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# *cis*-Dichloro[tris(2-benzimidazolylmethyl)amine]iron(III) chloride ethanol dihydrate: hydrogen bonding changing the arrangement of tapes built from $\pi$–$\pi$ and C—H$\cdots\pi$ interactions

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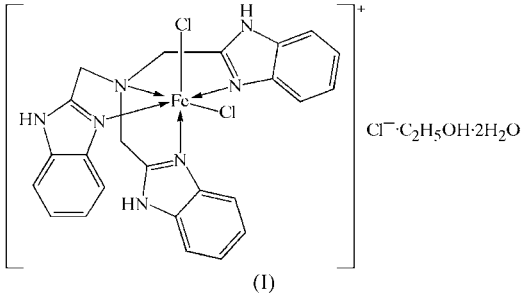
The title compound, $[FeCl_2(C_{24}H_{21}N_7)]Cl\cdot C_2H_5OH\cdot 2H_2O$, comprises an $[FeCl_2(C_{24}H_{21}N_7)]^+$ cation, a $Cl^-$ anion, an ethanol molecule and two water molecules. The cations are linked by $\pi$–$\pi$ and C—H$\cdots\pi$ interactions into one-dimensional tapes, and hydrogen bonding between the cations, $Cl^-$ anions, and ethanol and water molecules links these tapes into a three-dimensional network.

## Comment

Benzimidazole (Bzim) is an important chemical group in the design of antitumour agents (Arrowsmith *et al.*, 2002; Hay *et al.*, 2003), and its metal complexes have been reported as having the functions of the enzymes superoxide dismutase (SOD) (Nishida *et al.*, 1991; Kwak *et al.*, 1999; Liao *et al.*, 2001; Qin *et al.*, 2005) and nuclease (Liu *et al.*, 2004). Because of our interest in these areas, we have prepared the title compound, (I), and determined its crystal structure.




(I)

Compound (I) consists of a *cis*-$[FeCl_2(TBA)]^+$ cation [TBA is tris(2-benzimidazolylmethyl)amine], a $Cl^-$ anion, an ethanol solvent molecule and two water molecules (Fig. 1 and Table 1). In the cation, the four TBA N atoms and two mutually *cis* $Cl^-$ anions coordinate to $Fe^{3+}$. Three TBA N atoms (N1, N2 and N4) and atom Cl1 form an equatorial plane, from which the $Fe^{3+}$ ion is displaced by only 0.067 (1) Å in the direction of Cl2. The two axial sites are occupied by atoms Cl2 and N6 (from TBA). The Fe—N(Bzim) bond lengths [2.095 (2)–2.113 (2) Å] are much shorter than the Fe—N(amine) bond length [2.330 (2) Å]. This is due to the fact that the benzimidazole groups are good $\sigma$ donors and good $\pi$ acceptors compared with the amine (Li *et al.*, 2003).

The Fe—Cl2 bond [2.3299 (9) Å] is significantly longer than the Fe—Cl1 bond [2.2426 (9) Å], due to the different *trans* influences of the tertiary amine and benzimidazole groups (Horng & Lee, 1999). Three TBA N atoms coordinate to $Fe^{3+}$, with angles of 86.00 (9)° for N2—Fe1—N6 and 86.53 (9)° for N4—Fe1—N6, very similar to the values of 84.9 (1) and 86.1 (1)° in $[FeCl_2(TBA)]Cl\cdot 3CH_3OH$ (Pascaly *et al.*, 2000) and 86.9 (2) and 86.8 (2)° in $[FeCl_2(TBA)]ClO_4$ (Kwak *et al.*, 1999). Two benzimidazole rings (N2/N3/C2–C8 and N4/N5/C10–C16) are almost coplanar [dihedral angle = 9.6 (1)°], while the third (N6/N7/C18–C24) lies approximately orthogonal to them, with dihedral angles of 88.4 (1) and 78.9 (1)°, respectively. Overall, therefore, the cation in (I) is structurally very similar to those in the related complexes $[FeCl_2(TBA)]Cl\cdot 3CH_3OH$ and $[FeCl_2(TBA)]ClO_4$.

