

Poly[chlorido- μ_3 -1,2,4-triazolato-iron(II)]

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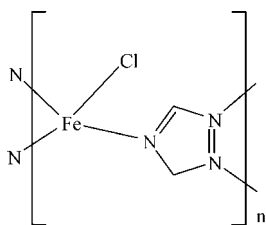
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{N}-\text{C}) = 0.007$ Å; R factor = 0.035; wR factor = 0.123; data-to-parameter ratio = 15.8.

The title compound, $[\text{Fe}(\text{C}_2\text{H}_2\text{N}_3\text{Cl})]_n$, was prepared from a hydrothermal reaction of iron(II) chloride and 1,2,4-triazole. It is isostructural with its Mn^{II} , Co^{II} , Ni^{II} and Zn^{II} analogues. The Fe^{II} cation shows a slightly distorted square-based pyramidal coordination environment, being surrounded by three crystallographically independent N atoms of three different triazolate ligands and a chloride ligand. A polymeric layer is formed by the triply bridging nature of the 1,2,4-triazolate ligand, which is bonded to three different Fe atoms through its three N atoms. The layer contains both binuclear units and tetranuclear units. In the binuclear units, two Fe atoms are bridged by two nearly coplanar triazolate groups through the 1,2-positions, affording a six-membered ring around an inversion center. Each binuclear unit is further connected to four parallel units through the coordination of the N atoms of the triazolate groups. Four adjacent units, which are pairwise parallel, afford 16-membered tetranuclear units, in each of which the two nearest-neighbor Fe atoms are bridged by a single triazolate group through the 1,4-positions.

Related literature

For background information, see: Evans *et al.* (2001); Evans & Lin (2001); Honma *et al.* (2001); Jannasch (2003); Javaid *et al.* (2001); Sudik *et al.* (2005); Kitaura *et al.* (2002); Rowsell *et al.* (2004); Sanchez *et al.* (2003); Vioux *et al.* (2004). For the isostructural compounds, see: Mn^{II} (Gao *et al.*, 2007a); Co^{II} (Ouellette *et al.*, 2006); Ni^{II} (Gao *et al.*, 2007b); Zn^{II} (Kröber *et al.*, 1995). For related literature, see: Ngo *et al.* (2004).



Experimental

Crystal data

$[\text{Fe}(\text{C}_2\text{H}_2\text{N}_3\text{Cl})]$	$V = 529.3$ (2) Å ³
$M_r = 159.37$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.202$ (2) Å	$\mu = 3.21$ mm ⁻¹
$b = 9.671$ (1) Å	$T = 293$ (2) K
$c = 8.947$ (1) Å	$0.15 \times 0.15 \times 0.15$ mm
$\beta = 99.49$ (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	4311 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	1025 independent reflections
$T_{\text{min}} = 0.644$, $T_{\text{max}} = 0.644$	927 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	65 parameters
$wR(F^2) = 0.123$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.69$ e Å ⁻³
1025 reflections	$\Delta\rho_{\text{min}} = -0.81$ e Å ⁻³

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2027).

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supplementary materials

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Comment

Hybrid organic-inorganic materials occupy a prominent position by virtue of their applications in catalysis, optical materials, membranes, and sorption (Ngo *et al.*, 2004; Evans *et al.*, 2001; Vioux *et al.*, 2004; Sanchez *et al.*, 2003; Evans & Lin, 2001; Jannasch, 2003; Javaid *et al.*, 2001; Honma *et al.*, 2001; Sudik *et al.*, 2005; Rowsell *et al.*, 2004; Kitaura *et al.*, 2002). The design of organic-inorganic hybrid materials is conceived of the metal, metal cluster, or metal oxide substructure as a node from which rigid or flexible multitopic organic ligands radiate to act as tethers to adjacent nodes in the bottom-up construction of complex extended architectures. While a variety of organic molecules have been investigated as potential tethers, materials incorporating multitopic carboxylates and pyridine ligands have witnessed the most significant development. However, ligands offering alternative tether lengths, different charge-balance requirements, and orientations of donor groups may afford advantages in the design of materials. One such ligand is 1,2,4- triazole, a member of the polyazaheteroaromatic family of compounds, which exhibit an extensively documented ability to bridge metal ions to afford polynuclear compounds. Triazole is an attractive ligand for the design of novel hybrid materials because of the unusual structural diversity associated with the di- and trinucleating properties of the neutral and anionic ligand forms, respectively. Herein, one new complex, [(1,2,4-triazolato) iron(II) chloride]_n, obtained from 1,2,4-triazole and iron dichloride under hydrothermal reaction is reported, which is iso-structural to reported ones (Gao *et al.*, 2007a,b; Ouellette *et al.*, 2006; Kröber *et al.*, 1995).

