

Hydrogen bonding and π - π stacking in methylaminium 4',7-dihydroxyisoflavone-3'-sulfonate dihydrate and hexaaquairon(II) bis(4',7-diethoxyisoflavone-3'-sulfonate) tetrahydrate

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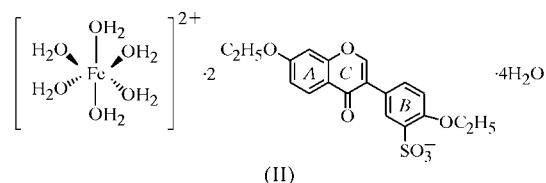
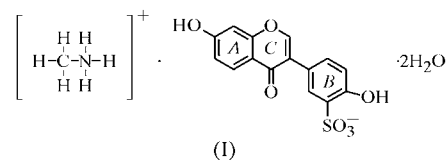
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In methylaminium 4',7-dihydroxyisoflavone-3'-sulfonate dihydrate, $\text{CH}_6\text{N}^+\cdot\text{C}_{15}\text{H}_9\text{O}_7\text{S}^-\cdot 2\text{H}_2\text{O}$, 11 hydrogen bonds exist between the methylaminium cations, the isoflavone-3'-sulfonate anions and the solvent water molecules. In hexaaquairon(II) bis(4',7-diethoxyisoflavone-3'-sulfonate) tetrahydrate, $[\text{Fe}(\text{H}_2\text{O})_6](\text{C}_{19}\text{H}_{17}\text{O}_7\text{S})_2\cdot 4\text{H}_2\text{O}$, 12 hydrogen bonds exist between the centrosymmetric $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ cation, the isoflavone-3'-sulfonate anions and the solvent water molecules. Additional π - π stacking interactions generate three-dimensional supramolecular structures in both compounds.

Comment

Daidzein (4',7-dihydroxyisoflavone), a natural soya isoflavone, is biologically active, with resistance to hypoxia and anoxemia (Meng *et al.*, 1999). However, because the solubility of this isoflavone is poor, its biological utilization rate is low so the dose required is high (Tang *et al.*, 1989). In order to increase



the solubility of the isoflavone, some sulfonated derivatives have been prepared. Sodium 4',7-dihydroxyisoflavone-sulfonate (Liu *et al.*, 2003) and sodium 7-methoxy-4'-hydroxyisoflavone-3'-sulfonate (Zhang *et al.*, 2002) have been synthesized and their crystal structures and biological activities have been studied. The results show that these compounds possess better biological activity than the parent compound daidzein. The water-soluble derivatives $\text{Co}(\text{H}_2\text{O})_6\cdot X_2\cdot 8\text{H}_2\text{O}$ (Zhang & Wang, 2005a), and $\text{Mg}(\text{H}_2\text{O})_6\cdot X_2\cdot 8\text{H}_2\text{O}$ and $\text{Zn}(\text{H}_2\text{O})_6\cdot X_2\cdot 8\text{H}_2\text{O}$ (Zhang & Wang, 2005b) (X is 4',7-diethoxyisoflavone-3'-sulfonate) have been reported. The title compounds, methylaminium 4',7-dihydroxyisoflavone-3'-sulfonate dihydrate, (I), and hexaaquairon(II) bis(4',7-diethoxyisoflavone-3'-sulfonate) tetrahydrate, (II), are water-soluble derivatives of daidzein.

