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catena-Poly[[diaquadichloroiron(II)]-μ-1,4-dioxane-κ^2O:O']

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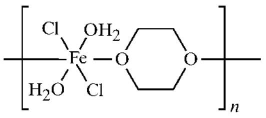
The crystal structure of the title compound, $[FeCl_2(C_4H_8O_2)(H_2O)_2]_n$, contains six-coordinate Fe^{II} atoms in approximately octahedral environments. The Fe^{II} atoms have $\overline{1}$ symmetry, *i.e.* all pairs of identical ligands are *trans*. The structure consists of polymeric chains made up of dioxane molecules, in the chair conformation with $\overline{1}$ symmetry, linking the Fe^{II} centers. The chains are crosslinked by $O-H\cdots Cl$ hydrogen bonds.

Comment

For many years, crystal engineering has utilized the hydrogen bond for the formation of extended networks, thus creating structures with a variety of pore shapes and sizes able to accommodate various guest molecules. Many of the networks that have been reported are neutral. An obvious alternative to neutral frameworks are ionic ones, in particular, cationic frameworks. These could then play host to a variety of negatively charged species of various sizes. It has been suggested that a metal-cation–dioxane network could achieve this (Hasche *et al.*, 2000). A number of structures have been reported involving alkali-metal–dioxane networks (Taube *et al.*, 1993; Eaborn *et al.*, 1997; Kühl *et al.*, 1999, 2000; Hasche *et al.*, 2000). These structures indicate the variety of structures obtainable as a result of variations in the coordination at the metal center; thus, one-dimensional chains, two-dimensional sheets, and three-dimensional networks have all been observed. The only other known extended dioxane–metal structures are chains with hard metal centers, for example, Al^{III} (Boardman *et al.*, 1983), Ga^{III} (Boardman *et al.*, 1984), Mg^{II} (Parvez *et al.*, 1988), Cd^{II} (Almond *et al.*, 1991), Tl^{III} (Jeffs *et al.*, 1983), Nd^{III} (Taube *et al.*, 1996), and Fe^{II} (Müller *et al.*, 1997). Recently, another type of chain structure has been reported where 1,4-dioxane links 1,2-diiodotetrafluoroethane molecules by coordination to the two I atoms (Chu *et al.*, 2001).



(I)

While attempting to extend our work on lithium-containing cationic networks to include iron(II)-containing anions by the reaction of LiCl and $FeCl_2$ in dioxane, only the lithium-free title compound, (I), a one-dimensional polymeric structure, was obtained. This compound contains a pseudo-octahedral six-coordinate Fe^{II} cation with $\overline{1}$ symmetry, coordinated by two *trans* Cl^- ions and two *trans* water molecules. The final two coordination sites are occupied by 1,4-dioxane rings bound through O atoms, as shown in Fig. 1. The O atoms of the dioxane ring, which adopts a chair conformation, bind to two Fe^{II} atoms on either side, with bond distances of 2.1830 (17) Å (Table 1). This coordination results in the formation of chains parallel to *a* and these chains build the backbone of the crystal structure, similar to the case in *catena*-poly[[bis(2,2,6,6-tetramethylheptane-3,5-dionato)iron(II)]-μ-1,4-dioxane] (Müller *et al.*, 1997). In the present case, the iron–dioxane chains are crosslinked by $O_{water}\cdots Cl$ hydrogen bonding (Fig. 2). The hydrogen bonding involves the H atoms located on the coordinated water molecules and the coordinated Cl^- ions on the Fe^{II} atoms of two adjacent chains (Table 2). Each water molecule hydrogen bonds to two Cl^- ions from two adjacent Fe^{II} centers, and each Cl^- ion accepts two hydrogen bonds from two adjacent Fe^{II} centers, *i.e.* an approximately square arrangement with the two Cl and two O atoms at opposite corners, each side representing a hydrogen bond, and each corner bound to a different Fe^{II} atom; an approximately

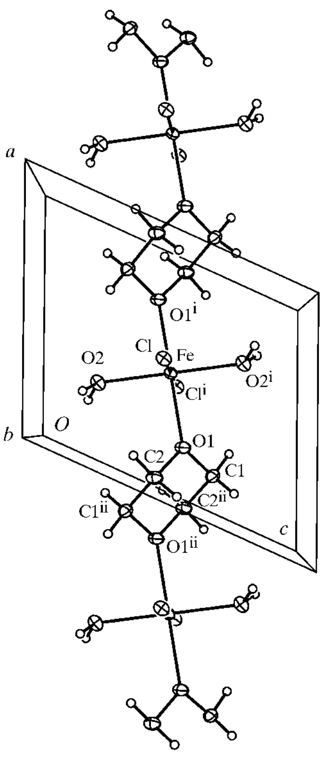


Figure 1
One polymeric chain in (I) parallel to *a*. [Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$.]

