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μ-Oxo-bis{chloro[*N*-(2-methoxyethyl)-*N*,*N*-bis(pyridin-2-ylmethyl)amine-κ^4-*N*,*N*′,*N*″,*O*]iron(III)} bis(trifluoromethanesulfonate) acetonitrile disolvate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.064
wR factor = 0.184
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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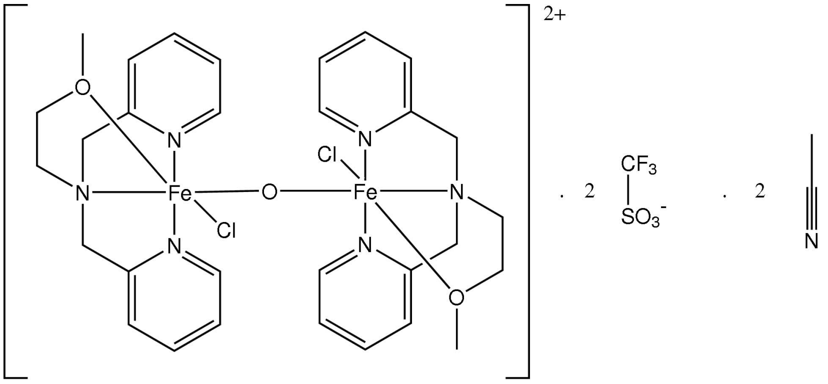
The main molecule of the title compound, $[Fe_2(C_{15}H_{19}ClN_3O)_2O](CF_3O_3S)_2\cdot 2C_2H_3N$, is located on a crystallographic inversion centre and displays disorder in the coordinated methoxyethyl group. The counter-ion and the cocrystallized solvent molecule are also disordered over multiple positions. The five-membered chelate rings involving the pyridine N atoms are in an envelope conformation. The chelate ring involving the ether O atom is in a half-chair conformation in both disorder components.

Comment

μ-Oxodiiron(III) complexes are known to catalyse the oxidation of a range of substrates, including alkanes and olefins (Costas *et al.*, 2000; Tanase *et al.*, 2004). The title compound, (I), was obtained by acid–base self-assembly synthesis during attempts to prepare chloride-free μ-oxodiiron(III) complexes with the ligand *N*-(2-methoxyethyl)-*N*,*N*-bis(pyridin-2-ylmethyl)amine (abbreviated as mebpa). Previously, the crystal structures of the dinuclear iron complex with perchlorate counter-ions were reported by Nishida *et al.* (1995), Ito *et al.* (1997) and Tanase *et al.* (2004). No atomic coordinates are available for the first two structures. In this paper, we report the crystal structure of an acetonitrile solvate of the dinuclear iron complex, with trifluoromethanesulfonate counter-ions. The ligand mebpa is known to be very stable as its hydrochloride (mebpa·HCl). From this study, it is clear that the addition of weak bases (such as Me_4NOH or Et_4NOH) does not prevent the formation of the strong Fe^{III}—Cl bond.



(I)

The structure of the $[Fe(mebpa)Cl]_2O$ complex in (I) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The bridging O atom of the complex is located on a crystallographic inversion centre. The Fe^{III} ion is in an octahedral coordination environment, which is somewhat

