Poly[diaqua(*μ₄*-squarato-*O,O′,O″,O‴*)iron(II)]

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In the title compound, [Fe(C₄O₄)(H₂O)₂], each Fe atom is coordinated by four squarate dianions and two water molecules within a slightly distorted octahedron. The Fe atoms and the squarate dianions are located in special positions, whereas the water molecules occupy general positions. There are two crystallographically independent squarate dianions in the asymmetric unit which exhibit a similar geometry. The compound represents a pseudo-polymorphic form of the previously reported Fe squarate dihydrate.

Comment

Recently, we became interested in the synthesis, structures and properties of coordination polymers based on transition metals and aromatic amine ligands. During these investigations, we obtained new transition metal squarates with 4,4′-bipyridine (Näther & Jeß, 2002; Greve, 2000) and pyrazine (Greve, 2000; Näther & Jeß, 2001) as ligands. In the bipyridine compounds, additional water molecules are present; these can be reversible deintercalated and reintercalated, a process which is accompanied by a change of the colour of the material (Näther *et al.*, 2002; Greve, 2000). Depending on the experimental conditions used in the synthesis of the metal squarates, mixtures of the desired compounds and additional phases are obtained. This is the case, for example, for the iron compound poly[[diaqua(*μ₂*-squarato-*O,O′*)(*μ₂*-4,4′-bipyridine)iron(II)] hydrate] (Greve, 2000). To identify the additional phase and to calculate a theoretical powder pattern, we have performed a single-crystal structure analysis. This analysis reveals that a new Fe squarate hydrate was formed. Two similar compounds are known, namely the dihydrate poly[diaqua(*μ₄*-squarato-*O,O′*,*O″*,*O‴*)iron(II)] (Lee *et al.*, 1996) and the tetrahydrate *catena*[tetraaqua(*μ₂*-squarato-*O,O′*)iron(II)] (Frankenbach *et al.*, 1992).

(I)
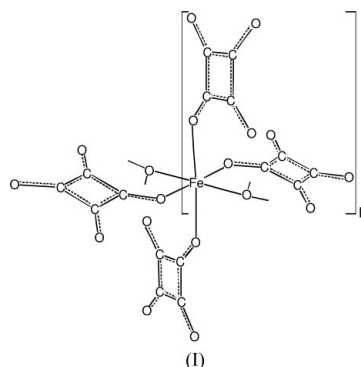
In the structure of the title compound, (I), the Fe atoms are surrounded by four O atoms of two pairs of symmetry-related
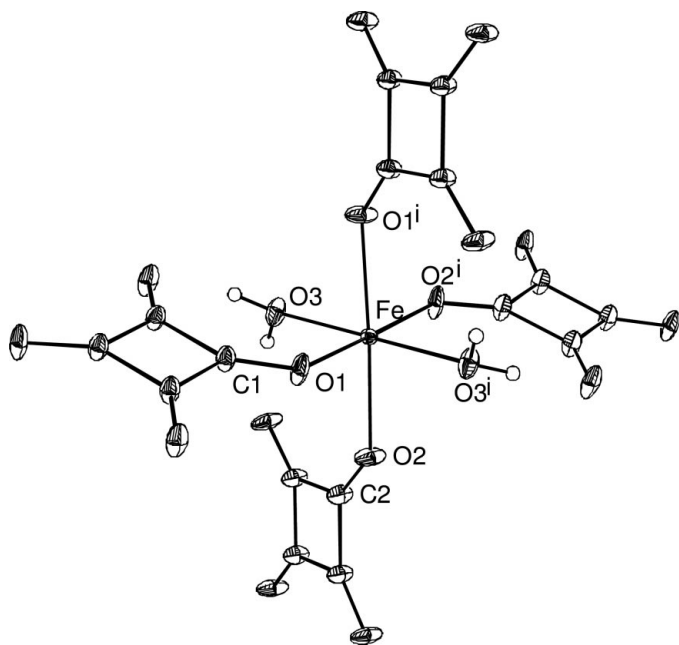
Figure 1
The crystal structure of the title compound, showing the iron coordination, with labelling and with displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) y, x, $-z + \frac{1}{2}$].
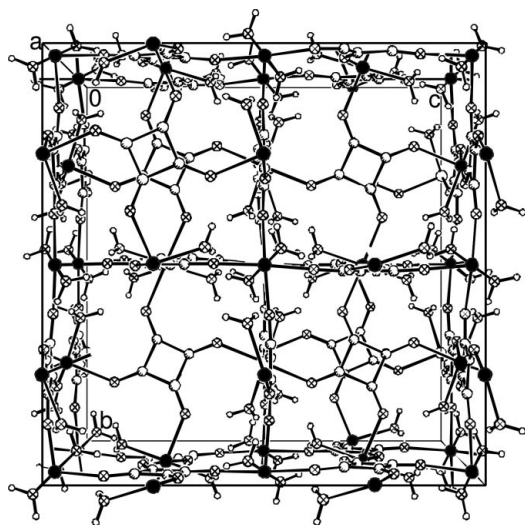
Figure 2
The crystal structure of the title compound, viewed along the crystallographic a axis.

