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Diaquo-2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12,3,1]octadeca-1(18),2,12,14,16-pentaeneiron(II) Chloride Perchlorate

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$Fe(N_5C_{15}H_{23})(H_2O)_2Cl.ClO_4$, $M=532{\cdot}15$, monoclinic, $a=7{\cdot}872$ (8), $b=27{\cdot}761$ (15), $c=10{\cdot}920$ (9) Å, $\beta=113{\cdot}6$ (1)°, $U=2191{\cdot}2$ Å^3, $Z=4$, $d_c=1{\cdot}52$, $d_m=1{\cdot}51$ (2), Mo $K\alpha$ radiation $\lambda=0{\cdot}7107$ Å, $\mu=9{\cdot}38$ cm^{-1}. Space group $I2/a$ [equivalent positions (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2})\pm(x,y,z;\ \frac{1}{2}-x,\frac{1}{2}+y,-z)$] from systematic absences hkl, $h+k+l=2n+1$; $h0l$, $h=2n+1$ and the successful structure determination. The cation has crystallographically imposed C_2 symmetry with the Fe atom in a distorted pentagonal bipyramidal environment. The five N atoms of the macrocycle form the pentagonal girdle [Fe–N 2·256 (7), 2·262 (6), 2·220 (7) Å] and the water molecules occupy the axial positions [Fe–O 2·218 (7) Å]. The perchlorate anion is disordered. 1285 independent reflexions, above background, measured by counter methods have been refined to R 0·073.

Introduction

A crystal with dimensions 0·25 × 0·35 × 0·40 mm was mounted with the c^* axis parallel to the instrument axis of a General Electric XRD5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium-filtered X-radiation was used. 2079 independent reflexions with $2\theta<50°$ were measured by the stationary-counter stationary-crystal method. No crystal decay was observed during the measurement of data. 1285 reflexions with $I>\sigma(I)$ were used in subsequent calculations. No extinction or absorption corrections were applied. The positions of the Fe atoms were determined from a Patterson function and Fourier syntheses were used to determine the positions of the remaining atoms. The positions of the non-methyl H atoms bonded to C, N and O were located from the difference Fourier map and/or calculated in tetrahedral or trigonal positions. These atoms were included in the structure factor calculation but not refined. The perchlorate anion was disordered in a complicated fashion which we approximated by taking two sets of tetrahedral positions for the O atoms with $\frac{1}{2}$ occupancy. The structure was refined by full-matrix least squares, all non-hydrogen atoms anisotropically except the oxygen atoms of the perchlorate which were refined isotropically to R 0·073. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflexions independent of values of F_o and $\sin\theta/\lambda$, was $\sqrt{w}=1$ for $F_o>35$ and $\sqrt{w}=35/F_o$ for $F_o<35$. Calculations were made on a C.D.C. computer at the University of London Computer Centre using the X-RAY set of programs (Stewart, 1970). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The anisotropic temperature factor is defined as $\exp\,[-0{\cdot}25\pi^2\sum_i\sum_j h_ih_jb_ib_jU_{ij}$ $(i,j=$

Table 1. *Atomic coordinates* (× 10^4) *with estimated standard deviations in parentheses*

	x	y	z
Fe	0*	1150 (4)	2500*
O(1)	1682 (8)	1153 (2)	1286 (5)
N(3)	−1657 (11)	506 (2)	1398 (8)
C(4)	−2524 (15)	606 (3)	−61 (10)
C(5)	−3546 (13)	1069 (4)	−260 (10)
N(6)	−2335 (9)	1436 (2)	649 (6)
C(7)	−2598 (11)	1880 (3)	437 (8)
C(8)	−1269 (10)	2188 (3)	1487 (7)
N(9)	0*	1950 (2)	2500*
C(17)	−523 (18)	68 (3)	1763 (12)
C(20)	−4125 (14)	2103 (4)	−789 (10)
C(21)	−1308 (13)	2692 (3)	1462 (9)
C(22)	0*	2937 (4)	2500*
Cl(1)	5000*	467 (1)	2500*
Cl(2)	0*	1492 (1)	7500*
O(21)	1399 (54)	1139 (13)	7679 (48)
O(22)	−379 (40)	1663 (10)	8542 (32)
O(23)	−1210 (37)	1300 (9)	6352 (27)
O(24)	1342 (30)	1856 (8)	7440 (24)
H(31)†	−2547	484	1749
H(41)	−1409	651	−388
H(42)	−3317	293	−507
H(51)	−4226	1151	−1284
H(52)	−4786	994	77
H(171)	379	51	1214
H(172)	−1473	−246	1413
H(21)	−2397	2889	636
H(22)	0	3322	2500
H(11)	2917	1000	1500
H(12)	888	1014	455

* Parameter fixed.

