

Chlorido{5,10,15,20-tetrakis[2-(2,2-dimethylpropanamido)phenyl]porphyrinato- $\kappa^4 N, N', N'', N'''$ }iron(III) chlorobenzene hemisolvate monohydrate

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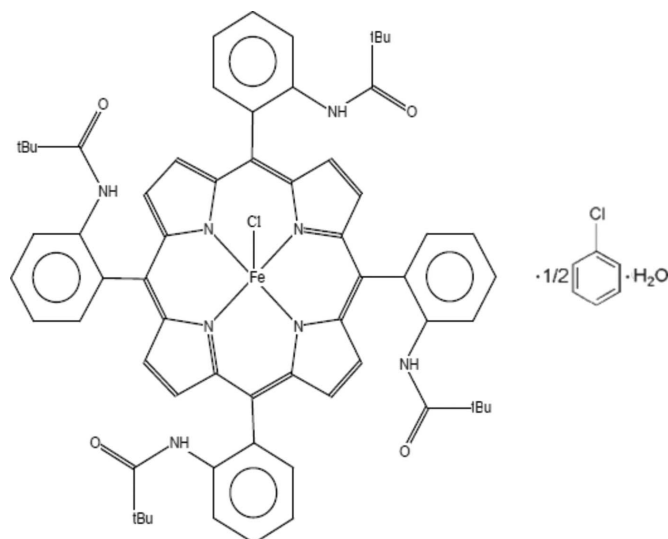
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Key indicators: single-crystal X-ray study; $T = 180$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; some non-H atoms missing; R factor = 0.060; wR factor = 0.180; data-to-parameter ratio = 17.0.

In the title complex, $[\text{Fe}(\text{C}_{64}\text{H}_{64}\text{N}_8\text{O}_4)\text{Cl}]\cdot 0.5\text{C}_6\text{H}_5\text{Cl}\cdot\text{H}_2\text{O}$, the equatorial iron–pyrrole N atom distance ($\text{Fe}-\text{N}_p$) is 2.065 (2) Å and the axial Fe–Cl distance is 2.207 (2) Å. The iron cation is displaced by 0.420 (4) Å from the 24-atom mean plane of the porphyrin core. The asymmetric unit contains a quarter of an $[\text{Fe}^{\text{III}}(\text{C}_{64}\text{H}_{64}\text{N}_8\text{O}_4)\text{Cl}]$ complex molecule, with a fourfold rotation axis passing through the central metal cation and the Cl ligand, along with disordered molecules of chlorobenzene and water of solvation; the solvent molecules were excluded from the refinement.

Related literature

For a review of porphyrin complexes, see: Scheidt (2000). For synthetic procedures, see: Gismelseed *et al.* (1990). For structural features of porphyrins, see: Schappacher *et al.* (1983). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$[\text{Fe}(\text{C}_{64}\text{H}_{64}\text{N}_8\text{O}_4)\text{Cl}]\cdot 0.5\text{C}_6\text{H}_5\text{Cl}\cdot\text{H}_2\text{O}$
 $M_r = 1206.84$
 Tetragonal, $P4/ncc$
 $a = 18.069$ (3) Å
 $c = 18.919$ (4) Å

$V = 6177$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.34$ mm⁻¹
 $T = 180$ K
 $0.22 \times 0.18 \times 0.16$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{\text{min}} = 0.842$, $T_{\text{max}} = 0.937$

43373 measured reflections
 3021 independent reflections
 2089 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.180$
 $S = 1.07$
 3021 reflections

178 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.81$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.34$ e Å⁻³

Data collection: APEX2 (Bruker, 2007); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SIR2004 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP3 (Burnett & Johnson, 1996), PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2389).

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supplementary materials

Acta Cryst. (2011). E67, m460-m461 [doi:10.1107/S1600536811009299]

Chlorido{5,10,15,20-tetrakis[2-(2,2-dimethylpropanamido)phenyl]porphyrinato- κ^4N,N',N'',N''' }iron(III) chlorobenzene hemisolvate monohydrate

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Comment

In the Cambridge Structural Database (CSD, Version 5.32; Allen, 2002) there are more than sixty structures of iron(III) chloride with many types of porphyrins. This large number of structures reflects the importance of this type of complex which is used as starting material in the synthesis of iron(III) and iron(II) porphyrin species.