squarate dianions and two water molecules within a slightly distorted octahedron. The Fe atom is located on a twofold rotation axis and the water molecules occupy general positions. There are two crystallographically independent squarate dianions in the asymmetric unit, of which the dianion formed by C1 and O1 is located around a fourfold rotation axis, whereas the second anion, formed by C2 and O2, is located around a fourfold rotoinversion axis. Bond lengths and angles around the Fe atoms are comparable to those obtained for the previously reported Fe squarate dihydrate and tetrahydrate (Lee *et al.*, 1996; Frankenbach *et al.*, 1992). The squarate dianions are coordinated by only one O atom to each metal

centre, and the Fe atoms are oriented in the direction of the lone pairs of the squarate dianions. Altogether, each squarate anion is coordinated to four Fe atoms, forming a three-dimensional coordination network. Within these networks, large cubic voids are found, which are bordered by six squarate dianions. There are hydrogen bonds in the structure between the O atoms of the squarate dianions and the H atoms of the water molecules. Bond lengths and angles indicate a strong interaction. The geometry of the two crystallographically independent squarate dianions is similar and comparable to that found in other metal squarate compounds retrieved from the Cambridge Structural Database (*Conquest*, Version 1.3 of 2002; Allen & Kennard, 1993).

The title compound (Fig. 1) is isotypic with the similar Co (Lee *et al.*, 1996) compound. In this structures, 0.33 molecules of water were found. Also, in (I), there is evidence for some additional solvent in the voids, which was not considered in the structure refinement due to disorder (see *Experimental*). We performed additional thermogravimetric measurements, which show that the compound decomposes completely at about 493 K. Only at this point can the additional water leave the crystal. Owing to its small amount relative to the complete mass loss observed, one cannot determine if additional water is present in the cavities. Therefore, it is difficult to decide whether this compound is a polymorphic form of the previously reported Fe squarate dihydrate (Lee *et al.*, 1996) or a pseudo-polymorphic form if additional solvent is present. In the structure determined by Lee *et al.* (1996), the stoichiometry of the compound is given exactly as $[Fe(C_4O_4)_2(H_2O)_2]$ and there is no evidence for additional solvent molecules or disorder in the structure. Interestingly, this structure is very similar to that of the title compound. In both compounds, the topology of the coordination network is very similar, but differences are found in the orientation of the squarate dianions between successive layers in the structures. This leads to a doubling of the translational period in (I) compared to the dihydrate determined by Lee *et al.* (1996). This is also reflected in the similarity of the lattice parameters. The previously reported dihydrate crystallizes with trigonal symmetry in space group $R\bar{3}$, with $a = 11.4395$ (19) Å and $c = 14.504$ (3) Å. This trigonal unit cell can be transformed into an approximately cubic unit cell with an a axis which is approximately half of that found for (I). However, to be sure that the previously reported Fe squarate dihydrate does not represent a substructure of our compound, we have tried to perform refinement in space group $R\bar{3}$ with the lattice parameters halved. In this case, strong disordering of the squarate dianions is found and the refinement does not work very well. The reason for the occurrence of two different dihydrates is not clear. It might be that the inclusion of solvent molecules into the voids is responsible for this. However, because we have prepared our compound at elevated temperatures, it might also be that our compound is the thermodynamically most stable form at higher temperatures, whereas the previously reported compound is more stable at lower temperatures. However, for a definite decision much more investigation is needed.

