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Dichloro[*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)benzene-1,4-diamine]iron(II)

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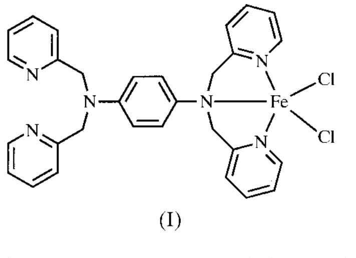
In the title complex, $[FeCl_2(C_{30}H_{28}N_6)]$, the Fe atom is five-coordinated by two terminal chloride ligands and one end of the bis-tridentate ligand. The complexes display intermolecular C—H⋯π, π-stacking and C—H⋯*X* (*X* = N, Cl) interactions.

Comment

The ligand *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)benzene-1,4-diamine (1,4-tpbd) is capable of forming both mono- and dinuclear complexes (Buchen *et al.*, 1997; Hazell *et al.*, 1998). Also, the coordination of octahedral metal ions as connectors between the tridentate bis(2-pyridylmethyl)amine ends of two 1,4-tpbd ligands should make possible the formation of one-dimensional coordination polymers. The title complex, (I), was obtained in the course of our efforts to access an iron(II)-containing polymer. Such a polymeric complex may be particularly interesting due to the similarity of the N_6 environment to well known mononuclear spin-crossover systems (Gütlich *et al.*, 1994). The reaction of several iron(II) salts with 1,4-tpbd has led to the precipitation of yellow powders which have shown a 1:1 ligand–metal stoichiometry by elemental analysis, commensurable with either mononuclear or coordination polymeric structures (dinuclear could be excluded on this basis). The title compound, (I), was obtained as a yellow crystalline material from the reaction of iron(II) chloride with 1,4-tpbd and the structure reported here shows it to be monomeric. The cell parameters and space group are similar to the Zn analogue (Hazell *et al.*, 1998), however, the packing of the complexes in the two structures differs to some extent, and thus the two structures are not strictly isostructural.



(I)

A search of the Cambridge Structural Database (update 5.19, April 2000; Allen & Kennard, 1993) reveals that (I) is only the third example of pentacoordinated iron(II) with an N_3Cl_2 ligand set (Small *et al.*, 1998; Britovsek *et al.*, 1998; Hemmert *et al.*, 1999). The geometry around the Fe atom (Table 1) is best described as being closer to square pyramidal (with Cl1 at the apex) than trigonal bipyramidal, although the geometry is more distorted from square pyramidal compared with the two other pentacoordinated iron(II) complexes with N_3Cl_2 coordination spheres. The sum of the C—N—C angles around the uncoordinated phenylenediamine N atom is 359.1 (9)°, and C16—N4 is only 1.386 (9) Å, indicating a π delocalization of this amine N atom lone pair with the aromatic system. In contrast, the corresponding values for the coordinated amine N atom are 335.8 (10)° and 1.475 (8) Å, respectively.

The H-shaped complexes are interdigitated and display C—H⋯π interactions between a CH group of a coordinated pyridyl ring of one complex and the benzene ring of another [closest contact: C4⋯C14^{iv} = 3.620 (9) Å, H4*A*⋯C14^{iv} = 2.69 Å, C4—H4*A*⋯C14^{iv} = 165°; symmetry code: (iv) *x* + 1, *y*, *z*]. This pyridyl ring also engages in π-stacking interactions with a coordinated pyridyl of this second complex [closest non-hydrogen interaction: C5⋯C12^{iv} = 3.34 (1) Å], which in turn engages in a π-stacking interaction with an uncoordinated pyridyl ring of a third complex [closest non-hydrogen interaction: C11⋯C24^{v} = 3.28 (1) Å; symmetry code: (v) *x*, *y*, *z* + 1]. There are also a number of close C—H⋯*X* intermolecular contacts between both aromatic and aliphatic H atoms and the uncoordinated pyridyl N atoms and the chloride ligands which connect the complexes (Table 2).