A formula unit of the title complex contains a molecule of $[\text{Fe}^{\text{III}}(\text{C}_{64}\text{H}_{64}\text{N}_8\text{O}_4)\text{Cl}]$ (Fig. 1), a half molecule of chlorobenzene and a molecule of water of solvation; the solvent molecules were disordered and were therefore, excluded from the refinement. The most important feature of the structure is the fact that the chloride ion is coordinated to the Fe(III) from the open side face of the picket fence porphyrin for which anionic axial ligands are known to be bound to the metal ion from the protected side of this porphyrin (Schappacher *et al.*, 1983). The square-pyramidal coordination of the central atom, with an equatorial iron-pyrrole nitrogen atom distance (Fe–N_p) of 2.065 (2) Å and 2.207 (2) Å for the axial Fe–Cl distance, is typical for penta-coordinated iron(III) high-spin ($S = 5/2$) chloride porphyrin species (Scheidt, 2000). The iron atom is displaced by 0.420 (4) Å from the 24 atom mean plane.

Experimental

The reaction of the $[\text{Fe}^{\text{III}}(\text{TpivPP})(\text{SO}_3\text{CF}_3)(\text{H}_2\text{O})]$ complex (Gismelseed *et al.*, 1990) (100 mg, 0.081 mmol) with an excess of potassium chlorite, KClO_3 (198 mg, 1.62 mmol) and 18-crown-6 (214 mg, 0.81 mmol) in chlorobenzene (5 ml) yields a reddish-brown solution. Crystals of the title complex were obtained as impurities by diffusion of hexanes through the chlorobenzene solution.

Refinement

Hydrogen atoms were placed in calculated positions with N–H = 0.86 Å and C–H = 0.93 and 0.96 Å for aryl and methyl type H-atoms, respectively, and refined in riding model with fixed isotropic displacement parameters: $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl-C})$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aryl-C/N})$.

The program *PLATON* (Spek, 2009) indicated solvent accessible void space of 757 Å³, corresponding to 161 electrons in a unit cell, equivalent to 2 molecules of chlorobenzene and 4 water molecules. Since the solvent molecules were grossly disordered and could not be modeled, their contribution was excluded using the subroutine SQUEEZE.

Figures

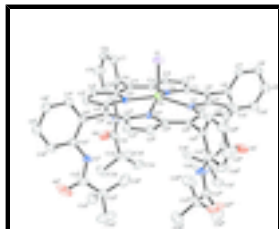


Fig. 1. A view of the structure of ion complex $[\text{Fe}^{\text{III}}(\text{C}_{64}\text{H}_{64}\text{N}_8\text{O}_4)\text{Cl}]$ showing the atom numbering scheme. Displacement ellipsoids are drawn at 50%. The H atoms have been omitted for clarity. Symmetry codes: (i) $-y + 1/2, x, z$; (ii) $y, -x + 1/2, z$; (iii) $-x + 1/2, -y + 1/2, z$.

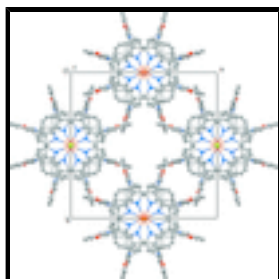


Fig. 2. A unit cell packing of the title complex viewed down the c -axis, solvents have been excluded.

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Crystal data

$[\text{Fe}(\text{C}_{64}\text{H}_{64}\text{N}_8\text{O}_4)\text{Cl}] \cdot 0.5\text{C}_6\text{H}_5\text{Cl} \cdot \text{H}_2\text{O}$

$M_r = 1206.84$

Tetragonal, $P4/ncc$

Hall symbol: $-P\ 4a\ 2ac$

$a = 18.069\ (3)\ \text{\AA}$

$c = 18.919\ (4)\ \text{\AA}$

$V = 6177\ (2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 2536$

$D_x = 1.298\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 43373 reflections

$\theta = 2.7\text{--}26.0^\circ$

$\mu = 0.34\ \text{mm}^{-1}$

$T = 180\ \text{K}$

Prism, dark purple

$0.22 \times 0.18 \times 0.16\ \text{mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer

3021 independent reflections

Radiation source: fine-focus sealed tube

2089 reflections with $I > 2\sigma(I)$

graphite

$R_{\text{int}} = 0.064$

φ and ω scans

$\theta_{\text{max}} = 26.0^\circ, \theta_{\text{min}} = 2.7^\circ$

Absorption correction: multi-scan

$h = -22 \rightarrow 22$

(*SADABS*; Bruker, 2007)