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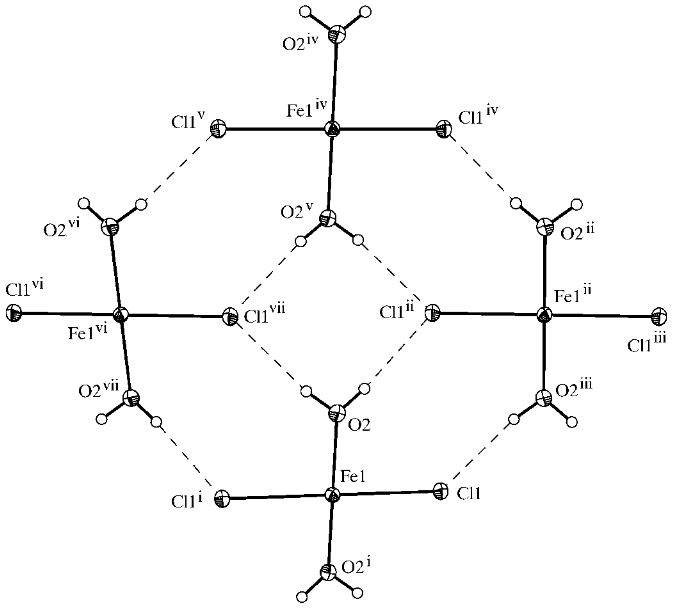

Figure 2
The hydrogen-bonded layer perpendicular to the Fe—O$_{dioxane}$ vector in the polymer chains of (I). Symmetry codes as in Tables 1 and 2, with the addition of (iii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1+x, y, 1+z$; (v) $1-x, 1-y, 1-z$; (vi) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$.

planar FeOClH layer is thus formed perpendicular to the Fe—O$_{dioxane}$ vector within the polymer chain.

Experimental

Anhydrous iron(II) chloride (0.50 g) and lithium chloride (0.50 g) were placed in a 100 ml beaker. 1,4-Dioxane (50 ml) was added and the solution was heated and stirred for 2 h. After filtering off unreacted starting material, the resulting solution was divided among 5 ml vials for evaporation and crystallization.

Crystal data

$[FeCl_2(C_4H_8O_2)(H_2O)_2]$
$M_r = 250.89$
Monoclinic, $P2_1/n$
$a = 6.8590\ (18)$ Å
$b = 9.273\ (2)$ Å
$c = 7.925\ (2)$ Å
$\beta = 114.082\ (5)^\circ$
$V = 460.2\ (2)$ Å^3
$Z = 2$
$D_x = 1.811$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1309 reflections
$\theta = 3.3$–29.2°
$\mu = 2.19$ mm^{-1}
$T = 100\ (1)$ K
Irregular, red–brown
0.20 × 0.20 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: empirical *via* multipole expansion (Blessing, 1995; Sheldrick, 1996)
$T_{min} = 0.364$, $T_{max} = 0.659$
1799 measured reflections
1058 independent reflections
965 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 29.2^\circ$
$h = -9 \rightarrow 7$
$k = -5 \rightarrow 12$
$l = -10 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.094$
$S = 1.05$
1058 reflections
76 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.1903P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	2.1830 (17)	Fe1—Cl1	2.4583 (8)
Fe1—O2	2.0934 (19)		
O1—Fe1—Cl1^{i}	88.65 (5)	O2—Fe1—O1	92.31 (7)
O1—Fe1—Cl1	91.35 (5)	O2—Fe1—Cl1^{i}	89.56 (4)
O2^{i}—Fe1—O1	87.69 (7)	O2—Fe1—Cl1	90.44 (4)

Symmetry code: (i) $-x, 1-y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1A···Cl1^{vii}	0.82 (4)	2.31 (4)	3.1202 (19)	171 (4)
O2—H1B···Cl1^{ii}	0.83 (4)	2.31 (4)	3.1280 (19)	173 (3)

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

Refined C—H distances were in the range 0.98 (3)–1.00 (3) Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1377). Services for accessing these data are described at the back of the journal.

References

Almond, M. J., Beer, M. P., Drew, M. G. B. & Rice, D. A. (1991). *J. Organomet. Chem.* **421**, 129–136.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Boardman, A., Jeffs, S. E., Small, R. W. H. & Worrall, I. J. (1984). *Inorg. Chim. Acta*, **87**, L27–28.
Boardman, A., Small, R. W. H. & Worrall, I. J. (1983). *Acta Cryst.* C**39**, 433–435.
Bruker (1999). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chu, Q., Wang, Z., Huang, Q., Yan, C. & Zhu, S. (2001). *J. Am. Chem. Soc.* **123**, 11069–11070.
Eaborn, C., Farook, A., Hitchcock, P. B. & Smith, J. D. (1997). *Acta Cryst.* C**53**, 1387–1388.
Hasche, S., Mock, C., Otto, J., Schweppe, F., Kirschbaum, K., Krebs, B. & Pinkerton, A. A. (2000). *Inorg. Chim. Acta*, **298**, 9–15.
Jeffs, S. E., Small, R. W. H. & Worrall, I. J. (1983). *Acta Cryst.* C**39**, 1628–1630.
Kühl, O., Sieler, J., Baum, G. & Hey-Hawkins, E. (2000). *Z. Anorg. Allg. Chem.* **626**, 605–607.
Kühl, O., Sieler, J. & Hey-Hawkins, E. (1999). *Z. Kristallogr.* **214**, 496–499.
Müller, H., Seidel, W. & Görls, H. (1997). *Z. Anorg. Allg. Chem.* **623**, 155–158.
Parvez, M., Pajerski, A. D. & Richey, H. G. Jr (1988). *Acta Cryst.* C**44**, 1212–1215.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Taube, R., Windisch, H., Görlitz, F. H. & Schumann, H. (1993). *J. Organomet. Chem.* **445**, 85–91.
Taube, R., Windisch, H., Maiwald, S., Hemling, H. & Schumann, H. (1996). *J. Organomet. Chem.* **513**, 49–61.