Although many crystal structures of TBA coordinated to transition metal ions have been reported, there has been little

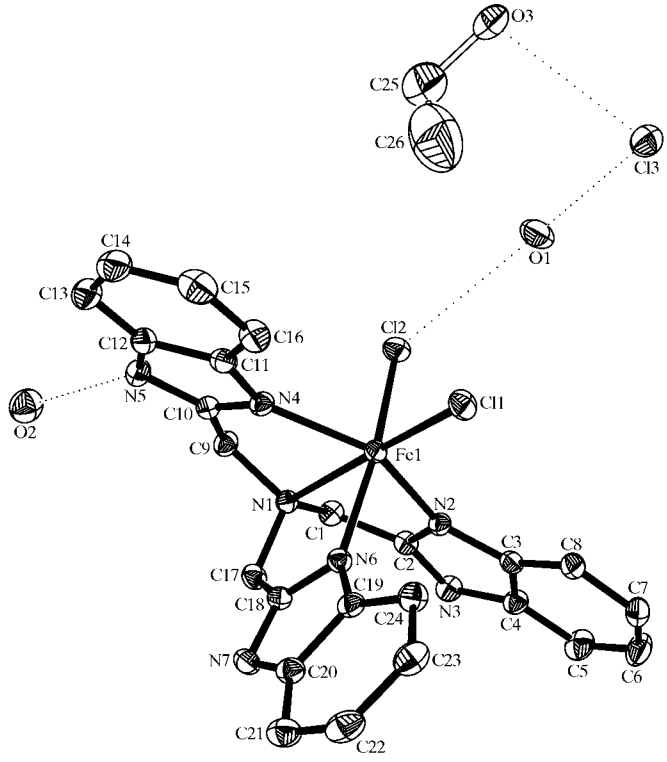



**Figure 1**
A view of the structure of (I), with displacement ellipsoids drawn at the 25% probability level. The minor disorder components and the H atoms have been omitted for clarity. Hydrogen bonds are indicated by dotted lines.

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investigation of non-covalent interactions. Several types of non-covalent interaction organize the molecules of (I) into the supramolecular architecture shown in Figs. 2 and 3. Firstly, two cations interact in an antiparallel tail-to-tail manner *via* $\pi$–$\pi$ and C—H$\cdots\pi$ interactions, which form a loop through four neighbouring benzimidazole groups, linking the $[FeCl_2(TBA)]^+$ cations into ladders which are then cross-linked to form tapes (Fig. 2). This is also observed in

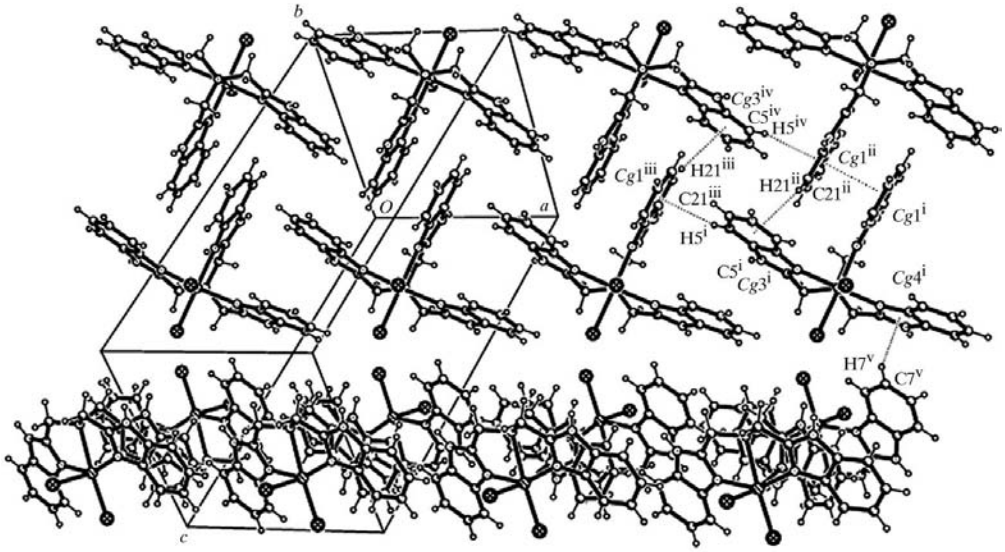


**Figure 2**
The face-to-face $\pi$–$\pi$ and edge-to-face C—H$\cdots\pi$ interactions (dotted lines) and the perpendicular arrangement of the tapes in (I). Fe atoms are shaded, N atoms have a central dot, Cl atoms are large and cross-hatched, C atoms are plain spheres and H atoms are small circles. The minor disorder components have been omitted for clarity. [Symmetry codes: (i) $3+x, y, z$; (ii) $3-x, 2-y, 1-z$; (iii) $2+x, y, z$; (iv) $2-x, 2-y, 1-z$; (v) $3-x, -\frac{1}{2}+y, \frac{3}{2}-z$.]