$k = -20 \rightarrow 22$

$T_{\text{min}} = 0.842, T_{\text{max}} = 0.937$

$l = -23 \rightarrow 23$

43373 measured reflections

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.060$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.180$	H-atom parameters constrained
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.115P)^2 + 0.6251P]$
3021 reflections	where $P = (F_o^2 + 2F_c^2)/3$
178 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -1.34 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe	0.2500	0.2500	0.12373 (4)	0.0222 (3)
Cl	0.2500	0.2500	0.24040 (7)	0.0335 (4)
O1	0.56932 (17)	0.3807 (2)	-0.12040 (12)	0.0677 (10)
N1	0.35198 (11)	0.20458 (11)	0.10034 (11)	0.0163 (5)
N2	0.49310 (14)	0.35229 (16)	-0.03138 (13)	0.0371 (7)
HN2	0.4488	0.3373	-0.0231	0.045*
C1	0.36920 (14)	0.13070 (14)	0.09954 (14)	0.0187 (6)
C2	0.44818 (15)	0.12135 (16)	0.09858 (15)	0.0250 (6)
H2	0.4735	0.0766	0.0981	0.030*
C3	0.47859 (15)	0.18914 (15)	0.09854 (15)	0.0249 (6)
H3	0.5289	0.2001	0.0980	0.030*
C4	0.41823 (14)	0.24197 (14)	0.09945 (14)	0.0190 (6)
C5	0.42756 (14)	0.31872 (14)	0.09900 (13)	0.0183 (6)
C6	0.50541 (14)	0.34772 (14)	0.09465 (14)	0.0200 (6)
C7	0.54726 (15)	0.35788 (16)	0.15514 (15)	0.0262 (7)
H7	0.5264	0.3482	0.1991	0.031*
C8	0.61929 (17)	0.38216 (18)	0.15117 (16)	0.0333 (7)
H8	0.6466	0.3890	0.1923	0.040*

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C9	0.65061 (18)	0.3961 (2)	0.08699 (18)	0.0433 (9)
H9	0.6995	0.4120	0.0845	0.052*
C10	0.61015 (18)	0.3869 (2)	0.02555 (17)	0.0412 (9)
H10	0.6316	0.3969	-0.0181	0.049*
C11	0.53757 (16)	0.36263 (17)	0.02937 (15)	0.0286 (7)
C12	0.50947 (19)	0.36235 (17)	-0.10004 (16)	0.0327 (7)
C13	0.44577 (19)	0.34785 (17)	-0.15323 (16)	0.0342 (8)
C14	0.4681 (2)	0.2800 (2)	-0.19598 (18)	0.0431 (8)
H14A	0.5152	0.2886	-0.2179	0.065*
H14B	0.4316	0.2707	-0.2317	0.065*
H14C	0.4715	0.2379	-0.1652	0.065*
C15	0.3714 (2)	0.3359 (3)	-0.11812 (18)	0.0494 (10)
H15A	0.3582	0.3791	-0.0915	0.074*
H15B	0.3742	0.2940	-0.0870	0.074*
H15C	0.3345	0.3268	-0.1536	0.074*
C16	0.4413 (3)	0.4155 (2)	-0.2017 (2)	0.0747 (15)
H16A	0.4271	0.4581	-0.1745	0.112*
H16B	0.4052	0.4068	-0.2380	0.112*
H16C	0.4887	0.4242	-0.2229	0.112*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe	0.0228 (3)	0.0228 (3)	0.0211 (4)	0.000	0.000	0.000
Cl	0.0409 (6)	0.0409 (6)	0.0188 (7)	0.000	0.000	0.000
O1	0.0669 (19)	0.111 (3)	0.0255 (13)	-0.0554 (19)	0.0096 (12)	-0.0067 (13)
N1	0.0157 (11)	0.0160 (11)	0.0171 (10)	0.0016 (9)	0.0025 (9)	-0.0008 (9)
N2	0.0264 (14)	0.0630 (19)	0.0220 (13)	-0.0182 (13)	-0.0021 (11)	0.0079 (12)
C1	0.0199 (14)	0.0203 (14)	0.0158 (12)	0.0021 (10)	0.0008 (10)	-0.0001 (10)
C2	0.0189 (14)	0.0226 (15)	0.0336 (15)	0.0052 (11)	0.0024 (12)	0.0002 (12)
C3	0.0167 (14)	0.0257 (15)	0.0323 (15)	0.0024 (11)	0.0038 (12)	-0.0042 (12)
C4	0.0172 (13)	0.0239 (15)	0.0158 (12)	0.0012 (10)	0.0018 (10)	-0.0014 (10)
C5	0.0184 (13)	0.0210 (14)	0.0155 (12)	-0.0026 (10)	0.0028 (10)	0.0009 (11)
C6	0.0166 (14)	0.0202 (14)	0.0232 (14)	-0.0010 (10)	0.0007 (11)	0.0002 (11)
C7	0.0244 (16)	0.0324 (17)	0.0219 (14)	-0.0009 (12)	0.0017 (12)	-0.0027 (12)
C8	0.0258 (16)	0.047 (2)	0.0271 (15)	-0.0057 (14)	-0.0049 (13)	-0.0102 (14)
C9	0.0231 (17)	0.063 (2)	0.0435 (19)	-0.0194 (16)	0.0014 (14)	-0.0035 (18)
C10	0.0304 (18)	0.067 (2)	0.0265 (16)	-0.0233 (16)	0.0047 (13)	0.0042 (15)
C11	0.0267 (16)	0.0364 (17)	0.0226 (15)	-0.0084 (12)	-0.0010 (12)	0.0025 (12)
C12	0.047 (2)	0.0288 (16)	0.0224 (15)	-0.0122 (14)	0.0016 (14)	0.0017 (13)
C13	0.052 (2)	0.0302 (17)	0.0209 (15)	-0.0009 (14)	-0.0103 (14)	0.0017 (12)
C14	0.047 (2)	0.048 (2)	0.0350 (18)	0.0001 (16)	-0.0096 (16)	-0.0104 (16)
C15	0.039 (2)	0.071 (3)	0.0376 (19)	0.0059 (18)	-0.0167 (16)	-0.0144 (18)
C16	0.132 (4)	0.046 (2)	0.046 (2)	0.013 (3)	-0.022 (3)	0.015 (2)

