Crystal Structure, Electron Spin Resonance, and Magnetism of Tris-(*o*-phenanthroline)iron(III) Perchlorate Hydrate

By **Joe Baker, Lutz M. Engelhardt, Brian N. Figgis,** and **Allan H. White,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia

The crystal structure of the title compound has been determined by the heavy-atom method from diffractometer data and refined by least-squares to R 0·082 for 3449 reflections. Crystals are monoclinic, space group $A2/a$, a = 23·252(6), b = 18·342(4), c = 17·824(5) Å, β = 92·45(2)°, Z = 8. The iron atom is surrounded by three bidentate ligands, the six Fe–N distances being equal (mean 1·973 Å). The geometries of two of the perchlorate ions are as expected but the third ion is badly disordered, and there may be additional partial occupancy of the lattice by further water molecules. The e.s.r. spectrum has been determined at *ca.* 85 K and the principal g values are found to be along the molecular pseudo-trigonal axis (g_1 1·459(5)) and in the plane normal to it [g_2, g_3 2·615(10), 2·727(10)]. The splitting of the $^2T_{2g}$ ground term of the Fe^{3+} ion (Δ_{A_g} *ca.* 800 cm^{-1}) is deduced to be opposite in sign to that predicted by crystal-field theory.

As part of a programme to investigate whether low-symmetry ligand-field components in transition-metal complex ions may be correlated with the details of the donor-ligand atom distribution about the central atom, we have determined the structure of the title compound by X-ray crystallographic methods and have defined the e.s.r. g tensor for the $[Fe(phen)_3]^{3+}$ cation in it. We discuss the relationship between the splitting of the ground $^2T_{2g}$ term of the t_{2g}^5 configuration and the g tensor axes of the Fe^{3+} ion and the details of the nitrogen donor-atom positions.

EXPERIMENTAL

(*a*) *Crystallography*.—The compound was prepared as described previously.[1] Suitable crystals were grown by slow evaporation of a nitric acid solution saturated with sodium perchlorate. The dimensions of the unit cell were obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ diffractometer. A unique data set in the range $2\theta < 100°$ was collected by a conventional 2θ—θ scan, yielding 3913 reflections of which 3449 having $I < 2\sigma(I)$ were used in the structure solution and refinement after correction for absorption, with weights proportional to $\sigma(I)^{-1}$. The crystal size was 0·23 × 0·19 × 0·20 mm.

Crystal data.—$C_{36}H_{26}Cl_3FeN_6O_{13}$, M = 912·9, Monoclinic, a = 23·252(6), b = 18·342(4), c = 18·824(5) Å, β = 92·45(2)°, U = 7594(3) Å^3, D_m (flotation) = 1·617(5), Z = 8, D_c = 1·60 g cm^{-3}, $F(000)$ = 3640. Ni-filtered Cu-$K_{\bar{\alpha}}$ radiation, λ = 1·5418 Å; μ(Cu-K_α) = 58·2 cm^{-1}. Space group $A2/a$ (transformation of No. 15, C_{2h}^6).

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares. In the final stages of refinement, the parameters of the FeN_6 cationic core were refined as a single block. The cationic hydrogen atoms were included as invariants, subject to the constraints C–H 1·08 Å, C–C–H 120°, U 0·01 Å^2. All other atoms were refined with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. In the final least-squares cycle, no parameter shift was $>0·5\sigma$, those of the cationic non-hydrogen atoms being an order of magnitude less, and the refinement converged at R 0·082, and R' 0·112 [$R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. Scattering factors employed were for the neutral atoms,[2] those for iron and chlorine being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[3] The structure refined normally, except for one of the perchlorate anions, which appeared to be disordered. Although several models were considered, no satisfactory approximation could be found for this ion. Its final geometry was considered as two highly distorted units located in a large hole in the structure and assigned populations of 0·5 each on the basis of the magnitudes of their respective peaks in a difference map. It is also possible that this region of disorder containing the third perchlorate group can accommodate additional water molecules as well as the one definitely located by difference. The results of analyses suggest that there are three molecules in all, while D_m suggests that there are two. In the absence of more exact evidence, the discussion of the structural features in this paper is conducted in terms of the crystallographic solution, namely, the monohydrate.