† Hydrogen atom parameters were fixed. The atoms were given thermal parameters equivalent to those of the atoms to which they were bonded.

1,2,3)] where b_i is the ith reciprocal cell dimension. The isotropic thermal parameter is $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. The 794 zero reflexions showed no large discrepancies. In the final cycle of refinement, all shifts were $< 0{\cdot}020\sigma$. The final list of positions is given in Table 1, thermal parameters in Table 2, bond lengths and angles in Table 3.*

Table 2. *Anisotropic thermal parameters* ($\times 10^3$) *with estimated standard deviations in parentheses*

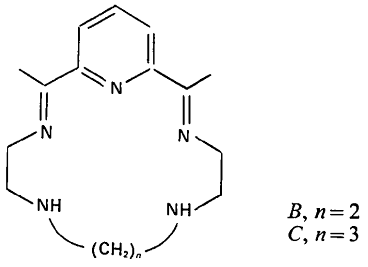
	U_{11}*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	51 (1)	36 (1)	45 (1)	0†	24 (1)	0†
O(1)	78 (4)	69 (3)	63 (3)	0 (3)	39 (3)	9 (3)
N(3)	93 (5)	59 (4)	103 (6)	−14 (4)	66 (5)	−22 (4)
C(4)	101 (8)	81 (6)	82 (7)	−39 (6)	43 (6)	−38 (6)
C(5)	70 (6)	113 (10)	65 (6)	−20 (6)	7 (5)	−31 (5)
N(6)	62 (4)	76 (5)	46 (3)	−4 (3)	18 (3)	−7 (4)
C(7)	61 (4)	72 (5)	47 (5)	18 (3)	26 (4)	10 (4)
C(8)	55 (4)	55 (4)	50 (4)	13 (3)	27 (3)	12 (3)
N(9)	60 (4)	40 (4)	47 (5)	0†	34 (4)	0†
C(17)	138 (10)	47 (5)	151 (10)	−14 (5)	100 (10)	−22 (4)
C(20)	76 (6)	153 (10)	65 (6)	35 (7)	19 (5)	43 (6)
C(21)	93 (6)	53 (5)	87 (6)	19 (4)	60 (6)	22 (4)
C(22)	119 (12)	39 (6)	123 (13)	0†	78 (11)	0†
Cl(1)	57 (2)	88 (2)	95 (2)	0†	20 (1)	0†
Cl(2)	85 (2)	58 (2)	46 (2)	0†	40 (2)	0†

* Isotropic parameters for O(21), O(22), O(23), O(24) are 256 (17), 190 (10), 164 (8), 144 (7).

† Parameter fixed.

Discussion

The analysis of the title compound, $[FeB(H_2O)_2]^{2+}Cl^-$, ClO_4^- was carried out as part of the studies (Drew, Othman, Hill, McIlroy & Nelson, 1975; Drew, Othman, McIlroy & Nelson, 1976*a*,*b*) of seven-coordination in metal complexes of pentadentate macrocyclic ligands. Crystal structures have been determined for four molecules in this series, namely, Fe*B*$(NCS)_2$, Fe*C*$(NCS)_2$ (Drew, Othman, Hill, McIlroy & Nelson, 1975; Drew *et al.*, 1976*b*) and $[FeB(NCS)_2]^+ClO_4^-$ and $[FeC(NCS)_2]^+ClO_4^-$ (Drew *et al.*, 1976*a*).



The structure of $[FeB(H_2O)_2]^{2+}Cl^-,ClO_4^-$ was determined in order to ascertain what effect, if any, a change in the nature of the anionic axial ligands might have upon the molecular geometry. The compound was prepared by dithionite reduction in the presence of an excess of sodium chloride, of the iron(III) complex $[FeB(NCS)_2]^{2+}ClO_4^-$ in aqueous solution. The royal

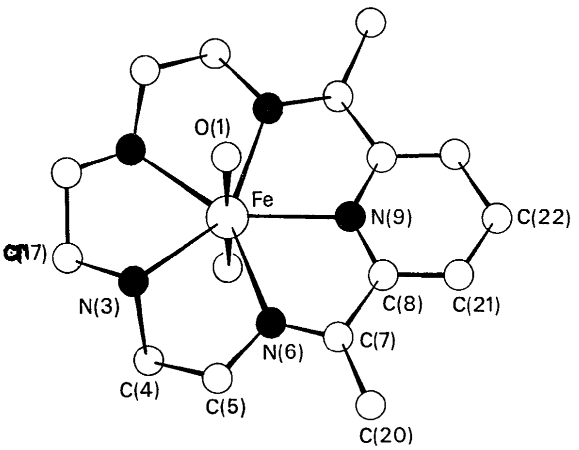


Fig. 1. The cation $[FeB(H_2O)]^{2+}$.

