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Hydrogen bonding and π–π stacking in hexaaquairon(II) bis(4′,7-dimethoxyisoflavone-3′-sulfonate) octahydrate

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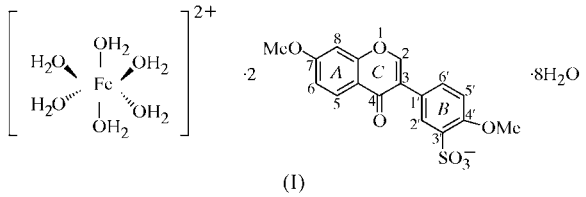
In the structure of the title compound, $[Fe(H_2O)_6](C_{17}H_{13}O_7S)_2\cdot 8H_2O$, 16 hydrogen bonds exist between the centrosymmetric $[Fe(H_2O)_6]^{2+}$ cation, the isoflavone-3′-sulfonate anions and the coordinated and solvent water molecules. π–π stacking interactions between the isoflavone units, hydrogen bonding and electrostatic interactions result in a three-dimensional supramolecular structure.

Comment

Dimethoxydaidzein (4′,7-dimethoxyisoflavone) is found mainly in Leguminosae plants, such as *Wisteria brachybotrys* (Konoshima *et al.*, 1988), the root of *Glycyrrhiza pallidiflora* Maxim (Fukai *et al.*, 1990) and the fruits of *Amorpha fruticosa* (Petkov *et al.*, 1983). It has been shown to be pharmacologically active as an inhibitor of phosphodiesterase (Petkov *et al.*, 1983) and of the Epstein–Barr virus (Konoshima *et al.*, 1988). Oka *et al.* (1989) also found that dimethoxydaidzein can be used to inhibit cancer cells. The biological utilization rate of isoflavonid is low and the dose is high because of its poor solubility. Thus, it is necessary to synthesize a water-soluble derivative of dimethoxydaidzein in order to study its possible biological effects. We have synthesized several derivatives of daidzein, namely sodium 7-methoxy-4′-hydroxyisoflavone-3′-sulfonate (Zhang *et al.*, 2002), sodium 4′,7-dihydroxyisoflavone-3′-sulfonate (Zhang *et al.*, 2003) and sodium 5,7-dihydroxy-4′,6-dimethoxyisoflavone-3′-sulfonate (Zhang *et al.*, 2004), and have studied their crystal structures and biological activities. The results show that isoflavonesulfonates possess better biological activities than their parent compounds. The title compound, (I), is a water-soluble derivative of isoflavone with potential medical applications.



(I)

A molecular representation of the structure of (I) is shown in Fig. 1. The Fe^{II} atom lies on an inversion centre and is coordinated by six water molecules, which form a slightly distorted octahedron. The Fe—O bond lengths fall in the range 2.043 (3)–2.155 (3) Å, and are close to those in both $[Fe(H_2O)_6](C_6H_2N_3O_7)_2\cdot 2H_2O$ and $[Fe(H_2O)_6](NO_3)_2\cdot 2C_6H_{12}N_4\cdot 4H_2O$ [2.024 (1)–2.164 (2) Å; Honda *et al.* (2003) and Zhu *et al.* (2003), respectively].

In the anion, the bond lengths and angles of the isoflavone units are similar to those in the isomorphic compounds $[Co(H_2O)_6]X_2\cdot 8H_2O$ (Zhang *et al.*, 2002) and $[Ni(H_2O)_6]X_2\cdot 8H_2O$ (Wang & Zhang, 2005) (*X* is 4′,7-dimethoxy-

