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Tetrakis(5-*tert*-butylpyrazole-1κN^2)-tetrachloro-1κCl,2$\kappa^3 Cl$-μ-oxo-1:2$\kappa^2 O$-diiron(III)

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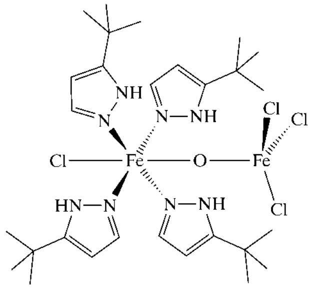
The title compound, $[Fe_2Cl_4O(C_7H_{12}N_2)_4]$, contains vertex-sharing distorted tetrahedral $[FeOCl_3]^-$ and octahedral $[FeOCl(Hpz^tBu)_4]^+$ moieties (Hpz^tBu is 5-*tert*-butylpyrazole), linked by a bent oxo bridging ligand. The two Fe^{III} centres are also bridged by intramolecular hydrogen bonds between the pyrazole N—H groups and the O^{2-} and Cl^- ligands.

Comment

We have recently reported that complexation of $CuCl_2$ by Hpz^tBu in basic MeOH affords a heptacopper aggregate with a double-cubane core structure, which is templated by N—H···Cl hydrogen bonding between the pyrazole ligands and non-coordinated Cl^- anions (Liu *et al.*, 2002). As an extension of this work, we were keen to determine the products of similar reactions using other transition metal halide precursors. We report here the title compound, (I), which we isolated in moderate yield from an otherwise identical procedure using $FeCl_3$ as starting material. Our isolation of (I) contrasts with a report of a very similar reaction using unsubstituted pyrazole as ligand, which instead afforded a unique octanuclear aggregate containing bridging oxo and pyrazolide groups (Raptis *et al.*, 1999). Unsymmetrical diiron complexes containing the $[FeOX_3]^-$ moiety (X^- is Cl^- or Br^-) have been described previously (Gómez-Romero *et al.*, 1989, 1990; Wang *et al.*, 1996; James *et al.*, 1997; Ondrejkovičová *et al.*, 1998*a*,*b*), most relevantly in $[Fe_2OCl_4tz_4]$ (tz is thiazole; James *et al.*, 1997).

The asymmetric unit of (I) contains one molecule of the complex lying on a general position, with the two Fe centres linked by a bent oxo bridge having an Fe1—O3—Fe2 angle that is within the usual range for compounds containing $[FeOCl_3]^-$ centres (tabulated in Ondrejkovičová *et al.*, 1998*b*). The failure of atom Fe1 to achieve perfect C_{3v} symmetry is seen in small variations in the Fe1—Cl bond lengths; the differences between individual Fe1—Cl distances are in the range 0.0042 (7)–0.0088 (7) Å. These differences may be related to the hydrogen bonds accepted by these three Cl^- donors (see below), since there is a perfect correlation between each Fe1—Cl bond length (Table 1) and the strength of the hydrogen bond accepted by that Cl atom, as expressed by its N—H···Cl angle (Table 2). However, this suggestion remains to be confirmed, since $[Fe_2OCl_4tz_4]$ (James *et al.*, 1997) and other compounds containing the $[FeOCl_3]^-$ moiety that do not possess hydrogen bonding to the Cl^- ligands (Ondrejkovičová *et al.*, 1998*b*) also show unequal Fe—Cl bond lengths.



(I)

The local geometry at Fe2 is approximately C_{4v}, but with a distribution of Fe2—N bond distances; while Fe2—N17 and Fe2—N35 are metrically equivalent, Fe2—N8 is shorter than the average of these two bonds by 0.012 (2) Å, and Fe2—N26 is longer by 0.019 (2) Å. A similar spread of Fe—N distances is also exhibited by $[Fe_2OCl_4tz_4]$ (James *et al.*, 1997). The Fe2—Cl7 bond is longer than the Fe1—Cl bonds by an average of 0.1755 (10) Å, which should reflect both the higher coordination number at Fe2 and the strong *trans* influence of the bridging oxo ligand.

While all the pyrazole rings are coordinated as the 5-substituted tautomer, the N35–C43 ligand is rotated by *ca* 180° about the Fe2—N35 bond relative to the other three Hpz^tBu ligands. This is related to the intramolecular hydrogen bonding within the compound (see below).