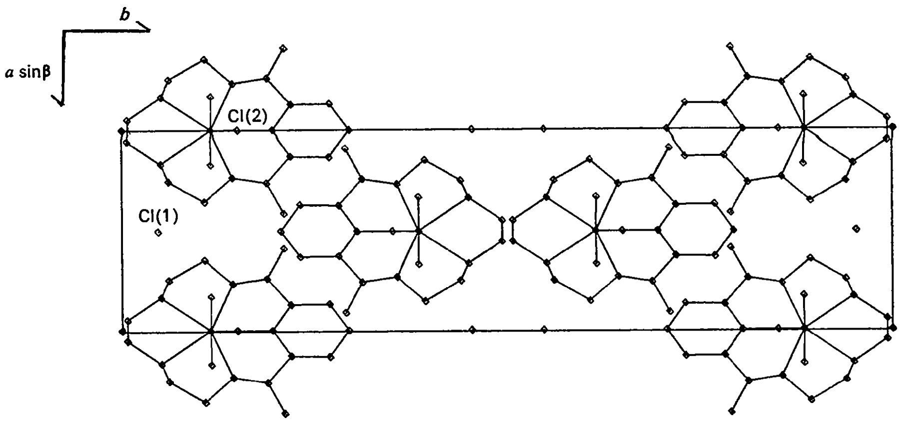


Fig. 2. The unit cell in the *c* projection. Oxygen atoms in the perchlorate ion are omitted for clarity.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31350 (6pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England

Table 3. *Bond lengths* (Å) *and angles* (°)

Fe——O(1)	2·218 (7)	O(1)—Fe——O(1$^{\rm I}$)*	179·7 (2)
Fe——N(3)	2·256 (7)	O(1)—Fe——N(3)	92·3 (3)
Fe——N(6)	2·262 (6)	O(1)—Fe——N(6)	96·0 (2)
Fe——N(9)	2·220 (7)	O(1)—Fe——N(9)	89·8 (1)
N(3)—C(4)	1·486 (13)	N(3)—Fe——N(6)	73·3 (2)
C(4)—C(5)	1·485 (15)	N(3)—Fe——N(9)	142·4 (2)
C(5)—N(6)	1·475 (11)	N(3)—Fe——N(3$^{\rm I}$)	75·1 (2)
N(6)—C(7)	1·255 (11)	N(3)—Fe——N(6$^{\rm I}$)	147·6 (2)
C(7)—C(8)	1·477 (10)	N(6)—Fe——N(9)	69·4 (2)
C(7)—C(20)	1·527 (12)	N(6)—Fe——N(6$^{\rm I}$)	138·9 (2)
C(8)—C(21)	1·398 (11)	Fe——N(3)—C(4)	110·0 (5)
C(8)—N(9)	1·332 (7)	Fe——N(3)—C(17)	110·7 (5)
C(21)–C(22)	1·368 (10)	C(4)—N(3)—C(17)	114·5 (9)
N(3)—C(17)	1·466 (12)	N(3)—C(4)—C(5)	107·9 (9)
C(17)–C(17$^{\rm I}$)	1·486 (16)	C(4)—C(5)—N(6)	109·5 (7)
		C(5)—N(6)—C(7)	122·7 (6)
Cl(2)–O(21)	1·43 (4)	Fe——N(6)—C(5)	115·7 (5)
Cl(2)–O(22)	1·37 (4)	Fe——N(6)—C(7)	121·6 (5)
Cl(2)–O(23)	1·34 (2)	N(6)—C(7)—C(8)	114·4 (6)
Cl(2)–O(24)	1·48 (2)	C(8)—C(7)—C(20)	120·6 (8)
O(21)–Cl(2)–C(22)	122 (2)	N(6)—C(7)—C(20)	125·0 (7)
O(21)–Cl(2)–O(23)	94 (2)	C(7)—C(8)—C(21)	124·2 (6)
O(21)–Cl(2)–O(24)	87 (2)	C(7)—C(8)—N(9)	114·7 (6)
O(22)–Cl(2)–O(23)	127 (2)	N(9)—C(8)—C(21)	121·1 (6)
O(22)–Cl(2)–O(24)	101 (2)	Fe——N(9)—C(8)	119·8 (4)
O(23)–Cl(2)–O(24)	119 (2)	C(8)—C(21)–C(22)	118·5 (7)
		C(21)–C(22)–C(21$^{\rm I}$)	120·4 (10)
		N(3)—C(17)–C(17$^{\rm I}$)	107·9 (9)
		C(8)—N(9)—C(8$^{\rm I}$)	120·4 (7)