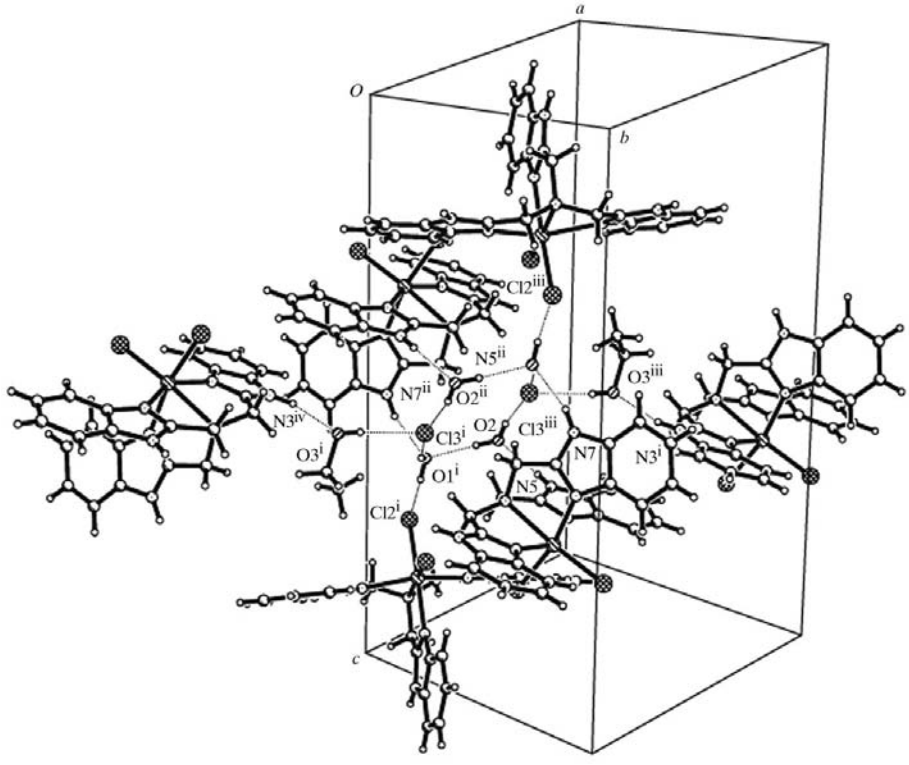


**Figure 3**
A view of the hydrogen-bonding motif in (I). Fe atoms are shaded, N atoms have a central dot, Cl atoms are large and cross-hatched, C atoms are plain spheres and H atoms are small circles. Dotted lines indicate hydrogen bonds. [Symmetry codes: (i) $-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ii) $-x, 1-y, 1-z$; (iii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (iv) $-1-x, 1-y, 1-z$; (v) $1+x, y, z$.]

$[FeCl_2(TBA)]Cl{\cdot}3CH_3OH$ (Pascaly *et al.*, 2000) and both $[FeCl_2(TBA)]ClO_4$ (Kwak *et al.*, 1999), indicating the role of the cation in directing the packing within the crystals. The centroid–centroid distance [$Cg1\cdots Cg2^{i}$; symmetry code: (i) $-x, 2-y, 1-z$] associated with the $\pi$–$\pi$ interaction between the six-membered (C19–C24; centroid *Cg*1) and five-membered rings (N6/C18/N7/C20/C19; centroid *Cg*2) of the antiparallel benzimidazoles is 3.704 (2) Å and the two rings have a perpendicular separation of 3.462 (2) Å. The C$\cdots$*Cg* distances involved in the C—H$\cdots\pi$ interactions are 3.647 (4) [$C5\cdots Cg1^{ii}$; symmetry code: (ii) $-1+x, y, z$] and 3.665 (4) Å [$C21\cdots Cg3^{i}$; *Cg*3 is the centroid of the ring C3–C8].