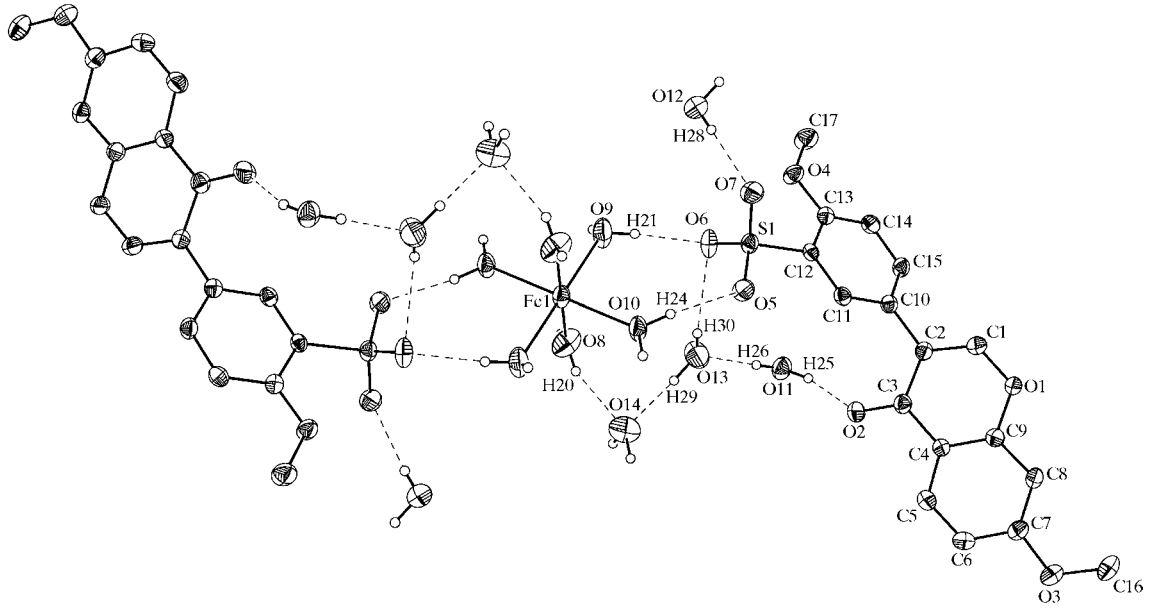


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Thin dashed lines indicate hydrogen bonds. For clarity, the H atoms of the isoflavone skeletons have been omitted.

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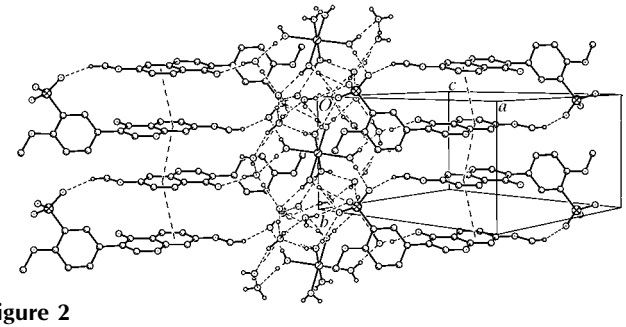

Figure 2
A partial packing diagram for (I), viewed appoximately along the *a* axis. Thin dashed lines indicate hydrogen bonds and π–π stacking interactions.

isoflavone-3′-sulfonate). The atoms of the benzopyranone moiety containing rings *A* (C4–C9) and *C* (C1–C4/C9/O1) display an almost coplanar configuration, with a mean deviation from the least-squares planes of 0.010 (3) Å. To avoid steric conflict, the two rigid ring systems, namely benzene ring *B* (C10–C15) and the benzopyranone moiety, are rotated by 58.09 (13)° with respect to each other. Methoxy atoms C17 and O4 bonded to atom C13 are nearly coplanar with the attached ring *B*, with mean deviations from the least-squares plane of 0.013 (4) and 0.012 (3) Å, respectively. Atom O3 of the other methoxy group bonded to atom C7 is nearly coplanar with its attached *A*/*C* rings, with a mean out-of-plane deviation of 0.012 (2) Å, while atom C16 of this methoxy group is slightly out of the plane [0.094 (4) Å].

One hydrogen-bond chain exists between carbonyl atom O2 and the Fe^{II}-coordinated water molecule O8, bridged by O11—H25···O2, O11—H26···O13, O13—H29···O14 and O8—H20···O14 hydrogen bonds (Fig. 1). Water atom O14 and sulfonate atom O6 are bifurcated and trifurcated, respectively, by hydrogen bonds (Table 1).