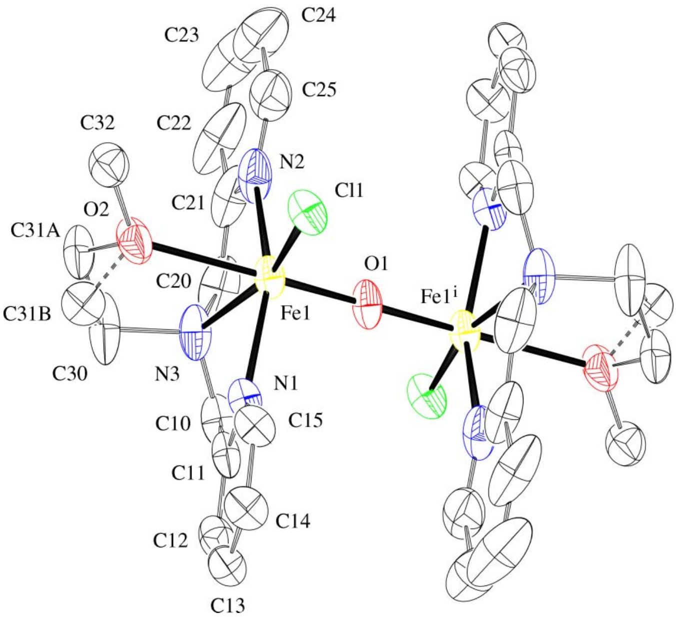


Figure 1
View of the main molecule in (I), showing 50% probability displacement ellipsoids (H atoms have been omitted for clarity). Disorder components with an occupation factor of less than 0.5 are drawn with dashed bonds. [Symmetry code: (i) $1 - x, -y, 1 - z$.]

deformed by the small bite angles of the mebpa ligand [75.08 (14)–77.47 (16)°]. These values are similar to the equivalent range found for the perchlorate structure [75.49 (11)–77.65 (11)°] by Tanase *et al.* (2004). Both disorder components of the five-membered chelate ring (see Fig. 1) involving the ether O atom are in a half-chair conformation, as is indicated by the asymmetry parameters (Duax & Norton, 1975) ΔC_2(C30—C31*A*) = 4.5 (3)° and ΔC_2(O2—C31*B*) = 5.2 (15)° for the major and minor components, respectively. The five-membered chelate rings involving the pyridine N atoms are in an envelope conformation, with N3 protruding from the plane of the other atoms, as is indicated by the asymmetry parameters ΔC_s(N3) = 6.5 (4) and 11.4 (5)° for the chelate rings involving N1 and N2, respectively. The chelate rings of the iron complex in the perchlorate structure (Tanase *et al.*, 2004) have the same conformation as the corresponding rings in the major component of the title compound.

Experimental

The ligand mebpa·HCl was prepared using the procedure reported by Wu *et al.* (2003). Compound (I) was obtained as dark-orange crystals by the slow diffusion of hexane into a tetrahydrofuran solution containing 0.1 mmol $Fe(CF_3SO_3)_2$, 0.1 mmol mebpa·HCl and 0.1 mmol Bu_4NOH. The resulting crystals were collected by filtration, washed with hexane and dried in a vacuum (yield: 65%). Elemental analysis calculated: C 39.54, H 4.06, N 10.25%; found: C 39.27, H 3.93, N 10.53%. IR (cm^{-1}): ν 3566 (*w*), 2925 (*m*), 2823 (*w*), 1608 (*s*), 1574 (*m*), 1482 (*m*), 1445 (*s*), 1252 (*s*), 1223 (*s*), 1142 (*s*), 1106 (*w*), 1076 (*w*), 1027 (*s*), 860 (*s*), 807 (*m*), 760 (*m*), 726 (*w*), 668 (*w*), 635 (*s*), 572 (*m*), 516 (*m*), 481 (*w*). UV–vis/NIR, λ_{max} (nm): 294, 355, 498 (*m*).

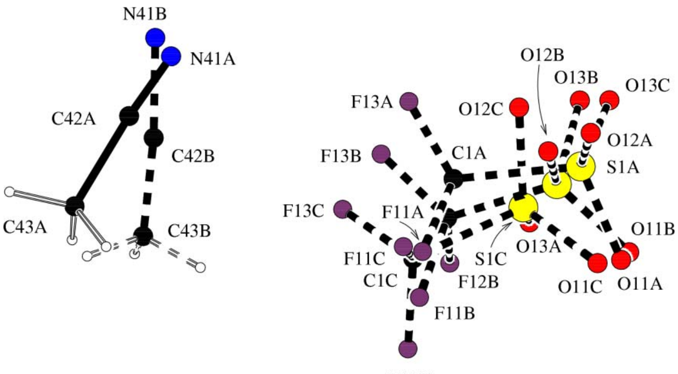


Figure 2
View of the disordered counter-ion and solvent molecules in (I). Disorder components with an occupation factor of less than 0.5 are drawn with dashed bonds.