Computation was carried out by a local adaptation of the 'X-Ray '72' system[4] on our CDC 6200. Structure factors are listed in Supplementary Publication No. SUP 21233 (21 pp., 1 microfiche).† Results are shown in Tables 1—3.

The atom numbering system within each ligand is shown in Figure 1, together with the mean ligand geometry. Unprimed nitrogen atoms [N(1)—(3), from ligands (1)—(3)] form an 'upper' triangle of the D_3 (approximate) co-ordination geometry, and primed atoms N(1')—(3') the lower triangle.

(*b*) *Electron Spin Resonances*.—Crystals were aligned by optical goniometry and cemented with epoxy resin to the end of a thin quartz tube. This fibre was mounted to rotate with its axis perpendicular to the magnetic field of the spectrometer, and the rotation could be measured relative to a fixed angular scale. A conventional e.s.r. spectrometer, operating in the X band, was used. Measurements were performed at *ca.* 85 K with crystals mounted to rotate about their a, b, and c^* axes.

There are two magnetically inequivalent molecules in the unit cell, related by a 180° rotation about b. The sym-

† For details, see Notice to Authors No. 7, in *J.C.S. Dalton*, 1973, Index issue.

[1] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.
[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **24A**, 321.
[3] D. T. Cromer, *Acta Cry* 1965, **18**, 17.
[4] '*X*-Ray System,' of crystal programs, Technical Report TR 192, University of Maryland, Computer Science Centre, 1972.