The isoflavone skeletons are arranged in an antiparallel fashion, with π–π stacking interactions between rings *A* in a column along the *b* axis (Fig. 2.). A normal range for such interactions is 3.3–3.8 Å (Janiak, 2000). In (I), rings *A* of the isoflavone skeleton form stacks with $Cg\cdots Cg^{i}$ = 3.683 (2) Å and $Cg\cdots Cg^{ii}$ = 3.799 (2) Å, where *Cg*, Cg^{i} and Cg^{ii} are the centroids of rings *A* at (x, y, z), $(1-x, -y, 2-z)$ and $(1-x, 1-y, 2-z)$, respectively. The C16—H16*A*···O5^{vi} hydrogen bond [symmetry code: (vi) $-x+1, -y+1, -z+2$] between isoflavone units builds a supramolecular $R_2^2(28)$ synthon (Etter, 1990). These isoflavone columns are also crosslinked by a C8—H8···O7^{v} hydrogen bond [symmetry code: (v) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$].

Thus, in the crystal structure of (I), the hydrophilic regions are dominated by classical hydrogen bonds, while the columns of isoflavone moieties generate hydrophobic areas, with the sulfonate group bridging the two regions. This combination of hydrogen bonds, π–π stacking and electrostatic interactions between the cations and anions leads to the formation of a three-dimensional supramolecular structure.

Experimental

Sodium 4′,7-dimethoxyisoflavone-3′-sulfonate was synthesized according to the method of Wang & Zhang (2005) and was dissolved (1.0 g) in water (10 ml) and then mixed with a saturated solution (5 ml) of $FeSO_4\cdot 7H_2O$ in water. Crystals of the title compound were obtained after 1 d. On recrystallization from water, single crystals of (I) suitable for X-ray diffraction analysis were obtained by slow evaporation (m.p. 593 K; decomposition).

Crystal data

$[Fe(H_2O)_6](C_{17}H_{13}O_7S)_2\cdot 8H_2O$
M_r = 1030.74
Monoclinic, $P2_1/c$
a = 18.892 (7) Å
b = 7.336 (3) Å
c = 18.357 (7) Å
β = 116.552 (5)°
V = 2275.8 (15) Å^3
Z = 2
D_x = 1.504 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2854 reflections
θ = 2.4–23.6°
μ = 0.52 mm^{-1}
T = 298 (2) K
Needle, colourless
0.46 × 0.18 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.797, T_{max} = 0.922
11468 measured reflections
4000 independent reflections
2643 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 25.0°
$h = -22 \rightarrow 19$
$k = -8 \rightarrow 8$
$l = -16 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.113
S = 1.01
4000 reflections
337 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.9561P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O11—H25···O2	0.87 (4)	1.88 (4)	2.729 (3)	166 (4)
O11—H26···O13	0.80 (4)	1.86 (4)	2.661 (4)	178 (5)
O12—H27···O11^{i}	0.87 (4)	1.92 (4)	2.785 (4)	172 (4)
O12—H28···O7	0.73 (4)	2.27 (4)	2.979 (4)	165 (5)
O8—H19···O6^{ii}	0.80 (2)	2.03 (3)	2.820 (4)	166 (4)
O8—H20···O14	0.76 (4)	1.99 (4)	2.711 (4)	157 (5)
O9—H21···O6	0.81 (4)	2.06 (4)	2.849 (3)	162 (4)
O9—H22···O13^{ii}	0.77 (4)	2.05 (4)	2.794 (5)	161 (5)
O10—H23···O11^{iii}	0.84 (4)	1.90 (4)	2.735 (4)	172 (4)
O10—H24···O5	0.88 (4)	1.96 (4)	2.836 (3)	172 (4)
O13—H29···O14	0.99 (4)	1.78 (4)	2.716 (5)	156 (3)
O13—H30···O6	0.72 (4)	2.33 (4)	2.966 (4)	149 (5)
O14—H31···O12^{iv}	0.97 (4)	1.83 (4)	2.736 (4)	156 (3)
O14—H32···O12^{ii}	0.90 (4)	2.03 (4)	2.843 (5)	149 (4)
C8—H8···O7^{v}	0.93	2.54	3.444 (5)	164
C16—H16*A*···O5^{vi}	0.96	2.51	3.405 (4)	155

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

Water H atoms were located in a difference Fourier map and their positions were refined; the O—H distances are in the range 0.72 (4)–0.97 (4) Å and the atoms were constrained with a common U_{iso}(H) value of 0.080 Å^2. All other H atoms were placed in calculated positions and treated as riding, with C—H distances in the range 0.93–0.96 Å and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1112). Services for accessing these data are described at the back of the journal.

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