The coordination polyhedron of the iron atom is shown in Fig. 1 and can be described as a slightly distorted tetrahedron. The iron cation is surrounded by three crystallographically independent nitrogen atoms belonging to three different triazolato ligands, and a chlorine atom. The Fe—N bond lengths are in the range of 1.998–2.022 Å, very close to each other. The Fe—Cl bond length is 2.238 Å. The bond angles around the iron atom are in the range of 106.47 to 113.23 Å. The polymeric layers as shown in Fig. 2 is formed due to the triply bridging nature of the 1,2,4-triazolato moieties. The 1,2,4-triazolato ligand is simultaneously bound to three different iron atoms through its three nitrogen atoms, and its symmetry is very close to C_{2v}. A layer contains both binuclear units and tetranuclear cavities. In the binuclear unit two iron atoms are bridged by two nearly coplanar triazolato groups through the 1,2-positions, affording a six-membered ring around an inversion center; the Fe···Fe separation within the binuclear unit is equal to 3.781 Å. The chlorine atoms bonded to the metals of a binuclear unit point out in opposite parallel directions. Each binuclear unit is further connected to four parallel units through the four positions of the triazolato groups. Four adjacent units, which are pairwise parallel, afford sixteen-membered tetranuclear cavities. In such a cavity the two nearest neighbor iron atoms are bridged by a single triazolato group through the 1,4 positions with Fe···Fe separations of 5.785 and 6.202 Å.

Experimental

All chemicals were used as purchased from Shanghai Chemical Co. Ltd. A mixture of iron(II) dichloride (0.5 mmol), potassium hydroxide (0.5 mmol), 1,2,4-triazole (0.5 mmol) and H₂O (8 ml) in a 25 ml Teflon-lined stainless steel autoclave was kept at 413 K for 2 d, and then cooled to room temperature. Colorless crystals of (I) were obtained in a yield of 36%. Anal. Calc. for C₂H₂ClN₃Fe: C 15.06, H 1.25, N 26.35%; Found: C 15.01, H 1.28, N 26.31%.

Refinement

H atoms were placed in calculated positions with a C—H bond distance of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ of the respective carrier atom.

Figures

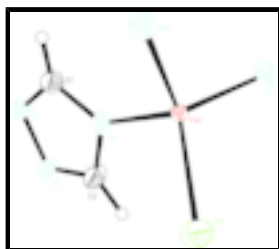


Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids for non-H atoms. Atoms labeled with *i* are at the symmetry position $(-x + 1/2, y - 1/2, -z + 3/2)$.

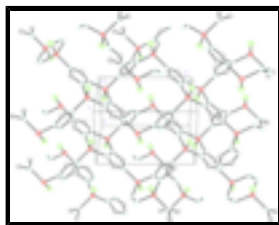


Fig. 2. View of a layer showing both the binuclear units and the tetranuclear cavities.

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Crystal data

[Fe(C₂H₂N₃)Cl]

$M_r = 159.37$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 6.202$ (2) Å

$b = 9.671$ (1) Å

$c = 8.947$ (1) Å

$\beta = 99.49$ (2)°

$V = 529.3$ (2) Å³

$Z = 4$

$F_{000} = 312$

$D_x = 2.000$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1025 reflections

$\theta = 3.1$ – 26.0 °

$\mu = 3.21$ mm⁻¹

$T = 293$ (2) K

Cube, colourless

$0.15 \times 0.15 \times 0.15$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

φ and ω scans

1025 independent reflections

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

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 26.0$ °

$\theta_{\text{min}} = 3.1$ °

Absorption correction: multi-scan
(SADABS; Bruker, 2001)
 $T_{\min} = 0.644$, $T_{\max} = 0.644$
4311 measured reflections

$h = -7 \rightarrow 7$
 $k = -11 \rightarrow 11$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.123$
 $S = 1.00$
1025 reflections
65 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0735P)^2 + 2.4001P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.011$
 $\Delta\rho_{\max} = 0.69 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.81 \text{ e } \text{\AA}^{-3}$
Extinction correction: SHELXL97 (Sheldrick, 1997),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.056 (6)

Special details

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2400 (9)	0.1685 (5)	0.7715 (6)	0.0378 (12)
H1	0.2470	0.1525	0.8747	0.045*
C2	0.2880 (9)	0.2541 (5)	0.5621 (6)	0.0416 (13)
H2	0.3366	0.3108	0.4906	0.050*
Cl1	0.8065 (3)	0.44652 (18)	0.67320 (19)	0.0532 (5)
Fe1	0.54401 (9)	0.41944 (6)	0.81489 (6)	0.0185 (3)
N1	0.3731 (8)	0.5915 (4)	0.8358 (5)	0.0356 (10)
N2	0.3415 (8)	0.6475 (5)	0.9728 (5)	0.0385 (11)
N3	0.3433 (7)	0.2724 (5)	0.7140 (5)	0.0368 (10)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.051 (3)	0.036 (3)	0.025 (2)	-0.004 (2)	0.003 (2)	-0.001 (2)
C2	0.055 (3)	0.035 (3)	0.033 (3)	-0.013 (3)	0.001 (2)	0.003 (2)
C11	0.0527 (9)	0.0605 (10)	0.0507 (9)	-0.0044 (7)	0.0211 (7)	0.0023 (7)
Fe1	0.0237 (4)	0.0162 (4)	0.0149 (4)	0.0005 (2)	0.0011 (2)	-0.0015 (2)
N1	0.043 (3)	0.035 (2)	0.027 (2)	0.0024 (18)	0.0013 (18)	-0.0041 (17)
N2	0.050 (3)	0.035 (2)	0.029 (2)	0.005 (2)	0.0025 (19)	-0.0028 (18)
N3	0.044 (2)	0.030 (2)	0.035 (2)	-0.0035 (18)	0.0032 (19)	-0.0020 (18)