TABLE 1

Final atomic fractional cell parameters (Fe, $\times 10^5$; others, $\times 10^4$) and thermal parameters ($\times 10^3$ Å^2), with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	37631(5)	02711(7)	21981(7)	37(1)	47(1)	45(1)	−1(1)	0(1)	2(1)
(*a*) Phenanthroline (1)									
N	3391(3)	1104(4)	1667(4)	43(4)	53(5)	47(4)	6(4)	9(3)	9(4)
N′	2967(3)	0063(4)	2487(4)	43(4)	60(5)	56(5)	−12(4)	10(4)	−17(4)
C(1)	3632(4)	1614(5)	1244(5)	70(7)	46(5)	40(5)	0(5)	−2(5)	7(4)
C(2)	3292(5)	2143(6)	0896(6)	94(8)	59(7)	49(6)	15(6)	−9(6)	1(5)
C(3)	2705(5)	2173(7)	0984(6)	82(8)	79(8)	66(7)	35(7)	−29(6)	−12(6)
C(4)	2451(5)	1627(6)	1408(6)	63(7)	68(7)	68(7)	11(6)	−8(5)	1(6)
C(5)	1836(5)	1564(7)	1518(7)	53(7)	98(9)	82(8)	22(6)	−19(6)	−20(7)
C(6)	2806(4)	1102(5)	1738(5)	36(5)	64(6)	54(6)	6(5)	−9(4)	−14(5)
C(1′)	2782(5)	−0467(6)	2919(6)	60(7)	67(7)	63(7)	−26(5)	12(5)	−7(5)
C(2′)	2207(5)	−0556(7)	3068(7)	65(7)	79(8)	93(9)	−6(6)	24(6)	−19(7)
C(3′)	1817(5)	−0078(8)	2765(8)	63(7)	105(10)	100(10)	−21(7)	26(7)	−49(8)
C(4′)	1992(4)	0482(7)	2303(7)	47(6)	85(8)	78(8)	1(6)	1(5)	−29(6)
C(5′)	1632(5)	1036(8)	1945(7)	46(6)	128(11)	82(8)	5(7)	0(6)	−30(8)
C(6′)	2574(4)	0542(6)	2185(5)	34(5)	80(7)	56(6)	18(5)	−7(4)	−20(5)
(*b*) Phenanthroline (2)									
N	4555(3)	0548(4)	1959(4)	35(4)	41(4)	42(4)	0(3)	−5(3)	−2(3)
N′	3918(3)	0916(4)	3067(4)	38(4)	53(5)	45(4)	−1(3)	0(3)	−10(4)
C(1)	4874(4)	0295(5)	1414(5)	42(5)	52(6)	58(6)	5(4)	8(4)	−2(5)
C(2)	5434(4)	0548(6)	1334(5)	51(6)	65(6)	53(6)	11(5)	7(5)	−4(5)
C(3)	5674(4)	1057(6)	1805(5)	48(6)	74(7)	44(5)	−8(5)	3(4)	0(5)
C(4)	5343(4)	1311(5)	2401(6)	49(6)	51(6)	62(6)	−10(5)	−4(5)	6(5)
C(5)	5544(5)	1816(6)	2964(6)	55(6)	64(7)	76(7)	−21(5)	−2(5)	1(5)
C(6)	4787(4)	1034(4)	2450(5)	38(5)	35(5)	42(5)	−5(4)	−5(4)	2(4)
C(1′)	3589(4)	1079(6)	3636(5)	47(6)	73(7)	52(6)	−4(5)	5(5)	−9(5)
C(2′)	3770(5)	1561(7)	4208(6)	58(6)	86(8)	53(6)	−13(6)	2(5)	−14(6)
C(3′)	4294(5)	1890(6)	4191(5)	63(7)	76(7)	43(6)	−5(5)	−10(5)	−9(5)
C(4′)	4653(4)	1728(6)	3610(6)	53(6)	62(6)	56(6)	−5(5)	4(5)	−6(5)
C(5′)	5216(5)	2030(6)	3540(6)	53(6)	75(7)	77(7)	−19(6)	−2(5)	−15(6)
C(6′)	4440(4)	1246(5)	3054(5)	41(6)	42(5)	42(5)	−8(4)	−5(4)	1(4)
(*c*) Phenanthroline (3)									
N	3638(3)	−0385(4)	1329(4)	38(4)	49(4)	58(5)	0(3)	1(4)	3(4)
N′	4087(3)	−0612(4)	2678(4)	39(4)	58(5)	54(5)	−3(4)	7(3)	6(4)
C(1)	3405(4)	−0247(6)	0646(6)	40(5)	76(7)	56(6)	−8(5)	6(5)	−4(5)
C(2)	3300(5)	−0786(7)	0109(6)	63(7)	97(9)	62(7)	−4(6)	5(5)	−31(6)
C(3)	3435(5)	−1497(7)	0275(7)	63(7)	79(8)	77(8)	−1(6)	0(6)	22(6)
C(4)	3683(4)	−1661(5)	0971(7)	45(6)	49(6)	91(8)	−11(5)	25(5)	−14(5)
C(5)	3852(6)	−2363(7)	1214(7)	87(9)	77(8)	78(8)	−16(7)	26(7)	−2(6)
C(6)	3781(4)	−1084(5)	1503(6)	37(5)	64(6)	67(6)	0(5)	11(5)	−4(5)
C(1′)	4314(5)	−0701(7)	3367(7)	70(7)	74(7)	74(8)	7(6)	−13(6)	24(6)
C(2′)	4508(6)	−1389(8)	3633(8)	75(8)	102(10)	89(9)	3(7)	−18(7)	39(8)
C(3′)	4435(5)	−1990(6)	3156(8)	66(7)	61(7)	120(10)	0(6)	7(7)	34(7)
C(4′)	4198(5)	−1911(6)	2443(7)	51(6)	54(6)	104(9)	10(5)	29(6)	20(6)
C(5′)	4102(5)	−2485(5)	1895(8)	75(8)	36(6)	139(11)	5(5)	57(8)	−3(6)
C(6′)	4024(4)	−1205(5)	2224(6)	43(5)	47(5)	66(6)	5(4)	10(5)	6(5)
(*d*) Perchlorate (1)									
Cl	2715(1)	2854(2)	3163(2)	52(2)	111(2)	82(2)	−2(2)	11(1)	23(2)
O(1)	2258(4)	2964(5)	2644(5)	66(5)	109(6)	101(6)	3(5)	−10(5)	−5(5)
O(2)	3218(4)	2637(6)	2797(6)	58(5)	141(8)	122(8)	7(5)	28(5)	4(6)
O(3)	2838(6)	3551(9)	3528(7)	156(11)	211(14)	109(9)	−31(10)	2(8)	−76(9)
O(4)	2579(5)	2354(11)	3703(11)	89(8)	308(21)	278(20)	53(11)	60(10)	22(18)
(*e*) Perchlorate (2)									
Cl	0338(1)	1413(1)	0419(1)	60(1)	69(2)	56(1)	5(1)	−2(1)	−7(1)
O(1)	0704(4)	0862(5)	0144(5)	105(7)	83(6)	93(6)	34(5)	29(5)	−10(5)
O(2)	0576(7)	2092(5)	0248(6)	233(14)	74(6)	106(8)	−12(7)	51(8)	18(6)
O(3)	0307(4)	1358(4)	1208(4)	108(6)	65(5)	60(5)	−5(4)	16(4)	−7(4)
O(4)	−0210(5)	1336(12)	0091(8)	77(7)	352(23)	141(10)	26(10)	−30(7)	−120(13)
(*f*) Perchlorate (3) (population 0·5)									
Cl	0727(4)	0118(6)	4332(5)	91(5)	187(9)	118(6)	20(6)	15(4)	−10(6)
O(1)	0988(11)	0795(12)	4043(15)	151(20)	91(14)	177(22)	−64(14)	60(17)	−22(14)
O(2)	0581(14)	0351(27)	3511(28)	124(23)	339(54)	357(52)	33(28)	131(29)	−173(45)
O(3)	0317(16)	0215(37)	4799(23)	135(26)	501(87)	191(35)	80(39)	66(24)	113(45)
O(4)	0477(15)	−0258(13)	3856(22)	206(31)	96(17)	267(37)	−53(18)	−91(28)	−74(20)
(*g*) Perchlorate (4) (population 0·5)									
Cl	1670(5)	3992(6)	0132(6)	174(10)	155(8)	115(7)	−14(7)	14(6)	−10(6)
O(1)	1726(10)	3491(10)	0591(11)	139(17)	71(11)	105(14)	24(11)	−3(12)	29(10)
O(2)	1412(15)	3851(16)	−0546(15)	204(29)	138(21)	126(19)	−18(20)	−29(18)	−26(16)
O(3)	1460(26)	4667(13)	0353(24)	521(80)	71(15)	229(38)	40(26)	213(48)	−47(19)
O(4)	2228(19)	3972(71)	0032(42)	115(27)	855(214)	431(84)	195(66)	−153(45)	−235(111)
(*h*) Water molecule									
O(5)	2170(14)	1075(17)	4279(17)	277(29)	315(30)	287(28)	−93(26)	82(23)	−63(24)