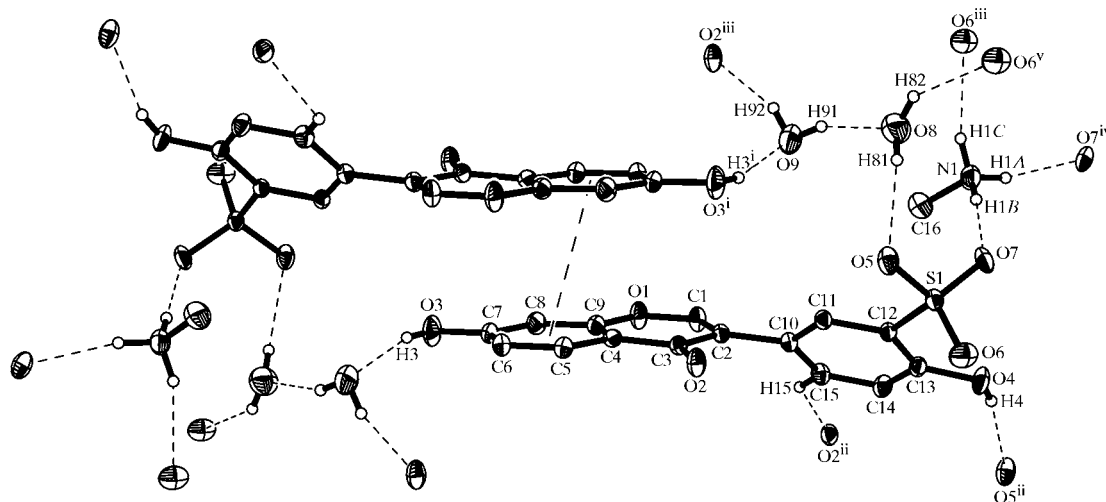


Figure 1

Part of the crystal structure of compound (I), showing the atom-numbering scheme, the dimer being generated by hydrogen bonds and other intermolecular interactions (dashed lines). Displacement ellipsoids are drawn at the 30% probability level. For clarity, some H atoms bonded to atoms not involved in the motif shown have been omitted. For symmetry codes, see Table 1. Unlabelled atoms are related to labelled atoms by the symmetry code $(1-x, 1-y, 1-z)$.

Compound (I) is composed of one CH_3NH_3^+ cation, one 4',7-dihydroxyisoflavone-3'-sulfonate anion and two solvent water molecules (Fig. 1). In the anion, the bond lengths and angles of the isoflavone units are similar to those of the sodium

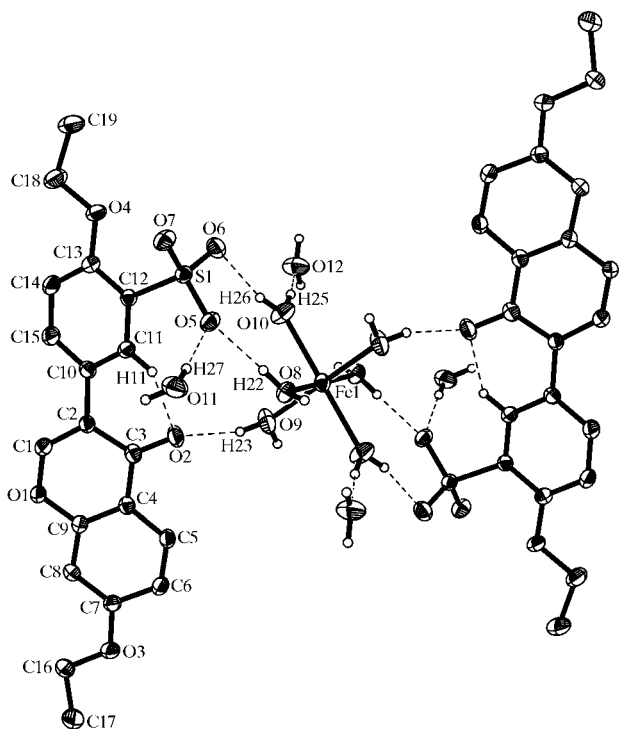


Figure 2

The molecular structure of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Thin dashed lines indicate hydrogen bonds. For clarity, some H atoms of the isoflavone skeletons have been omitted. Unlabelled atoms are related to labelled atoms by the symmetry code $(1-x, 1-y, 1-z)$.

salt (Liu *et al.*, 2003). The atoms of the benzopyranone moiety constitute planar rings *A* (C4–C9) and *C* (C1–C4/C9/O1) [mean out-of-plane deviations are 0.006 (3) and 0.013 (3) Å, respectively], with an interplanar angle of 2.8 (1)°. To avoid intramolecular steric conflicts, the two rigid ring systems, *viz.* benzene ring *B* (C10–C15) and the benzopyranone moiety, are rotated by 43.2 (1)° with respect to one another.