Geometric parameters (\AA , $^\circ$)

Fe—N1 ⁱ	2.065 (2)	C7—C8	1.376 (4)
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Fe—N1 ⁱⁱ	2.065 (2)	C7—H7	0.9300
Fe—N1	2.065 (2)	C8—C9	1.363 (5)
Fe—N1 ⁱⁱⁱ	2.065 (2)	C8—H8	0.9300
Fe—Cl	2.2073 (16)	C9—C10	1.383 (4)
O1—C12	1.195 (4)	C9—H9	0.9300
N1—C1	1.371 (3)	C10—C11	1.385 (4)
N1—C4	1.375 (3)	C10—H10	0.9300
N2—C12	1.345 (4)	C12—C13	1.551 (4)
N2—C11	1.415 (4)	C13—C15	1.515 (5)
N2—HN2	0.8600	C13—C14	1.523 (5)
C1—C5 ⁱⁱ	1.393 (4)	C13—C16	1.530 (5)
C1—C2	1.437 (4)	C14—H14A	0.9600
C2—C3	1.343 (4)	C14—H14B	0.9600
C2—H2	0.9300	C14—H14C	0.9600
C3—C4	1.449 (4)	C15—H15A	0.9600
C3—H3	0.9300	C15—H15B	0.9600
C4—C5	1.397 (4)	C15—H15C	0.9600
C5—C1 ⁱ	1.393 (4)	C16—H16A	0.9600
C5—C6	1.503 (4)	C16—H16B	0.9600
C6—C7	1.384 (4)	C16—H16C	0.9600
C6—C11	1.391 (4)		
N1 ⁱ —Fe—N1 ⁱⁱ	155.25 (12)	C9—C8—H8	120.0
N1 ⁱ —Fe—N1	87.37 (3)	C7—C8—H8	120.0
N1 ⁱⁱ —Fe—N1	87.37 (3)	C8—C9—C10	120.4 (3)
N1 ⁱ —Fe—N1 ⁱⁱⁱ	87.37 (3)	C8—C9—H9	119.8
N1 ⁱⁱ —Fe—N1 ⁱⁱⁱ	87.37 (3)	C10—C9—H9	119.8
N1—Fe—N1 ⁱⁱⁱ	155.25 (12)	C9—C10—C11	119.7 (3)
N1 ⁱ —Fe—Cl	102.38 (6)	C9—C10—H10	120.2
N1 ⁱⁱ —Fe—Cl	102.38 (6)	C11—C10—H10	120.2
N1—Fe—Cl	102.38 (6)	C10—C11—C6	120.2 (3)
N1 ⁱⁱⁱ —Fe—Cl	102.38 (6)	C10—C11—N2	122.5 (3)
C1—N1—C4	106.3 (2)	C6—C11—N2	117.3 (2)
C1—N1—Fe	126.29 (17)	O1—C12—N2	123.2 (3)
C4—N1—Fe	125.75 (17)	O1—C12—C13	120.6 (3)
C12—N2—C11	130.0 (3)	N2—C12—C13	116.2 (3)
C12—N2—HN2	115.0	C15—C13—C14	110.6 (3)
C11—N2—HN2	115.0	C15—C13—C16	109.3 (3)
N1—C1—C5 ⁱⁱ	126.0 (2)	C14—C13—C16	109.8 (3)
N1—C1—C2	109.9 (2)	C15—C13—C12	113.5 (3)
C5 ⁱⁱ —C1—C2	124.1 (2)	C14—C13—C12	106.5 (3)
C3—C2—C1	107.4 (2)	C16—C13—C12	107.0 (3)
C3—C2—H2	126.3	C13—C14—H14A	109.5
C1—C2—H2	126.3	C13—C14—H14B	109.5
C2—C3—C4	107.0 (2)	H14A—C14—H14B	109.5
C2—C3—H3	126.5	C13—C14—H14C	109.5
C4—C3—H3	126.5	H14A—C14—H14C	109.5