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses

(*a*) Cation

(i) Distances

Ligand fragment:	(1)	(1′)	(2)	(2′)	(3)	(3′)	⟨ ⟩
Fe–N	1·976(8)	1·980(8)	1·974(8)	1·968(7)	1·972(8)	1·967(8)	1·973
N–C(1)	1·34(1)	1·32(1)	1·33(1)	1·33(1)	1·34(1)	1·32(1)	1·33
N–C(6)	1·37(1)	1·36(1)	1·35(1)	1·36(1)	1·36(1)	1·36(1)	1·36
C(1)–C(2)	1·38(1)	1·38(2)	1·39(1)	1·40(2)	1·39(2)	1·41(2)	1·39
C(2)–C(3)	1·38(2)	1·36(2)	1·36(1)	1·36(2)	1·37(2)	1·40(2)	1·37
C(3)–C(4)	1·40(2)	1·39(2)	1·42(1)	1·39(1)	1·38(2)	1·37(2)	1·39
C(4)–C(5)	1·46(2)	1·45(2)	1·43(1)	1·43(1)	1·41(2)	1·45(2)	1·44
C(4)–C(6)	1·38(1)	1·38(1)	1·40(1)	1·40(1)	1·43(1)	1·41(2)	1·40
C(5)–C(5′)	1·33(2)		1·36(2)		1·34(2)		1·34
C(6)–C(6′)	1·42(1)		1·43(1)		1·40(1)		1·42
C(1)–N–Fe	128·6(6)	128·6(7)	128·5(6)	130·0(6)	129·9(7)	129·3(7)	129·2
C(6)–N–Fe	111·7(6)	113·0(6)	112·4(6)	112·9(6)	111·7(6)	111·7(6)	112·2
C(6)–N–C(1)	119·6(8)	118·4(8)	119·1(7)	117·0(8)	118·2(8)	118·8(9)	118·5
N–C(1)–C(2)	119·9(10)	122·6(10)	120·7(8)	122·2(9)	123·1(0)	122·0(11)	121·8
C(1)–C(2)–C(3)	121·8(10)	118·8(12)	121·7(9)	120·3(10)	119·7(10)	118·0(12)	120·0
C(2)–C(3)–C(4)	118·3(11)	120·5(11)	117·8(9)	119·3(10)	119·1(11)	120·9(11)	119·3
C(3)–C(4)–C(5)	124·7(11)	127·1(10)	124·5(9)	124·3(10)	125·2(10)	126·3(10)	125·4
C(3)–C(4)–C(6)	118·0(10)	117·6(10)	117·5(9)	117·2(9)	118·9(10)	117·0(10)	117·7
C(5)–C(4)–C(6)	117·3(10)	115·3(10)	118·0(9)	118·5(9)	115·9(10)	116·5(10)	116·9
N–C(6)–C(4)	122·4(9)	122·1(10)	123·1(8)	123·9(8)	121·2(9)	123·2(9)	122·6