In compound (II), the Fe^{II} atom lies on an inversion centre and is coordinated by six water molecules, which form a slightly distorted octahedron (Fig. 2). The Fe–O bond lengths are in the range 2.066 (2)–2.157 (2) Å, and are close to those in $[\text{Fe}(\text{H}_2\text{O})_6](\text{C}_{17}\text{H}_{13}\text{O}_7\text{S})_2 \cdot 8\text{H}_2\text{O}$ [2.043 (3)–2.155 (3) Å; Zhang & Cheng, 2005]. The atoms of the benzopyranone moiety constitute rings *A* (C4–C9) and *C* (C1–C4/C9/O1) [mean out-of-plane deviations are 0.003 (1) and 0.013 (2) Å, respectively], with an interplanar angle of 0.7 (1)°. The two rigid ring systems, *viz.* benzene ring *B* (C10–C15) and the benzopyranone moiety, are rotated by 24.8 (1)° with respect to each other. One independent C11–H11...O2 intramolecular hydrogen bond forms a characteristic intramolecular *S*(6) motif.

Fig. 1 shows how a cyclic dimer is formed in (I) by O–H...O hydrogen bonding and π – π stacking interactions. One hydrogen-bond chain exists between hydroxyl atom H3ⁱ of one molecule [symmetry code: (i) $1-x, 1-y, 1-z$] and sulfonate atom O5 of another molecule, *viz.* O3ⁱ–H3ⁱ...O9–H9ⁱ...O8–H8ⁱ...O5, pairs of which build a dimeric unit described by the $R_6^6(34)$ synthon (Etter, 1990). Details of other hydrogen bonds are given in Table 1. In the dimer, the isoflavone skeletons are in an antiparallel mode, with π – π stacking interactions between their *A* rings, with an offset distance of 1.127 Å and a $C_g \cdots C_g^i$ distance of 3.610 (5) Å, where C_g and C_g^i are the centroids of rings *A* at (x, y, z) and

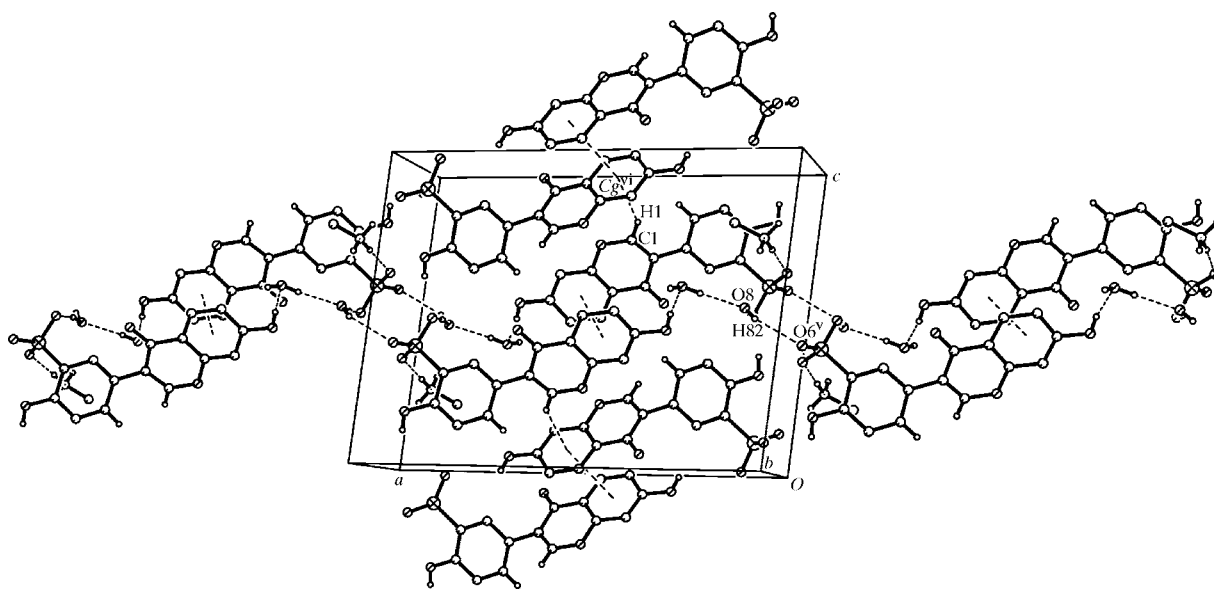


Figure 3

Part of the crystal structure of compound (I), showing the (011) sheet linked by hydrogen bonds to form the three-dimensional supramolecular structure. For clarity, some H atoms bonded to atoms not involved in the motif shown have been omitted. Thin dashed lines indicate hydrogen-bonding and π – π stacking interactions. C_g is the centroid of the C4–C9 ring. See Table 1 for symmetry codes.

