |

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

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Fe(A) | 512(2) | −3 126(1) | 2 942(1) | Fe(B) | 4 441(2) | 85(1) | 2 538(1) |
| O(1A) | 1 737(10) | −3 091(4) | 2 123(5) | O(1B) | 3 039(9) | 89(4) | 3 264(5) |
| C(1A) | 2 727(13) | −2 768(5) | 1 928(8) | C(1B) | 2 228(13) | −267(5) | 3 536(7) |
| C(2A) | 3 321(16) | −2 853(6) | 1 217(9) | C(2B) | 1 602(15) | −165(6) | 4 227(9) |
| C(3A) | 4 386(17) | −2 544(6) | 985(9) | C(3B) | 755(18) | −528(7) | 4 529(11) |
| C(4A) | 4 880(16) | −2 187(7) | 1 462(9) | C(4B) | 496(16) | −964(6) | 4 148(10) |
| C(5A) | 4 340(15) | −2 095(6) | 2 177(9) | C(5B) | 1 108(16) | −1 060(6) | 3 476(10) |
| C(6A) | 3 216(14) | −2 401(5) | 2 404(8) | C(6B) | 2 036(14) | −707(5) | 3 165(8) |
| C(7A) | 2 728(14) | −2 311(6) | 3 151(8) | C(7B) | 2 684(16) | −838(6) | 2 475(8) |
| N(1A) | 1 706(12) | −2 561(4) | 3 430(7) | N(1B) | 3 602(13) | −583(4) | 2 162(7) |
| C(8A) | 1 371(18) | −2 445(6) | 4 230(9) | C(8B) | 4 128(23) | −768(7) | 1 435(10) |
| C(9A) | −212(19) | −2 413(7) | 4 217(10) | C(9B) | 5 298(22) | −462(6) | 1 169(10) |
| N(2A) | −825(13) | −2 856(5) | 3 853(8) | N(2B) | 6 046(14) | −221(5) | 1 817(7) |
| C(10A) | −2 254(18) | −2 748(8) | 3 510(12) | C(10B) | 7 015(20) | −524(6) | 2 307(11) |
| C(11A) | −2 145(18) | −2 514(7) | 2 756(12) | C(11B) | 7 362(18) | −296(8) | 3 024(12) |
| N(3A) | −1 172(14) | −2 765(5) | 2 262(8) | N(3B) | 6 003(13) | −176(5) | 3 399(7) |
| C(12A1) | −2 103(34) | −3 145(11) | 1 839(21) | C(12B) | 6 127(20) | 252(7) | 3 981(10) |
| C(13A1) | −1 330(33) | −3 631(10) | 1 730(18) | C(13B) | 6 408(18) | 703(7) | 3 594(9) |
| N(4A) | −612(13) | −3 717(5) | 2 482(8) | N(4B) | 5 563(12) | 719(4) | 2 845(6) |
| C(14A) | −560(15) | −4 182(6) | 2 694(9) | C(14B) | 5 740(14) | 1 079(6) | 2 406(8) |
| C(15A) | 272(14) | −4 354(5) | 3 339(8) | C(15B) | 5 043(13) | 1 161(5) | 1 686(7) |
| C(16A) | 119(16) | −4 828(6) | 3 536(10) | C(16B) | 5 421(15) | 1 561(6) | 1 264(9) |
| C(17A) | 889(18) | −5 043(6) | 4 163(10) | C(17B) | 4 819(17) | 1 655(6) | 557(10) |
| C(18A) | 1 809(17) | −4 706(6) | 4 590(9) | C(18B) | 3 720(17) | 1 378(6) | 268(9) |
| C(19A) | 1 946(16) | −4 252(6) | 4 397(8) | C(19B) | 3 266(17) | 955(6) | 674(8) |
| C(20A) | 1 191(14) | −4 031(5) | 3 779(8) | C(20B) | 3 969(14) | 836(5) | 1 372(8) |
| O(2A) | 1 329(10) | −3 578(3) | 3 615(6) | O(2B) | 3 573(10) | 451(3) | 1 739(5) |
| P(A) | −147(5) | −1 612(2) | 1 130(3) | P(B) | 4 075(6) | 3 603(2) | 486(3) |
| F(1A) | 248(12) | −1 785(4) | 1 967(6) | F(1B) | 2 782(25) | 3 365(8) | 168(16) |
| F(2A) | 189(17) | −1 091(5) | 1 383(9) | F(2B) | 3 153(21) | 4 075(6) | 352(10) |
| F(3A) | −1 627(15) | −1 489(8) | 1 369(9) | F(3B) | 4 186(18) | 3 575(6) | −392(8) |
| F(4A) | −109(26) | −2 174(6) | 906(10) | F(4B) | 4 556(21) | 3 077(7) | 687(11) |
| F(5A) | −500(12) | −1 455(5) | 290(6) | F(5B) | 4 676(25) | 3 717(8) | 1 293(10) |
| F(6A) | 1 421(14) | −1 636(6) | 947(9) | F(6B) | 3 083(27) | 3 571(9) | 1 126(15) |
| F(7A) | −1 357(32) | −1 965(13) | 1 018(17) | F(7B) | 4 864(31) | 4 090(9) | 466(15) |
| C(12A2) | −1 381(39) | −3 177(21) | 1 567(24) | F(8B) | 5 534(25) | 3 523(10) | 280(18) |
| C(13A2) | −1 940(46) | −3 533(15) | 1 952(23) | | | | |