(ii) Angles

Ligand	(1)	(2)	(3)	⟨ ⟩
C(4′)–C(5′)–C(5)	123·4(10)	119·9(10)	122·5(10)	121·9
C(4)–C(5)–C(5′)	120·7(11)	122·5(10)	122·3(11)	
C(4′)–C(6′)–C(6)	122·7(9)	120·8(8)	120·1(9)	121·1
C(4)–C(6)–C(6′)	120·6(9)	120·2(8)	122·4(9)	
N′–C(6′)–C(6)	115·1(8)	115·1(8)	116·6(8)	116·1
N–C(6)–C(6′)	117·0(8)	116·6(7)	116·5(9)	
N–Fe–N′	83·0(3)	82·8(3)	83·1(3)	83·0

N(1)–Fe–N(2′)	88·5(3)	N(1)–Fe–N(2)	95·2(3)
N(2)–Fe–N(3′)	87·8(3)	N(2)–Fe–N(3)	95·5(3)
N(3)–Fe–N(1′)	88·7(3)	N(3)–Fe–N(1)	92·8(3)
N(1)–Fe–N(3′)	175·1(3)	N(1′)–Fe–N(2′)	93·0(3)
N(2)–Fe–N(1′)	175·5(3)	N(2′)–Fe–N(3′)	95·6(3)
N(3)–Fe–N(2′)	177·9(3)	N(3′)–Fe–N(1′)	94·2(3)

(*b*) Perchlorate ions

(i) Distances

Ion	(1)	(2)	(3)	(4)
Cl–O(1)	1·39(1)	1·42(1)	1·48(3)	1·23(2)
Cl–O(2)	1·42(1)	1·40(1)	1·55(5)	1·38(3)
Cl–O(3)	1·46(2)	1·42(1)	1·30(4)	1·42(4)
Cl–O(4)	1·38(2)	1·39(1)	1·22(3)	1·25(5)

(ii) Angles

Ion	(1)	(2)	(3)	(4)
O(1)–Cl–O(2)	110·8(6)	107·9(7)	61·1(20)	116·8(17)
O(1)–Cl–O(3)	107·4(7)	110·5(5)	115·4(32)	118·4(20)
O(1)–Cl–O(4)	111·8(7)	109·6(9)	114·8(20)	93·0(51)
O(2)–Cl–O(3)	107·4(7)	108·4(6)	115·4(24)	103·0(24)
O(2)–Cl–O(4)	110·6(8)	111·4(10)	54·5(23)	108·2(38)
O(3)–Cl–O(4)	108·6(10)	109·0(7)	100·5(29)	117·8(63)

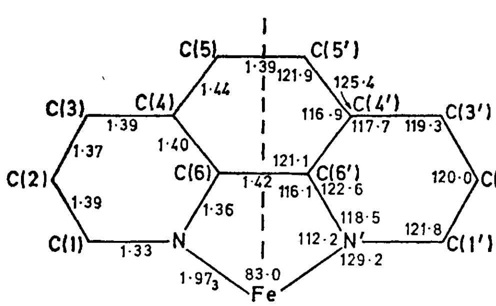

FIGURE 1 Mean ligand geometry (distances Å, angles °) and numbering system within each ligand; ligands are numbered (1)—(3), so that the N atoms of each are N(1)—(3) and N(1′)—(3′)

metry relations of the g^2 tensors for the two species have been discussed by Hill.[5] They differ only in the sign of the *xy* and *yz* elements. The e.s.r. spectra of the two species should coincide in the *ac* plane and this was observed experimentally.