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

C1—N1 ⁱ	1.322 (7)	Fe1—N1	1.998 (4)
C1—N3	1.339 (7)	Fe1—N3	2.004 (4)
C1—H1	0.9300	Fe1—N2 ⁱⁱ	2.022 (4)
C2—N2 ⁱ	1.312 (7)	N1—C1 ⁱⁱⁱ	1.322 (7)
C2—N3	1.356 (7)	N1—N2	1.383 (6)
C2—H2	0.9300	N2—C2 ⁱⁱⁱ	1.312 (7)
C11—Fe1	2.2375 (17)	N2—Fe1 ⁱⁱ	2.022 (4)
N1 ⁱ —C1—N3	112.0 (4)	N2 ⁱⁱ —Fe1—C11	113.23 (14)
N1 ⁱ —C1—H1	124.0	C1 ⁱⁱⁱ —N1—N2	106.7 (4)
N3—C1—H1	124.0	C1 ⁱⁱⁱ —N1—Fe1	128.9 (4)
N2 ⁱ —C2—N3	112.6 (5)	N2—N1—Fe1	124.3 (3)
N2 ⁱ —C2—H2	123.7	C2 ⁱⁱⁱ —N2—N1	105.5 (4)
N3—C2—H2	123.7	C2 ⁱⁱⁱ —N2—Fe1 ⁱⁱ	125.6 (4)
N1—Fe1—N3	109.48 (19)	N1—N2—Fe1 ⁱⁱ	128.9 (3)
N1—Fe1—N2 ⁱⁱ	106.75 (18)	C2—N3—C1	103.2 (4)
N3—Fe1—N2 ⁱⁱ	106.97 (19)	C2—N3—Fe1	125.4 (4)
N1—Fe1—C11	113.72 (15)	C1—N3—Fe1	131.3 (4)
N3—Fe1—C11	106.47 (14)		

Symmetry codes: (i) $-x+1/2, y-1/2, -z+3/2$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+1/2, y+1/2, -z+3/2$.

Fig. 1

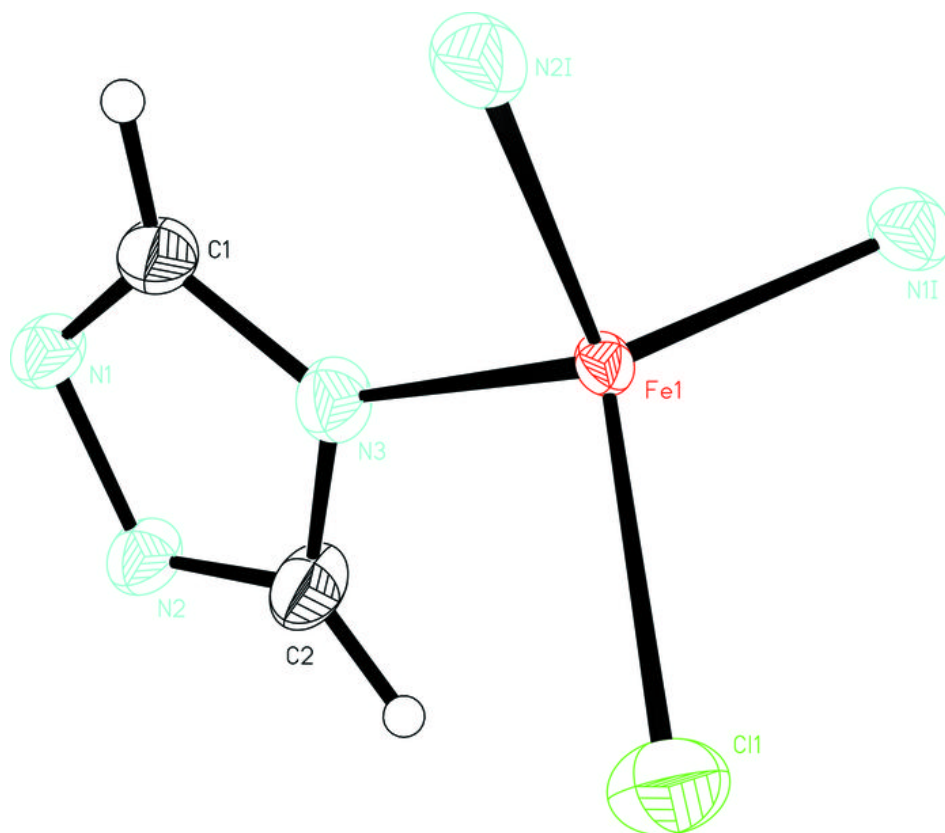


Fig. 2

