C(24)	0.1840 (12)	0.5328 (12)	−0.1181 (7)	4.8 (6)
C(25)	0.2379 (13)	0.5915 (11)	−0.0727 (8)	5.1 (7)
C(26)	0.2868 (12)	0.5092 (11)	0.0140 (7)	4.6 (6)
C(31)	0.2548 (9)	0.1279 (9)	0.2129 (6)	2.8 (4)
C(32)	0.1104 (11)	0.1763 (10)	0.2615 (7)	3.9 (5)
C(33)	0.0281 (12)	0.0888 (13)	0.2896 (8)	5.6 (7)
C(34)	0.0903 (12)	−0.0521 (11)	0.2713 (7)	4.5 (6)
C(35)	0.2312 (11)	−0.1038 (11)	0.2266 (7)	4.2 (6)
C(36)	0.3143 (10)	−0.0128 (10)	0.1955 (7)	3.7 (5)
C(40)	0.3034 (13)	0.1292 (13)	0.4444 (8)	6.0 (7)
C(41)	0.2174 (15)	0.1328 (17)	0.5354 (11)	11.1 (10)

Table 2. *Selected geometric parameters* (Å, °)

Re—O(1)	1.691 (6)	Re—O(2)	1.885 (6)
Re—Cl(1)	2.427 (2)	Re—Cl(2)	2.385 (2)
Re—P	2.463 (2)	Re—N(7)	2.185 (7)
P—C(11)	1.817 (9)	P—C(21)	1.826 (9)
P—C(31)	1.821 (8)	O(2)—C(40)	1.383 (12)
C(40)—C(41)	1.40 (2)		
Cl(1)—Re—P	94.30 (8)	Cl(1)—Re—O(1)	89.5 (2)
Cl(1)—Re—O(2)	84.7 (2)	Cl(1)—Re—N(7)	85.8 (2)
Cl(2)—Re—P	91.49 (8)	Cl(2)—Re—O(1)	95.5 (2)
Cl(2)—Re—O(2)	90.3 (2)	Cl(2)—Re—N(7)	88.2 (2)
P—Re—O(1)	90.7 (2)	P—Re—O(2)	89.4 (2)
O(1)—Re—N(7)	91.7 (3)	O(2)—Re—N(7)	88.3 (3)
Cl(1)—Re—Cl(2)	172.30 (9)	P—Re—N(7)	177.6 (2)
O(1)—Re—O(2)	174.2 (3)	Re—O(2)—C(40)	148.8 (6)
O(2)—C(40)—C(41)	115.3 (10)	C(11)—P—C(21)	105.1 (4)
Re—P—C(11)	113.4 (3)	C(11)—P—C(31)	104.4 (4)
Re—P—C(21)	114.4 (3)	C(21)—P—C(31)	104.3 (4)
Re—P—C(31)	114.2 (3)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	H···*A*	*D*···*A*	*D*—H···*A*
N(1)	H(1)	O(1)	2.305	2.922 (9)	120.5
N(1)	H(1)	Cl(1)	2.737	3.212 (8)	111.3

The intensities were corrected for Lp effects. No symmetry higher than triclinic was indicated by axial photographs and Niggli matrix. The structure was solved in space group $P\bar{1}$ by direct methods (Sheldrick, 1985). The *NRCVAX* package (Gabe, Le Page, Charland, Lee & White, 1989) was used for all other calculations. The non-H atoms were refined anisotropically by full-matrix least-squares methods. H-atom positions were fixed at idealized geometries (C—H = 0.95 Å). Isotropic temperature factors were refined for ring H atoms, but were fixed at $U_H = (U_C + 0.01)$ Å^2 for those on the ethyl group.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, and bond distances and angles of the phosphine and 7-azaindole ligands, as well as a stereoview of the unit cell, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71769 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1050]

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Tris(1,10-phenanthroline)iron(II) Diperchlorate Hemihydrate

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Abstract

Crystals of $[Fe(phen)_3](ClO_4)_2.0.5H_2O$ (phen = 1,10-phenanthroline) are nearly isostructural with those of the Co^{II} and Cu^{II} analogues, with similar disorder of the perchlorate groups. The Fe^{II} complex ion is less distorted than the Co^{II} and Cu^{II} complex ions. The average Fe—N distance is 1.978 (3) Å and the average N—Fe—N bidentate angle is 82.6 (4)°. The phenanthroline ligands are planar.

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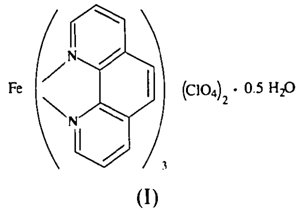
Comment

The crystal structures of the Co^{II} and Cu^{II} analogues of the title compound have been reported previously (Boys, Escobar & Wittke, 1984; Anderson, 1973). We now report the structure of the title compound (I).