Experimental

The title compound was prepared by the reaction of 0.5 mmol iron(II) chloride, 0.5 mmol squaric acid and 0.5 mmol 4,4′-bipyridine in 5 ml of water in a Teflon-lined steel autoclave at 423 K under hydrothermal conditions. After 5 d, the reaction mixture was cooled to room temperature, filtered and washed with water. The precipitate consisted of a mixture of large red crystals of the 4,4′-bipyridine compound poly[[diaqua(μ_2-squarato-O,O')(μ_2-4,4′-bipyridine)iron(II)] hydrate] (Greve, 2000), which were embedded in a yellow microcrystalline powder of the title compound. The compositions of the different phases were determined by X-ray powder diffraction, using Co $K\alpha$ radiation.

Crystal data

[Fe(C$_4$O$_4$)(H$_2$O)$_2$]	Cell parameters from 800
$M_r = 203.92$	reflections
Cubic, $Pn\bar{3}n$	$\theta = 2.5–28°$
$a = 16.3606\ (9)$ Å	$\mu = 2.05$ mm^{-1}
$V = 4379.2\ (4)$ Å^3	$T = 293\ (2)$ K
$Z = 24$	Irregular polyhedron, yellow
$D_x = 1.856$ Mg m^{-3}	$0.30 \times 0.05 \times 0.05$ mm
Mo $K\alpha$ radiation	

Data collection

Stoe IPDS diffractometer	$R_{int} = 0.026$
ω scans	$\theta_{max} = 28.0°$
27 710 measured reflections	$h = -21 \rightarrow 21$
881 independent reflections	$k = -20 \rightarrow 20$
750 reflections with $I > 2\sigma(I)$	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0991P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 5.2645P]$
$wR(F^2) = 0.178$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.18$	$(\Delta/\sigma)_{max} = 0.001$
881 reflections	$\Delta\rho_{max} = 1.08$ e Å^{-3}
51 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Fe—O3^i	2.0819 (17)	Fe—O2^i	2.1414 (17)
Fe—O1	2.1260 (16)		
O3^i—Fe—O3	179.52 (9)	O1^i—Fe—O2^i	87.42 (7)
O3^i—Fe—O1	84.17 (7)	O3^i—Fe—O2	85.69 (7)
O3—Fe—O1	96.18 (7)	O3—Fe—O2	93.98 (7)
O1—Fe—O1^i	90.31 (10)	O1—Fe—O2	87.42 (7)
O3—Fe—O2^i	85.69 (7)	O2^i—Fe—O2	94.92 (10)
O1—Fe—O2^i	176.91 (7)		

Symmetry code: (i) $y, x, \frac{1}{2} - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H1$\cdots$O1^i	0.86	1.91	2.735 (2)	160
O3—H2$\cdots$O2^{ii}	0.86	1.91	2.745 (2)	164

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

The positions of the O—H H atoms were located from a difference Fourier map and then refined as rigid groups with idealized O—H bond lengths of 0.86 Å and fixed isotropic displacement parameters [U_{iso}(H) $= 1.5U_{eq}$(O)]. In the last refinement, significant residual electron density was found in voids of the structure, which presumably corresponds to incorporated clathrate water molecules. The distance between the highest peak in the difference map and the next adjacent atom is 3.74 Å. Several peaks are found with extremely short distances, indicating strong disorder of the clathrate water molecules. A structure refinement using a split model or using the SQUEEZE option for disordered solvent in *PLATON* (Spek, 2002) leads only to slightly improved realibility factors. Therefore, the disordered solvent was not considered in the structure refinement.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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