The nearest-neighbour Fe ··· Fe distance is 11·7 Å, implying reasonable magnetic dilution; nevertheless, the resonance absorptions were quite broad (200—500 gauss). Consequently the spectra of the two species were only poorly resolved in the *bc** and not at all in the *ab* plane. No hyperfine structure was observed. Principal *g* values and their directions were deduced from the maximum and minimum *g* values in the three orthogonal planes using the relations of

[5] N. J. Hill, *J.C.S. Faraday II*, 1972, **68**, 427.

TABLE 3

(*a*) Least-squares planes in the form $pX + qY + rZ = S$,* with deviations (Å) of relevant atoms from the plane in square brackets

	10^4p	10^4q	10^4r	S	σ/Å
Plane (i): Phenanthroline (1) and Fe					
	872	5805	8096	4·240	0·02

[Fe −0·03, N 0·02, N′ 0, C(1) 0, C(2) 0·01, C(3) 0·04, C(4) 0·01, C(5) −0·02, C(6) 0, C(1′) 0·02, C(2′) 0·02, C(3′) 0·01, C(4′) −0·02, C(5′) −0·02, C(6′) 0]

	10^4p	10^4q	10^4r	S	σ/Å
Plane (ii): Phenanthroline (2) and Fe					
	−3521	7550	−5532	−4·885	0·04

[Fe 0·07, N 0·04, N′ 0·01, C(1) −0·05, C(2) −0·08, C(3) −0·03, C(4) 0·03, C(5) 0·02, C(6) 0·05, C(1′) −0·04, C(2′) −0·07, C(3′) −0·03, C(4) 0·01, C(5) 0·03, C(6) 0·05]

	10^4p	10^4q	10^4r	S	σ/Å
Plane (iii): Phenanthroline (3) and Fe					
	9239	1681	−3437	6·753	0·03

[Fe −0·08, N 0·04, N′ 0·01, C(1) 0·04, C(2) 0·02, C(3) −0·02, C(4) −0·01, C(5) −0·03, C(6) 0·01, C(1) 0, C(2′) 0·02, C(3′) 0·01, C(4′) 0·01, C(5′) 0, C(6′) 0]

(*b*) Angles (°) between planes:

(i)–(ii)	87·7	(ii)–(iii)	89·5
(i)–(iii)	84·3		

* $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$

Schonland.[6] The g values, together with their direction cosines (l, m, n) in the a, b, c^* co-ordinate system are:

	g	l	m	n
g_1	1·459(5)	−0·2331	−0·2550	0·9384
g_2	2·615(10)	−0·1190	0·9652	0·2328
g_3	2·727(10)	0·9652	0·0574	0·2553

DISCUSSION

Consideration of the unit-cell contents (Figure 2) shows that the disposition of the perchlorate anions and tris(*o*-phenanthroline)iron(III) cations within the cell is generally in the form of alternating sheets parallel to the *ab* plane, the third perchlorate ion lying rather loosely between the bulky cations, very poorly resolved and apparently disordered between two sites. The considerable amount of unoccupied space in its vicinity suggests that there may be unobserved disordered water molecules present, although the evidence for them from difference maps, density, and analysis is very equivocal. The geometries of the two well-ordered perchlorate groups are normal within the rather large limits of error and high thermal motion.

The cation is comprised of a central iron atom co-ordinated by three symmetrically bidentate *o*-phenanthroline ligands, all Fe–N distances lying within a σ of their mean, 1·973 Å. This value is identical with that found in the iron(II) analogue in L-tris(*o*-phenanthroline)-iron(II) bis(antimony(III) D-tartrate) octahydrate,[7] as also is the mean angular geometry. The FeN_6 unit approaches a regular octahedron, and in particular possesses a *pseudo* C_3 axis, whose direction cosines in the abc^* co-ordinate system are l −0·2658, m −0·2622, n 0·9275. The triangle N(1),N(2),N(3) is out of phase about the *pseudo*-trigonal axis with respect to the N(1′),N(2′),N(3′) triangle by 55·6°, so that the 'twist' distortion from octahedral geometry is 4·4°. This value correlates well with the mean ligand bite of 83·0° when compared with the curve derived from the ligand-repulsion model[8] of stereochemical interactions. There is also a compression along the three-fold axis, since the N–Fe–(C_3-axis) angle is increased to a mean of 57·8° from the octahedral value of 54·7°.