(I)

Crystals were obtained from an aqueous dioxane solution containing Fe^{2+}, 1,10-phenanthroline and $NaClO_4$. The crystal structure was found to be isomorphous with those of the Co^{II} and Cu^{II} analogues. The cell dimensions and the atomic positions of the title compound are essentially the same as those of the analoguous Co^{II} and Cu^{II} complexes.

The asymmetric unit contains one $Fe(phen)_3^{2+}$ cation, two perchlorate anions and a site partially occupied by a water molecule. As in the Co^{II} and Cu^{II} analogues, the perchlorate ions appear to be disordered; therefore various disordered models were tried. That used finally was a slight modification of the model reported for the Cu^{II} analogue (Anderson, 1973). One ClO_4^- anion is located on a crystallographic twofold axis and is disordered over two sites, each with a site occupancy factor of 0.5. At one of these sites [Cl(1)] the twofold crystallographic axis coincides with one of the twofold axes of the perchlorate tetrahedron. At the other site [Cl(1′)] an O atom [O(1′)] is located on the crystallographic twofold axis. The second ClO_4^- anion is in a general position. One O atom [O(5)] is ordered but the other three are disordered over two sites, each with site occupancy factors of 0.5. As in the case of the Co^{II} analogue, there is a residual peak of about 1.5 e $Å^{-3}$ which is attributed to a water molecule. This water molecule [O(10)], which is hydrogen bonded to O(8) with an O···O distance of 2.77 (1) Å, is given a site occupancy factor of 0.5, which is same as that of O(8).

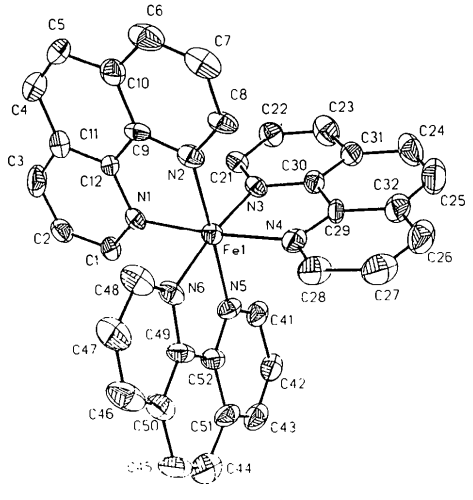


Fig. 1. Atomic numbering of the complex cations.

The $Fe(phen)_3^{2+}$ ion is similar to its Co^{II} analogue. As expected, it does not show any Jahn–Teller distortion, which was found to be quite prominent in the Cu^{II} analogue. A comparison of the geometries of the three complex ions is given in Table 3. With shorter *M*—N bond lengths and larger bidentate N—*M*—N angles, the Fe^{II} complex ion is less distorted than the Co^{II} complex. Bond lengths and angles of the $Fe(phen)_3^{2+}$ ion are similar to those of other $Fe(phen)_3^{2+}$ salts (Johansson, Molund & Oskarsson, 1978; Fujiwara, Iwamoto & Yamamoto, 1984) as well as those of $Fe^{III}(phen)_3(ClO_4)_3$ (Baker, Engelhardt, Figgis & White, 1975).

Each phenanthroline ligand is coplanar to within 0.04 Å. The average dihedral angle between pairs of phenanthroline planes is 94 (1)°. Bond lengths and angles in the phenanthroline ligands (Fig. 2) are identical to those found in other structures (Anderson, 1973; Baker, Engelhardt, Figgis & White, 1975; Nishigaki, Yoshioka & Nakatsu, 1978).

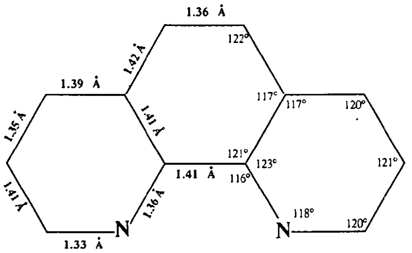


Fig. 2. Average bond lengths and angles in the phen ligands.