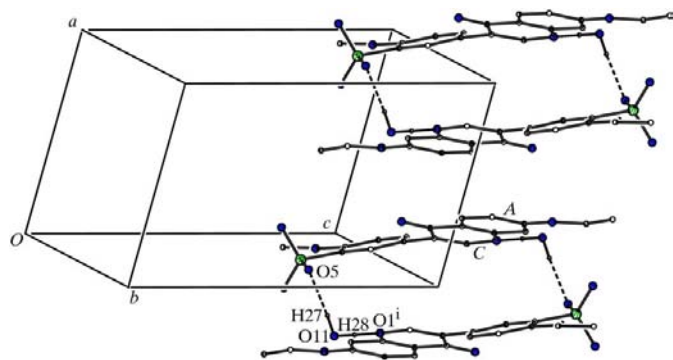


Figure 4
The stacking of the organic anions in compound (II), showing the column along the *a* axis. For clarity, some H atoms have been omitted. [Symmetry code: (i) $-x, 2 - y, 2 - z$.]

($1 - x, 1 - y, 1 - z$), respectively. A normal range for such interactions is 3.3–3.8 Å (Janiak, 2000). The C–H... π (arene), O–H...O and C–H...O hydrogen bonds, which exist between the dimers, assemble the isoflavone units into an approximately two-dimensional (011) sheet linked by paired O8–H82...O6^v hydrogen bonds [symmetry code: (v) $-x, 1 - y, 1 - z$] (Fig. 3). Atom C1 in the molecule at (*x, y, z*) acts as hydrogen-bond donor, *via* axial atom H1, to ring A in the molecule at ($1 - x, \frac{1}{2} + y, \frac{3}{2} - z$), with a H...centroid distance of 2.650 Å. Crosslinks between the sheets are provided by strong N–H...O hydrogen bonds, leading to a three-dimensional supramolecular structure.

In compound (II), each H atom of the six water molecules coordinated to the Fe^{II} atom and of the two solvent water molecules acts as a donor, leading to the formation of hydrogen bonds (Fig. 2). Atoms O2, O5, O6 and O7 are all trifurcated by hydrogen bonds; details of the hydrogen-bond geometry are given in Table 2. Similarly, the isoflavone skeletons of compound (II) are in an almost antiparallel mode and π – π stacking interactions, forming dimers, exist between rings A and C of one molecule and rings C and A of another, with a centroid–centroid distance of 3.720 (2) Å (Fig. 4). The dimers are further linked by paired O11–H27...O5 and O11–H28...O1ⁱ [symmetry codes: (i) $-x, 2 - y, 2 - z$] hydrogen bonds and a column is built along the *a* axis. These columns are also crosslinked by paired C6–H6...O3^{vi} [symmetry code: (vi) $1 - x, 3 - y, 2 - z$] hydrogen bonds, which form an $R_2^2(8)$ synthon, and a three-dimensional supramolecular structure of (II) is generated.

Experimental

Sodium 4',7-dihydroxyisoflavone-3'-sulfonate and sodium 4',7-dithoxyisoflavone-3'-sulfonate were prepared as described by Liu *et al.* (2003) and Zhang & Wang (2005a), respectively. They were dissolved (1 g) in water (10 ml) and then separately mixed with a saturated CH₃NH₃⁺·Cl⁻ solution (5 ml) or an FeSO₄·7H₂O solution (5 ml) in water. Crystals of (I) and (II) were obtained after 2 and 3 d, respectively. On recrystallization from water, single crystals suitable for X-ray diffraction were obtained by slow evaporation (m.p. 585 and 611 K, respectively; decomposition).