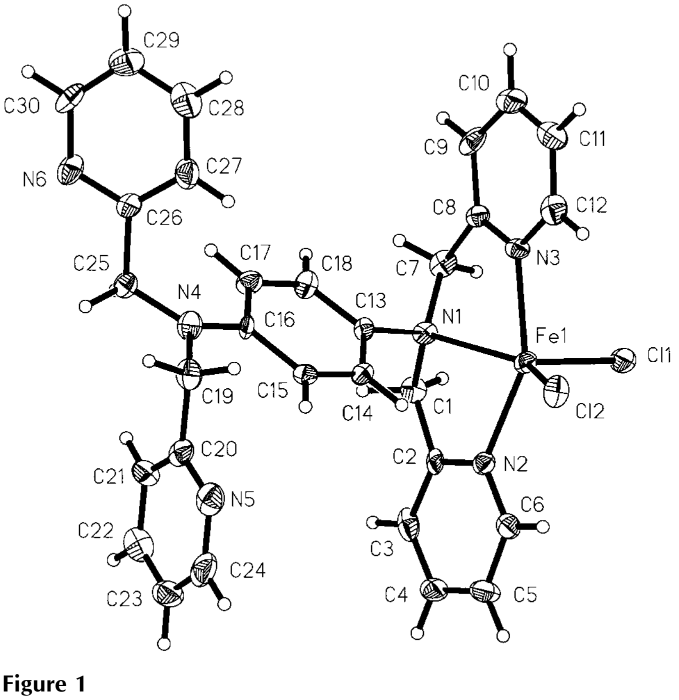


Figure 1
A view of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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Experimental

The title compound was prepared from the 1:1 reaction of anhydrous $FeCl_2$ and 1,4-tpbd in acetonitrile under an inert atmosphere (Hazell *et al.*, 1998). Yellow single crystals suitable for analysis were obtained directly from the reaction mixture.

Crystal data

$[FeCl_2(C_{30}H_{28}N_6)]$
$M_r = 599.33$
Monoclinic, $P2_1$
$a = 8.4470\ (6)$ Å
$b = 12.9100\ (12)$ Å
$c = 12.9850\ (13)$ Å
$\beta = 105.270\ (6)^\circ$
$V = 1366.0\ (2)$ Å^3
$Z = 2$
$D_x = 1.457$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11554 reflections
$\theta = 3.16$–28.26°
$\mu = 0.780$ mm^{-1}
$T = 123\ (2)$ K
Irregular block, yellow
$0.125 \times 0.125 \times 0.075$ mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
11514 measured reflections
3479 independent reflections (plus 1813 Friedel-related reflections)
3608 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.110$
$\theta_{\rm max} = 28.26^\circ$
$h = -9 \rightarrow 11$
$k = -12 \rightarrow 17$
$l = -17 \rightarrow 17$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.080$
$wR(F^2) = 0.156$
$S = 1.061$
5292 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 3.2934P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.03$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.66$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.01 (3)

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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Table 1
Selected geometric parameters (Å, °).

Fe1—N3	2.141 (5)	Fe1—Cl2	2.321 (2)
Fe1—N2	2.152 (5)	Fe1—Cl1	2.329 (2)
Fe1—N1	2.251 (6)		
N3—Fe1—N2	151.4 (2)	N1—Fe1—Cl2	136.3 (2)
N3—Fe1—N1	75.7 (2)	N3—Fe1—Cl1	95.8 (2)
N2—Fe1—N1	75.8 (2)	N2—Fe1—Cl1	96.3 (2)
N3—Fe1—Cl2	98.8 (2)	N1—Fe1—Cl1	110.4 (2)
N2—Fe1—Cl2	100.0 (2)	Cl2—Fe1—Cl1	113.24 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*A*···Cl1$^{\rm i}$	0.95	2.76	3.556 (7)	142
C23—H23*A*···Cl1$^{\rm ii}$	0.95	2.80	3.666 (8)	152
C25—H25*A*···Cl2$^{\rm iii}$	0.99	2.75	3.730 (8)	169
C17—H17*A*···N5$^{\rm iii}$	0.95	2.55	3.42 (1)	153

Symmetry codes: (i) $x-1, y, z$; (ii) $x, y, z-1$; (iii) $-x, \frac{1}{2}+y, -z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1490). Services for accessing these data are described at the back of the journal.

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