Experimental

Crystal data

$[Fe(C_{12}H_8N_2)_3](ClO_4)_2$.-
$0.5H_2O$
M_r = 804.4
Monoclinic
$C2/c$
a = 36.378 (7) Å
b = 15.890 (3) Å
c = 12.115 (2) Å
β = 102.07 (3)°
V = 6848 (3) $Å^3$
Z = 8

D_x = 1.558 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 3.1–11.0°
μ = 0.66 mm^{-1}
T = 298 K
Prisms
0.4 × 0.4 × 0.3 mm
Deep red

Data collection

Siemens *R*3*m*/*V* diffractometer
ω scans
Absorption correction: empirical
T_{min} = 0.747, T_{max} = 0.798
6170 measured reflections
6071 independent reflections
2706 observed reflections [$F > 4.0\sigma(F)$]

R_{int} = 0.028
θ_{max} = 22.5°
$h = 0 \rightarrow 42$
$k = 0 \rightarrow 18$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 97 reflections
intensity variation: ±1.5%

Refinement

Refinement on *F*
R = 0.080
wR = 0.081
S = 1.71
2706 reflections
521 parameters
H-atom parameters not refined; disordered water H atoms not located

$w = 1/[\sigma^2(F) + 0.0007F^2]$
$(\Delta/\sigma)_{max}$ = 0.234
$\Delta\rho_{max}$ = −0.53 e Å^{-3}
$\Delta\rho_{min}$ = 0.67 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	*x*	*y*	*z*	U_{eq}
Fe(1)	1.0	−0.1217 (1)	0.2812 (1)	0.1244 (1)	0.046 (1)
N(1)	1.0	−0.0986 (2)	0.2108 (4)	0.0232 (6)	0.048 (3)
N(2)	1.0	−0.1662 (2)	0.2745 (5)	−0.0018 (7)	0.057 (3)
N(3)	1.0	−0.1069 (2)	0.3884 (5)	0.0626 (7)	0.049 (3)
N(4)	1.0	−0.1478 (2)	0.3573 (6)	0.2124 (7)	0.058 (3)
N(5)	1.0	−0.0776 (2)	0.2830 (6)	0.2523 (6)	0.054 (3)
N(6)	1.0	−0.1338 (2)	0.1797 (5)	0.2025 (7)	0.052 (3)
C(1)	1.0	−0.0648 (3)	0.1780 (6)	0.0386 (8)	0.052 (4)
C(2)	1.0	−0.0532 (3)	0.1311 (7)	−0.0463 (10)	0.070 (5)
C(3)	1.0	−0.0768 (4)	0.1195 (7)	−0.1475 (11)	0.085 (6)
C(4)	1.0	−0.1395 (5)	0.1437 (8)	−0.2689 (11)	0.107 (7)
C(5)	1.0	−0.1746 (5)	0.1753 (9)	−0.2813 (12)	0.105 (7)
C(6)	1.0	−0.2213 (4)	0.2573 (8)	−0.1969 (14)	0.092 (6)
C(7)	1.0	−0.2281 (3)	0.2996 (8)	−0.1066 (12)	0.083 (6)
C(8)	1.0	−0.2003 (3)	0.3078 (6)	−0.0115 (9)	0.067 (4)
C(9)	1.0	−0.1591 (3)	0.2308 (6)	−0.0917 (8)	0.051 (4)
C(10)	1.0	−0.1858 (3)	0.2206 (8)	−0.1937 (10)	0.074 (5)
C(11)	1.0	−0.1123 (4)	0.1539 (7)	−0.1675 (10)	0.075 (5)
C(12)	1.0	−0.1230 (3)	0.1983 (5)	−0.0801 (8)	0.050 (4)
C(21)	1.0	−0.0862 (3)	0.4021 (7)	−0.0141 (8)	0.057 (4)
C(22)	1.0	−0.0771 (3)	0.4814 (8)	−0.0467 (9)	0.066 (5)
C(23)	1.0	−0.0906 (4)	0.5489 (8)	−0.0016 (12)	0.090 (6)
C(24)	1.0	−0.1287 (4)	0.6074 (8)	0.1322 (14)	0.104 (7)
C(25)	1.0	−0.1505 (4)	0.5867 (12)	0.2087 (14)	0.110 (8)
C(26)	1.0	−0.1808 (4)	0.4867 (12)	0.3176 (14)	0.104 (7)
C(27)	1.0	−0.1852 (3)	0.4065 (14)	0.3406 (10)	0.106 (7)
C(28)	1.0	−0.1688 (3)	0.3399 (9)	0.2869 (9)	0.086 (5)
C(29)	1.0	−0.1425 (3)	0.4388 (8)	0.1887 (9)	0.060 (4)
C(30)	1.0	−0.1206 (3)	0.4569 (7)	0.1075 (8)	0.052 (4)
C(31)	1.0	−0.1128 (3)	0.5398 (8)	0.0795 (10)	0.074 (5)
C(32)	1.0	−0.1585 (4)	0.5041 (10)	0.2412 (13)	0.083 (6)
C(41)	1.0	−0.0499 (3)	0.3392 (8)	0.2766 (9)	0.067 (5)
C(42)	1.0	−0.0231 (3)	0.3368 (8)	0.3807 (10)	0.070 (5)
C(43)	1.0	−0.0255 (4)	0.2752 (11)	0.4562 (10)	0.082 (6)
C(44)	1.0	−0.0583 (4)	0.1497 (11)	0.5076 (12)	0.098 (7)
C(45)	1.0	−0.0871 (5)	0.0942 (10)	0.4821 (12)	0.101 (7)
C(46)	1.0	−0.1459 (4)	0.0491 (9)	0.3449 (12)	0.096 (7)
C(47)	1.0	−0.1699 (4)	0.0596 (8)	0.2438 (14)	0.099 (7)
C(48)	1.0	−0.1632 (3)	0.1268 (8)	0.1717 (10)	0.080 (5)
C(49)	1.0	−0.1103 (3)	0.1649 (8)	0.3025 (9)	0.064 (5)
C(50)	1.0	−0.1144 (4)	0.1015 (8)	0.3789 (11)	0.076 (5)
C(51)	1.0	−0.0533 (3)	0.2174 (10)	0.4344 (9)	0.072 (5)
C(52)	1.0	−0.0797 (3)	0.2230 (8)	0.3303 (9)	0.061 (4)
Cl(1)	0.5	0	0.5907 (3)	1/4	0.086 (2)
O(1)	1.0	0.0297 (3)	0.6400 (8)	0.2464 (15)	0.256 (10)
O(2)	1.0	0.0061 (5)	0.5439 (13)	0.3399 (13)	0.347 (13)
Cl(1′)	0.5	0	0.0394 (3)	1/4	0.091 (2)
O(1′)	0.5	0	0.1266 (6)	1/4	0.181 (9)
O(2′)	0.5	−0.0042 (6)	0.0101 (12)	0.1425 (11)	0.146 (11)
O(3′)	0.5	−0.0301 (8)	0.0177 (12)	0.2967 (32)	0.273 (20)
O(4′)	0.5	0.0333 (6)	0.0101 (13)	0.3125 (16)	0.292 (23)
Cl(2)	1.0	0.2613 (1)	0.5210 (3)	0.4472 (3)	0.123 (2)
O(5)	1.0	0.2314 (3)	0.4966 (8)	0.4901 (10)	0.258 (11)
O(6)	0.5	0.2510 (3)	0.5626 (8)	0.3449 (9)	0.096 (7)
O(7)	0.5	0.2806 (6)	0.4464 (10)	0.4282 (16)	0.244 (18)
O(8)	0.5	0.2856 (5)	0.5696 (10)	0.5219 (14)	0.285 (11)
O(6′)	0.5	0.2599 (5)	0.4825 (15)	0.3435 (12)	0.346 (15)
O(7′)	0.5	0.2576 (5)	0.6095 (6)	0.4267 (16)	0.187 (12)
O(8′)	0.5	0.2956 (3)	0.5106 (11)	0.5154 (12)	0.149 (11)
O(10)	0.5	0.2096 (10)	0.2321 (20)	0.0569 (17)	0.253 (19)