Compound (I)

Crystal data

CH₆N⁺·C₁₅H₉O₇S⁻·2H₂O
M_r = 401.38
 Monoclinic, $P2_1/c$
a = 17.852 (13) Å
b = 7.365 (5) Å
c = 13.558 (10) Å
 β = 96.194 (11)°
V = 1772 (2) Å³
Z = 4

D_x = 1.504 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2270 reflections
 θ = 2.3–25.2°
 μ = 0.24 mm⁻¹
T = 298 (2) K
 Rhomboid, colourless
 0.53 × 0.45 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
T_{min} = 0.886, *T_{max}* = 0.952
 8930 measured reflections

3123 independent reflections
 2147 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
 θ_{max} = 25.0°
h = -21 → 10
k = -8 → 8
l = -15 → 16

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.043
wR(*F*²) = 0.123
S = 1.01
 3123 reflections
 246 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.3658P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.27 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °) for (I).

C_g is the centroid of the C4–C9 ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O3–H3...O9 ⁱ	0.82	1.88	2.664 (3)	160
O4–H4...O5 ⁱⁱ	0.82	1.99	2.774 (3)	160
N1–H1B...O7	0.89	2.06	2.950 (4)	174
N1–H1C...O6 ⁱⁱⁱ	0.89	2.09	2.946 (4)	162
N1–H1A...O7 ^{iv}	0.89	2.04	2.918 (3)	168
O8–H81...O5	0.84	2.23	3.043 (4)	163
O8–H82...O6 ^v	0.82	2.30	2.998 (3)	144
O9–H92...O2 ⁱⁱⁱ	0.83	2.09	2.883 (3)	158
O9–H91...O8	0.84	1.98	2.787 (4)	159
C15–H15...O2 ⁱⁱ	0.93	2.49	3.201 (4)	134
C1–H1...C _g ^{vi}	0.93	2.66	3.440 (4)	143

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

Compound (II)

Crystal data

[Fe(H₂O)₆](C₁₉H₁₇O₇S)₂·4H₂O
M_r = 1014.78
 Triclinic, $P\bar{1}$
a = 8.827 (3) Å
b = 10.422 (3) Å
c = 12.803 (4) Å
 α = 88.888 (4)°
 β = 84.952 (4)°
 γ = 74.255 (4)°
V = 1129.2 (6) Å³

Z = 1
D_x = 1.492 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1771 reflections
 θ = 2.6–24.3°
 μ = 0.51 mm⁻¹
T = 298 (2) K
 Needle, colourless
 0.47 × 0.21 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
T_{min} = 0.794, *T_{max}* = 0.913
 5966 measured reflections

3935 independent reflections
 2698 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
 θ_{max} = 25.0°
h = -9 → 10
k = -12 → 11
l = -15 → 15

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.125$
 $S = 1.03$
 3935 reflections
 295 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.3331P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$

Table 2
 Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11–H27 \cdots O5	0.85	2.01	2.853 (4)	175
O11–H28 \cdots O1 ⁱ	0.85	2.57	3.237 (3)	137
O8–H21 \cdots O7 ⁱⁱ	0.85	2.01	2.858 (3)	176
O8–H22 \cdots O5	0.85	1.92	2.773 (3)	178
O9–H23 \cdots O2	0.85	1.84	2.665 (3)	164
O9–H24 \cdots O11 ⁱⁱⁱ	0.85	1.91	2.749 (3)	170
O12–H29 \cdots O7 ⁱⁱⁱ	0.85	2.14	2.885 (3)	147
O12–H30 \cdots O6 ^{iv}	0.85	2.11	2.933 (4)	162
O10–H25 \cdots O12	0.85	1.90	2.723 (4)	164
O10–H26 \cdots O6	0.85	2.11	2.943 (3)	166
C11–H11 \cdots O2	0.93	2.25	2.813 (4)	118
C6–H6 \cdots O3 ^v	0.93	2.57	3.500 (4)	174

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

All H atoms were placed in calculated positions and treated as riding, with $N-H = 0.89 \text{ \AA}$, $O-H = 0.82 \text{ \AA}$, $C-H = 0.93-0.96 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$ for compound (I), and with $O-H = 0.84-0.85 \text{ \AA}$, $C-H = 0.93-0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,O})$ for compound (II).

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3002). Services for accessing these data are described at the back of the journal.

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