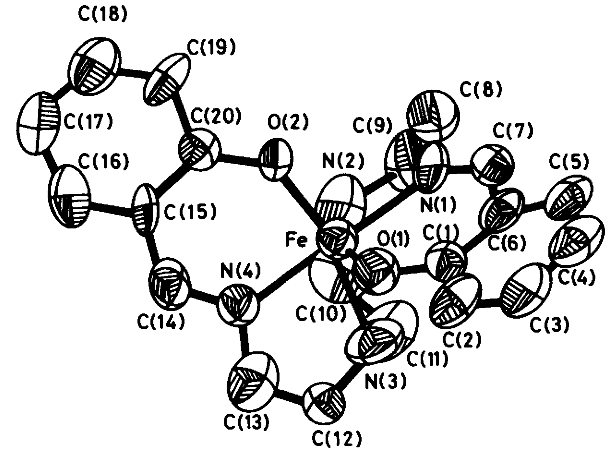

**Figure 4.** ORTEP drawing of [Fe(saltrien)]$PF_6$ (**3A**)

*Z* in the space group $P2_1/c$), the lattice of (**3**) contains two crystallographically independent complex entities. Figure 4 shows the ORTEP drawing of one of the two cations. The atomic co-ordinates and selected bond distances and angles of the two independent cations are listed in Tables 5 and 3, respectively. As shown in Table 3, the structures of the two independent cations [hereafter (**3A**) and (**3B**), respectively] are essentially the same, and are similar to that of compound (**2**). Slight differences exist in the bond lengths and angles as seen in Table 3; O(1)–Fe–N(2), N(1)–Fe–N(4), and N(3)–Fe–O(2) deviate considerably from 180° [157.6(5), 177.0(5), and 157.3(5)° for (**3A**); 157.5(5), 171.4(5), and 161.4(4)° for (**3B**)]. The average ligand field of (**3A**) appears to be slightly larger than that of (**3B**) from the mean metal–ligand bond lengths of (**3A**) (2.066 Å) and (**3B**) (2.070 Å).

## Discussion

Surveying the crystallographic studies so far reported,[8,13,20–22] we found that the metal–imine nitrogen bond distance closely relates to the spin state of the iron(III) ion of Schiff bases,[23] *i.e.* 2.00—2.10 Å for a high-spin state and 1.93—1.96 Å for a low-spin state. Based on this criterion, we assume that compounds (**2**), (**3A**), and (**3B**) are essentially of the high-spin type at room temperature. This is, in fact, consistent with the observed magnetic data.

In the present structural analysis, only a single species of complex cation was detected in the crystal of (**2**) at 293 K and was classified as high-spin on the basis of bond distances. However, this must be an averaged structure of high-spin and low-spin states between which rapid interconversion is occurring, since the magnetic moment is already lower than the spin-only value of $S = \frac{5}{2}$ at room temperature. As the temperature is lowered the high-spin/low-spin ratio gradually drops so that $\mu_{eff.}$ monotonously decreases as shown in Figure 1. In the case of compound (**3**) both complex species in the crystal are distinctly high-spin at > 200 K as is evident from the constant $\mu_{eff.}$ value corresponding to the spin-only value of $S = \frac{5}{2}$. Since $\mu_{eff.}$ gradually decreases from 200 K with lowering of temperature, one of the complex species is likely to reach the crossover point of high-spin and low-spin states at *ca.* 200 K. The other species seems to reach the crossover point at a temperature lower than 100 K. Thus, the complicated $\mu_{eff.}$ *versus* $T$ curve as shown in Figure 1 is brought about.

In the course of this study Hendrickson and co-workers[24] reported a room-temperature *X*-ray structure determination of an iron(III) crossover complex which showed the presence of two crystallographically independent complex cations in the solid state; one is low-spin, and the other part high-spin and part low-spin, and concluded that the 'incomplete' spin-crossover transformation of this complex should be attributed to 'two site' transitions. Our present compound (**3**) is quite similar to that of Hendrickson and co-workers in magnetic behaviour and the presence of two independent complex cations in its crystal. Thus, it provides another example of a crossover complex whose unusual magnetic behaviour can be explained in terms of such 'two site' transitions.

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