* The superscript I refers to atoms with coordinates $-x,y,\frac{1}{2}-z$ compared to the x,y,z reference set in Table 1.

blue crystals are stable to oxidation for long periods in the solid state and in solution in the absence of oxygen; unlike the parent iron(III) complex, however, the reduced compound is decomposed by acid solution of moderate concentration. Preliminary physico-chemical measurements (infrared and visible spectra, electrical conductance, magnetic susceptibility) were fully consistent (Drew *et al.*, 1976*b*) with the formulation of the complex in the solid state as containing the high spin ($S=2$) seven-coordinate cation $[\mathrm{Fe}B(\mathrm{H_2O})_2]^{2+}$.

The cation, $[\mathrm{Fe}B(\mathrm{H_2O})_2]^{2+}$, which has crystallographically imposed C_2 symmetry with Fe, N(9), C(22) on the twofold axis, is shown in Fig. 1 together with the atomic numbering scheme. The $\mathrm{FeN_5}$ atoms are not coplanar, the N atoms being displaced from the least-squares plane (Table 4) in an identical fashion to those in $\mathrm{Fe}B(\mathrm{NCS})_2$ and $[\mathrm{Fe}B(\mathrm{NCS})_2]^+\mathrm{ClO_4^-}$. However, there are differences in the deviations of the C atoms from the $\mathrm{FeN_5}$ plane in that (*inter alia*) in $[\mathrm{Fe}B(\mathrm{H_2O})_2]^{2+}$, C(22) is perforce on the plane but in $\mathrm{Fe}B(\mathrm{NCS})_2$ this atom is 0·28 Å away. It may well be that the thiocyanate groups in the latter structure affect the relative position of the pyridine ring. The Fe, N(3), C(4), C(5), N(6) ring has the asymmetric puckered conformation with C(4) 0·68 and C(5) 0·07 Å from the $\mathrm{FeN_2}$ plane. By contrast, the Fe, N(3), C(17), C(17$^{\rm I}$), N(3$^{\rm I}$) ring has the symmetric puckered conformation in that C(17) and C(17$^{\rm I}$) are ±0·37 Å from the plane of $\mathrm{FeN_2}$.*

Table 4. *Least-squares planes in the form* $Ax+By+Cz=D$, *where* x,y,z *are the crystallographic fractional coordinates of the atoms*

Distances (Å) of the relevant atoms from each plane are given in square brackets.

Fe, N(3), N(6), N(9), N(6$^{\rm I}$), N(3$^{\rm I}$)

$A=-6{\cdot}73,\ B=-0{\cdot}00,\ C=8{\cdot}94,\ D=2{\cdot}23$

[Fe 0·00, N(3) 0·13, N(6) −0·08, N(9) 0·00, C(7) −0·10, C(8) −0·05, C(20) −0·17, C(21) −0·05, C(22) 0·00, C(4) −0·59, C(5) −0·08, C(17) −0·31 Å]

Bond lengths in $[\mathrm{Fe}B(\mathrm{H_2O})_2]^+\mathrm{Cl^-},\mathrm{ClO_4^-}$ are similar to those in $\mathrm{Fe}B(\mathrm{NCS})_2$; Fe–N(9) is the shortest bond at 2·220 (7) Å and the other four are equivalent 2·256 (7), 2·262 (6) Å. There is little difference between Fe(II)–N and Fe(III)–N bond lengths in complexes formed with macrocycle *B* suggesting that the size of the cation has little effect on the bond lengths. There is a much wider range of Fe–N lengths in complexes of macrocycle *C* presumably due to the greater steric strain set up by the six-membered ring. For the present complex the inclusion of the axial $\mathrm{H_2O}$ groups instead of the pseudohalide –NCS groups has made little difference in the amount of distortion in the macrocycle.

The Fe–O bond lengths of 2·218 (7) Å are longer than the axial bond found in another pentagonal bipyramidal structure, that of the chloroaquo-(2,6-diacetylpyridine)bis(semicarbazone)iron(II) cation (2·153 Å, Wester & Palenik, 1973). The chloride ion is hydrogen bonded to the axial oxygen *via* H(11) [Cl(1)···H(11) 2·15 Å, O(1)–H(11)···Cl 151·9°]. There are no intermolecular contacts significantly less than the sum of van der Waals radii. The unit cell is shown in the *c* projection in Fig. 2.

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* As expected, atoms Fe, N(6), C(7), C(8), N(9), C(20), C(21), C(22) are coplanar within experimental error.

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