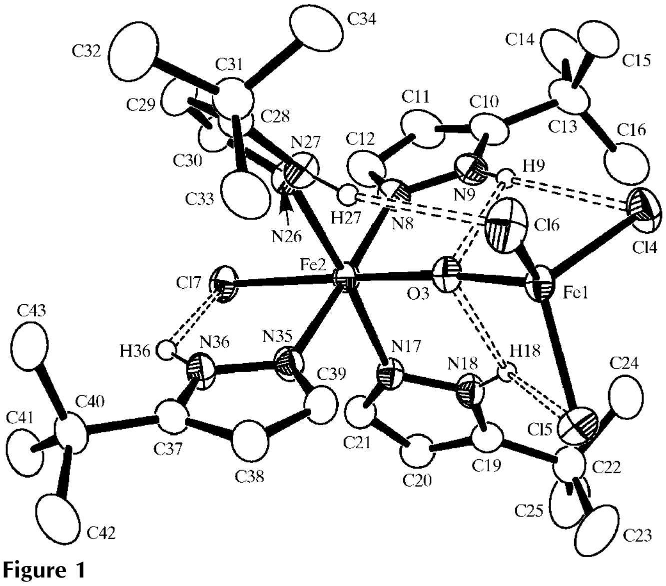


Figure 1
A view of the molecular structure of (I) with 50% probability displacement ellipsoids, showing the atom-numbering scheme employed. All C-bound H atoms have been omitted for clarity.

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The four pyrazole ligands in (I) form intramolecular N—H···*X* (*X* is O or Cl) hydrogen bonds to different acceptors in the molecule. Three of these NH groups interact with atom O3 and/or a Cl^- ligand bound to Fe1. Atoms H9 and H18 form bifurcated hydrogen bonds to atom O3 and atoms Cl4 and Cl5, respectively. While the N9—H9···Cl4 interaction is quite short and close to being linear, the N18—H18···Cl5 contact is much longer and is substantially bent, to the extent that this should be considered a very weak interaction. In contrast, atom H27 forms a near-linear hydrogen bond to atom Cl6 only. The irregularity of the hydrogen bonds formed by these three pyrazole groups reflects the poor complementarity between hydrogen-bond donors bound to a near-C_{4v}-symmetric metal centre, with N—Fe2—N angles of *ca* 90°, and hydrogen-bond acceptors at a C_{3v}-symmetric centre, related by *ca* 109.5°. The fourth pyrazole N—H atom, H36, forms a hydrogen bond to Cl7. There are no noteworthy intermolecular contacts within the crystal lattice.

Experimental

To a solution of $FeCl_3$ (0.32 g, 2.0 mmol) in MeOH (30 ml) was added an MeOH (30 ml) solution of 3{5}-*tert*-butylpyrazole (0.49 g, 4.0 mmol) and NaOH (0.080 g, 2.0 mmol). The mixture was stirred at room temperature for 2 h and then evaporated to dryness. The residue was dissolved in a minimum volume of CH_2Cl_2, and the filtered extracts were layered with pentane to give dark-brown crystals of (I) (yield: 0.28 g, 37%). Analysis found: C 43.9, H 6.2, N 14.8%; calculated for $C_{28}H_{48}Cl_4Fe_2N_8O$: C 43.9, H 6.3, N 14.6%.

Crystal data

$[Fe_2Cl_4O(C_7H_{12}N_2)_4]$
$M_r = 766.24$
Triclinic, $P\bar{1}$
$a = 10.3075$ (1) Å
$b = 10.9284$ (1) Å
$c = 17.3424$ (2) Å
$\alpha = 87.5556$ (4)°
$\beta = 88.8661$ (4)°
$\gamma = 89.3366$ (5)°
$V = 1951.25$ (3) $Å^3$
$Z = 2$
$D_x = 1.304$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 44 449 reflections
$\theta = 2.7$–27.5°
$\mu = 1.05$ mm^{-1}
$T = 150$ (2) K
Rectangular prism, brown
0.43 × 0.30 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Area-detector scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.661$, $T_{max} = 0.818$
44 449 measured reflections
8944 independent reflections
8129 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.091$
$S = 1.03$
8944 reflections
401 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 1.185P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.68$ e $Å^{-3}$
$\Delta\rho_{min} = -0.46$ e $Å^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0074 (11)

Table 1
Selected interatomic distances (Å).

Fe1—O3	1.7710 (11)	Fe2—N8	2.1280 (14)
Fe1—Cl5	2.2168 (5)	Fe2—N17	2.1395 (14)
Fe1—Cl6	2.2214 (5)	Fe2—N26	2.1592 (14)
Fe1—Cl4	2.2256 (5)	Fe2—N35	2.1407 (14)
Fe2—O3	1.8243 (11)	Fe2—Cl7	2.3968 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N9—H9···O3	0.88	2.45	2.8885 (19)	112
N9—H9···Cl4	0.88	2.76	3.6265 (16)	170
N18—H18···O3	0.88	2.46	2.9122 (18)	113
N18—H18···Cl5	0.88	3.03	3.7117 (16)	135
N27—H27···Cl6	0.88	2.54	3.3945 (15)	165
N36—H36···Cl7	0.88	2.59	3.1392 (15)	122

All H atoms were placed in calculated positions and were refined using a riding model. The constraints employed were as follows: Csp^2—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, C_{methyl}—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, and N—H = 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1491). Services for accessing these data are described at the back of the journal.

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