Crystal data

$[Fe_2(C_{15}H_{19}ClN_3O)_2O](CF_3O_3S)_2\cdot 2C_2H_3N$
M_r = 1093.53
Triclinic, $P\bar{1}$
a = 8.6773 (10) Å
b = 11.585 (2) Å
c = 12.068 (2) Å
α = 77.137 (14)°
β = 79.072 (14)°
γ = 79.279 (14)°
V = 1148.1 (3) Å^3
Z = 1
D_x = 1.582 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 244 reflections
θ = 2.0–25.0°
μ = 0.92 mm^{-1}
T = 150 K
Block, dark orange
0.20 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans and ω scans with κ offset
Absorption correction: none
36 193 measured reflections
5000 independent reflections
3784 reflections with $I > 2\sigma(I)$
R_{int} = 0.167
θ_{max} = 27.0°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 4\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.185
S = 1.07
5000 reflections
304 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0791P)^2 + 1.96P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—Cl1	2.2751 (13)	Fe1—N1	2.132 (4)
Fe1—O1	1.7801 (7)	Fe1—N2	2.135 (5)
Fe1—O2	2.305 (4)	Fe1—N3	2.183 (4)
Cl1—Fe1—O1	102.53 (4)	O1—Fe1—N3	95.09 (10)
Cl1—Fe1—O2	87.50 (11)	O2—Fe1—N1	89.33 (13)
Cl1—Fe1—N1	100.75 (10)	O2—Fe1—N2	80.67 (16)
Cl1—Fe1—N2	102.96 (13)	O2—Fe1—N3	75.08 (14)
Cl1—Fe1—N3	162.33 (10)	N1—Fe1—N2	153.76 (16)
O1—Fe1—O2	168.56 (11)	N1—Fe1—N3	76.52 (14)
O1—Fe1—N1	94.11 (10)	N2—Fe1—N3	77.47 (16)
O1—Fe1—N2	91.59 (13)		

The 2-methoxyethyl group of the mebpa ligand displayed conformational disorder, which could be described with a two-site model for atom C31. The site-occupancy ratio (sum constrained to unity) for

Acta Cryst. (2005). E**61**, m1042–m1044 Kooijman *et al.* • $[Fe_2(C_{15}H_{19}ClN_3O)_2O](CF_3O_3S)_2\cdot 2C_2H_3N$ **m1043**

C31 refined to 0.796 (10):0.204 (10). A model with three disorder components was introduced to describe the disorder in the trifluoromethanesulfonate counter-ion (Fig. 2). Mild restraints were applied to ensure equal values for chemically equivalent bond lengths and angles. The occupancies of the components refined to 0.406 (3):0.317 (3):0.277 (2) (sum restrained to unity). The disorder in the acetonitrile solvent molecule was described with a two-site disorder model, with occupancy ratio 0.668 (12):0.332 (12). The methyl groups of the mebpa ligand and the acetonitrile solvent molecule were refined as rigid groups, allowing for rotation around the O—C and C—C bonds, respectively. All other H atoms were introduced at calculated positions (C—H = 0.95–0.99 Å) and refined as riding on their carrier atoms. The non-H atoms of the solvent molecule and the minor disorder component of the iron complex were refined with isotropic displacement parameters. The disordered counter-ion was refined with common isotropic displacement parameters for each element type. All other non-H atoms were refined with anisotropic displacement parameters. The constraint $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(carrier) or $1.5U_{\rm eq}$(methyl carrier) was applied.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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