Equivalent distances and angles between ligands are similar and little significance can be attached to the majority of the variations, in the absence of an accurate knowledge of the structure of the unco-ordinated ligand, and a suitable correction for the effects of thermal motion. The latter are probably large in view of the general observation that the peripheral C–C distances in the ligands are appreciably shorter than those in the centre where the thermal motion is less. The planarity of all the systems (phenanthroline–iron) is generally good; for the phenanthroline ligands (2) and (3) the iron atom exhibits a slight deviation and in the latter case the ligand itself shows a slight 'butterfly' distortion.

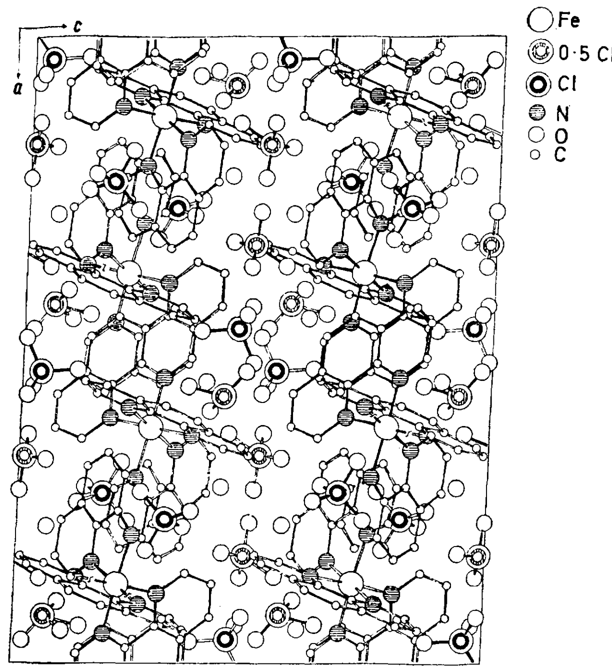

FIGURE 2 Unit cell contents projected down *b*

The e.s.r. results show that the direction of g_1 is almost parallel to the mean *pseudo* C_3 axis through the iron atom, the difference being *ca.* 2°. The directions of g_2 and g_3 relative to the two triangles are shown in Figure 3(a). The direction of g_2 almost bisects the N ··· N vector of relative to the two triangles are shown in Figure 3. The direction of g_2 almost bisects the N ··· N vector of phenanthroline (3), the direction cosines from the iron atom to the centre of which are l −0·1668, m 0·9575, and n 0·2350. That g_2 and g_3 are not exactly equal implies a small distortion from C_3 symmetry, such as might be

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accounted for qualitatively by the slight inequivalences observed in the crystal structure, for example in the N $\cdots$ N distances shown in Figure 3(a).

The mean magnetic susceptibility of the compound has been studied from 4 to 300 K and the results were interpreted along with some of the present e.s.r. data to yield a splitting of the orbital degeneracy of the $^2T_{2g}$ ground term of the Fe^{3+} ion, with the $^2A_{1g}$ orbital singlet lying

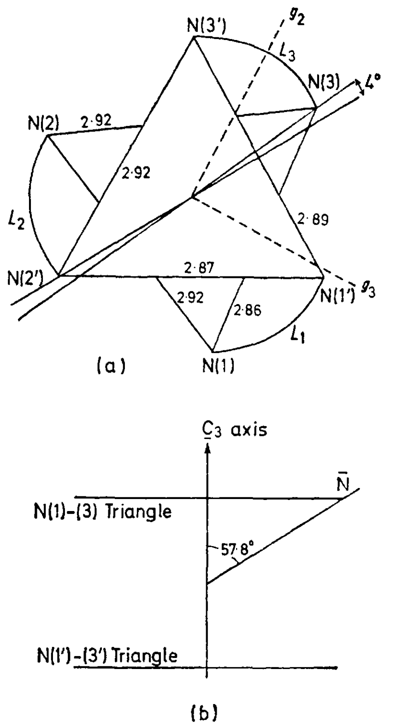

FIGURE 3 Definition of the octahedral stereochemistry and orientation of the principal axes of the g tensor within the complexion. (a) Projection down and (b) normal to the three-fold axis

lowest and the ^2E_g orbital doublet some 800 cm^{-1} higher ($\Delta^{E_g}_{A_{1g}}$ 800 cm^{-1}).[9] The fact that the g tensor is not quite axial indicates that there must be some small splitting of the ^2E_g term.