Table 2. *Selected geometric parameters* (Å, °)

Fe(1)—N(1)	1.973 (8)	Fe(1)—N(2)	1.982 (7)
Fe(1)—N(3)	1.980 (8)	Fe(1)—N(4)	1.981 (9)
Fe(1)—N(5)	1.984 (7)	Fe(1)—N(6)	1.965 (8)
N(1)—Fe(1)—N(2)	82.8 (3)	N(3)—Fe(1)—N(4)	83.0 (4)
N(5)—Fe(1)—N(6)	82.0 (3)	N(1)—Fe(1)—N(4)	174.3 (3)
N(2)—Fe(1)—N(5)	177.7 (4)	N(3)—Fe(1)—N(6)	173.6 (3)

Table 3. *Comparison of the geometries of* Fe(phen)$_3^{2+}$, Co(phen)$_3^{2+}$ *and* Cu(phen)$_3^{2+}$ *in their perchlorate salts*

	Fe^{II}	Co^{II}*	Cu^{II}†
Average *M*—N (Å)	1.978 (3)	2.127 (14)	2.33 (1) (axial) 2.04 (1) (equatorial)
Bidentate N—*M*—N (°)	82.6 (4)	78.1 (3)	81.6 (5) 76.9 (5)
Opposite N—*M*—N (°)	175 (2)	172 (3)	179.2 (5) (axial) 168 (1) (equatorial)

* Boys, Escobar & Wittke (1984).
† Anderson (1973).

The structure was solved by direct methods and refined by full-matrix least squares using programs in the *SHELXTL-Plus* package (Sheldrick, 1990).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, along with a packing diagram, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71767 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1068]

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