Secondly, $R_6^6(12)$ hydrogen-bonded rings [$O1/Cl3/O2^{iii}/O1^{iv}/Cl3^{iv}/O2^{v}$; symmetry codes: (iii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $-x, 2-y, 2-z$; (v) $x, \frac{3}{2}-y, \frac{1}{2}+z$] consisting of four water molecules and two $Cl^-$ anions directly connect four and indirectly another two neighbouring cations through ethanol molecules *via* hydrogen bonds (Fig. 3), arranging neighbouring tapes perpendicular to each other and leading to the C—H$\cdots\pi$ interaction, with a $C7\cdots Cg4^{iii}$ (*Cg*4 is the centroid of the ring N4/C10/N5/C12/C11) distance of 3.332 (4) Å between the tapes (Fig. 2).

As a result of the hydrogen-bonding and C—H$\cdots\pi$ interactions, compound (I) forms a three-dimensional supramolecular network. This structural motif is clearly different from those in $[FeCl_2(TBA)]Cl{\cdot}3CH_3OH$ and $[FeCl_2(TBA)]ClO_4$, where the different hydrogen-bonding patterns give tapes arranged in a head-to-head parallel manner *via* $\pi$–$\pi$ interactions, rather than the C—H$\cdots\pi$ interaction ($C7\cdots Cg4$) seen in (I) between the horizontal benzimidazoles of the tapes. Therefore, the $R_6^6(12)$ hydrogen-bonded rings, together with the hydrogen bonds involving ethanol molecules, change the arrangement of the tapes, resulting in C—H$\cdots\pi$ interactions between the cations of the tapes in (I).

## Experimental

All chemicals were of reagent grade, were commercially available and were used without further purification. For the synthesis of the ligand tris(2-benzimidazolylmethyl)amine (TBA), nitrilotriacetic acid (0.479 g, 2.50 mmol) and 1,2-diaminobenzene (0.812 g, 7.50 mmol) were dissolved in glycol (10 ml) and the mixture irradiated intermittently (15 × 1 min) using a WP700 LG microwave oven with an output power of 350 W. The solution was cooled to room temperature, and when distilled water (*ca* 80 ml) was added a yellow precipitate formed immediately. This was filtered off, washed with distilled water and dried in air. IR data (KBr pellet, $\nu$, $cm^{-1}$): 3000–3500 (*w*), 1624 (*ms*), 1591.2 (*ms*), 1436.9 (*s*), 1325 (*ms*), 1274.9 (*s*), 1220.9 (*ms*), 1116.7 (*s*), 1024.1 (*ms*), 968.2 (*ms*), 740.6 (*s*). $FeCl_3{\cdot}6H_2O$ (0.0344 g, 0.125 mmol) was added to a solution of TBA (0.0514 g, 0.125 mmol) in absolute ethanol (10 ml) and the mixture was stirred for 1 h. The clear solution was left at room temperature and red needles of (I) were obtained by slow evaporation of the solvent over several days. IR data (KBr pellet, $\nu$, $cm^{-1}$): 3446 (*w*), 1629.7 (*w*), 1593.1 (*w*), 1548.7 (*w*), 1471.6 (*s*), 1450.4 (*s*), 1390.6 (*ms*), 1325 (*ms*), 1274.9 (*s*), 1218.9 (*ms*), 1049.2 (*s*), 995.2 (*w*), 894.9 (*ms*), 756 (*s*). Elemental analysis found: C 47.79, H 4.80, N 14.70%; calculated for $C_{26}H_{31}Cl_3FeN_7O_3$: C 47.91, H 4.79, N 15.05%.