If this result is examined from the point of view of crystal-field theory, a discrepancy may be apparent. An examination of the effects of a distortion of an octahedron on the $^2T_{2g}$ ground term of the d^1 configuration have shown that in that model the effect of the ' twist ' of the octahedron about the C_3 axis on the energy levels of the term is negligible for an angle as small as 4°. On the other hand, the compression of the octahedron along the C_3 axis so as to raise the C_3–Fe–N angle, θ, by 3·1° from the regular octahedral value (θ_o) should have a rather large effect.[10,11]

The t_{2g} orbital set is split by an amount which is determined by the relationship between integrals involving the d electron radial wave functions, $\langle\overline{r^4}\rangle$ (Dq) and $\langle\overline{r^2}\rangle$ (Cp) [11]. The $^5T_{2g}$ ground term of the high-spin d^6 configuration has been shown to be split by

$$\Delta^{E_g}_{A_{1g}} = -\frac{10}{7}Dqf_1(\theta) - \frac{9}{2}Cpf(\theta) - 20^{\frac{1}{2}}Dqf_2(\theta)$$

where $f_1(\theta)$, $f(\theta)$, and $f_2(\theta)$ are functions of (θ) and are defined elsewhere.[11] If Cp is small ($\lesssim Dq$) and $\theta > \theta_o$ the sign of $\Delta^{E_g}_{A_{1g}}$ should be negative, so that the ^5E_g term would be lowest. In the more likely event that Cp is large ($\gtrsim 2Dq$) $\Delta^{E_g}_{A_{1g}}$ is positive and the $^5A_{1g}$ term should lie lowest in crystal-field theory. Provided that Cp is not $\sim Dq$, $\Delta^{E_g}_{A_{1g}}$ changes sign at θ_o. The studies on the magnetic properties of the $[Fe(H_2O)_6]^{2+}$ ion in iron(II) fluorosilicate confirmed that Cp was large and that the positive sign of $\Delta^{E_g}_{A_{1g}}$ deduced was opposite to that predicted by crystal-field theory from the experimental value of θ ($<\theta_o$).

For the $^2T_{2g}$ term of the $t_{2g}{}^5$ configuration, where there is a ' hole ' in the filled $t_{2g}{}^6$ shell rather than one electron above the half-filled shell as in the d^6 configuration, the splitting should be of the opposite sign. Therefore, for the same type of relationship between Cp and Dq, it would have been expected that $\Delta^{E_g}_{A_{1g}}$ for the $[Fe(phen)_3]^{3+}$ ion in $[Fe(phen)_3][ClO_4]_3{\cdot}H_2O$ would have been negative. In this compound, as in iron(II) fluorosilicate, the sign deduced for the splitting of the T_{2g} term is opposite to that expected from crystal-field theory. It may be surmised that the orbital singlet A_{1g} term lies lowest in each case because of the operation of the Jahn–Teller theorem, but that the required raising of orbital degeneracy is arranged by electronic distributions within the central-metal–ligand-atom system which are not determined principally by the positions of the ligand donor-atoms. It has been observed that the studies of most systems possessing a T-type ground term indicate that the term is split with Δ^E_A positive. It seems likely that this happens because the operation of the Jahn–Teller theorem is not directed by the fine details of the ligand donor-atom positions. However, the fact that in $[Fe(phen)_3][ClO_4]_3{\cdot}H_2O$, the axes of the g tensor correlate well with the obvious geometrical features of the $[Fe(phen)_3]^{3+}$ ion indicates that the axes of the low-symmetry crystal-field component which arises from the Jahn–Teller effect are fairly closely tied to the gross features of the ligand distribution about the central iron atom.

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