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N1—C4—C5	126.4 (2)	H14B—C14—H14C	109.5
N1—C4—C3	109.4 (2)	C13—C15—H15A	109.5
C5—C4—C3	124.2 (2)	C13—C15—H15B	109.5
C1 ⁱ —C5—C4	124.0 (2)	H15A—C15—H15B	109.5
C1 ⁱ —C5—C6	118.6 (2)	C13—C15—H15C	109.5
C4—C5—C6	117.3 (2)	H15A—C15—H15C	109.5
C7—C6—C11	118.7 (2)	H15B—C15—H15C	109.5
C7—C6—C5	120.8 (2)	C13—C16—H16A	109.5
C11—C6—C5	120.5 (2)	C13—C16—H16B	109.5
C8—C7—C6	120.9 (3)	H16A—C16—H16B	109.5
C8—C7—H7	119.5	C13—C16—H16C	109.5
C6—C7—H7	119.5	H16A—C16—H16C	109.5
C9—C8—C7	120.0 (3)	H16B—C16—H16C	109.5

Symmetry codes: (i) $-y+1/2, x, z$; (ii) $y, -x+1/2, z$; (iii) $-x+1/2, -y+1/2, z$.

Fig. 1

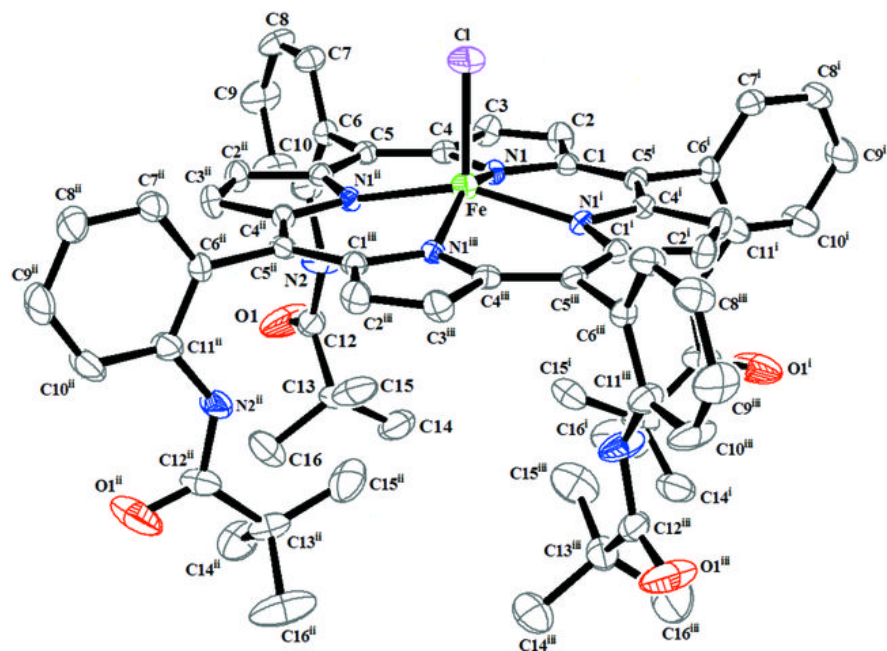


Fig. 2