*Crystal data*

| | |
|---|---|
| $[FeCl_2(C_{24}H_{21}N_7)]Cl{\cdot}C_2H_6O{\cdot}2H_2O$ | $D_x$ = 1.457 Mg $m^{-3}$ |
| $M_r$ = 651.78 | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 2889 reflections |
| $a$ = 10.3541 (12) Å | $\theta$ = 2.4–23.2° |
| $b$ = 13.5873 (15) Å | $\mu$ = 0.82 $mm^{-1}$ |
| $c$ = 21.746 (3) Å | $T$ = 298 (2) K |
| $\beta$ = 103.791 (5)° | Needle, red |
| $V$ = 2971.1 (6) $Å^3$ | 0.44 × 0.06 × 0.06 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART 1K CCD area-detector diffractometer | 5216 independent reflections |
| $\omega$ scans | 3851 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000) | $R_{int}$ = 0.040 |
| $T_{min}$ = 0.715, $T_{max}$ = 0.953 | $\theta_{max}$ = 25.0° |
| 13948 measured reflections | $h = -12 \rightarrow 12$ |
| | $k = -16 \rightarrow 15$ |
| | $l = -25 \rightarrow 14$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)]$ = 0.044 | $w = 1/[\sigma^2(F_o^2) + (0.0616P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.113 | $(\Delta/\sigma)_{max}$ = 0.001 |
| $S$ = 0.97 | $\Delta\rho_{max}$ = 0.45 e $Å^{-3}$ |
| 5216 reflections | $\Delta\rho_{min}$ = −0.27 e $Å^{-3}$ |
| 395 parameters | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Fe1—Cl1 | 2.2426 (9) | Fe1—N2 | 2.095 (2) |
| Fe1—Cl2 | 2.3299 (9) | Fe1—N4 | 2.110 (2) |
| Fe1—N1 | 2.330 (2) | Fe1—N6 | 2.113 (2) |
| | | | |
| Cl1—Fe1—Cl2 | 95.70 (4) | Cl2—Fe1—N6 | 167.44 (7) |
| Cl1—Fe1—N1 | 175.43 (6) | N1—Fe1—N2 | 74.30 (9) |
| Cl1—Fe1—N2 | 107.46 (7) | N1—Fe1—N4 | 74.26 (9) |
| Cl1—Fe1—N4 | 103.77 (7) | N1—Fe1—N6 | 79.03 (9) |
| Cl1—Fe1—N6 | 96.81 (7) | N2—Fe1—N4 | 148.52 (9) |
| Cl2—Fe1—N1 | 88.51 (6) | N2—Fe1—N6 | 86.00 (9) |
| Cl2—Fe1—N2 | 89.21 (7) | N4—Fe1—N6 | 86.53 (9) |
| Cl2—Fe1—N4 | 91.56 (7) | | |

**Table 2**
Geometry of short contacts (Å).

*Cg*1 is the centroid of ring C19–C24, *Cg*2 is the centroid of ring N6/C18/N7/C20/C19, *Cg*3 is the centroid of ring C3–C8 and *Cg*4 is the centroid of ring N4/C10/N5/C12/C11.

| | | | |
|---|---|---|---|
| $Cg1\cdots Cg2^{i}$ | 3.704 (2) | $C7—H7\cdots Cg4^{iii}$ | 3.332 (4) |
| $C5—H5\cdots Cg1^{ii}$ | 3.647 (4) | $C21—H21\cdots Cg3^{i}$ | 3.665 (4) |

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

**Table 3**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N3—H3$\cdots$O3$B^{iv}$ | 0.86 | 1.86 | 2.701 (9) | 165 |
| N3—H3$\cdots$O3$A^{iv}$ | 0.86 | 1.94 | 2.779 (16) | 164 |
| O3$A$—H3$A\cdots$Cl3 | 0.82 | 2.31 | 3.104 (16) | 164 |
| O3$B$—H3$B\cdots$Cl3 | 0.82 | 2.40 | 3.145 (8) | 151 |
| N5—H5$A\cdots$O2 | 0.86 | 2.02 | 2.828 (4) | 156 |
| N7—H7$A\cdots$O1$^{v}$ | 0.86 | 2.00 | 2.831 (4) | 162 |
| O1—H32$\cdots$Cl3 | 0.85 | 2.32 | 3.113 (3) | 155 |
| O1—H31$\cdots$Cl2 | 0.85 | 2.42 | 3.193 (3) | 151 |
| O2—H33$\cdots$O1$^{vi}$ | 0.85 | 2.03 | 2.877 (4) | 170 |
| O2—H34$\cdots$Cl3$^{v}$ | 0.85 | 2.34 | 3.153 (3) | 162 |

Symmetry codes: (iv) $x-1, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (vi) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$.

Atoms C25, C26 and O3 of the ethanol solvent molecule were found to be disordered and were modelled over two sets of positions using restraints on their anisotropic displacement parameters. The major and minor disorder components had refined occupancies of 0.638 (11) and 0.362 (11), respectively. The H atoms attached to C, N and alcohol O atoms of (I) were placed in geometrically idealized positions, with C—H = 0.93–0.97 Å, N—H = 0.86 Å and O—H = 0.82–0.85 Å, and refined with $U_{iso}(H) = 1.2U_{eq}$(parent), except for the H atoms on the O and methyl C atoms of the ethanol molecule, which were refined with $U_{iso}(H) = 1.5U_{eq}$(parent). The water H atoms were located in a difference Fourier map and refined with a global $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3001). Services for accessing these data are described at the back of the journal.

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