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Hexaaquanickel(II) bis(4′,7-dimethoxyisoflavone-3′-sulfonate) octahydrate

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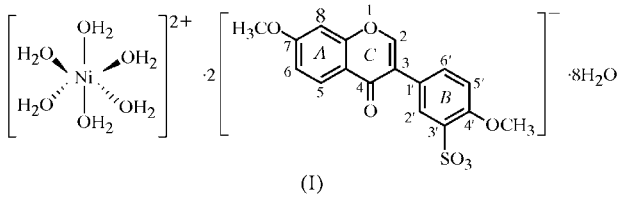
In the title compound, $[Ni(H_2O)_6](C_{17}H_{13}O_7S)_2\cdot 8H_2O$, the Ni^{II} atom is located on an inversion centre in the space group $P2_1/c$. The $[Ni(H_2O)_6]^{2+}$, $C_{17}H_{13}O_7S^-$ and H_2O components form many hydrogen bonds and there are π–π stacking interactions betweeen the isoflavone units. The hydrogen bonds, π–π stacking interactions and electrostatic interactions between the cation and anions link the components into a three-dimensional structure.

Comment

Daidzein (4′,7-dihydroxyisoflavone) is one of the effective principles of soy isoflavone. It has been pharmacologically shown to be antidysrhythmic (Fan *et al.*, 1985) and antioxidant (Meng *et al.*, 1999; Tlkkanen *et al.*, 1998), to remove hyperkinesias (Guo *et al.*, 1995), to inhibit the growth of cancer cells (Jing & Han, 1992; Sarhyyamoonhy & Wang, 1997; Jing *et al.*, 1993), to accelerate the formation of bone cells (Emi & Masayoshi, 2000) and to mimic a female hormone (Miksicek, 1993). Because the solubility of daidzein is poor, its biological utilization rate is low (Tang *et al.*, 1989). Thus, it is necessary to synthesize a water-soluble derivative of daidzein 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 showed that they possess better biological activities than daidzein. The title compound, (I), is a water-soluble derivative of daidzein with potential medical applications, and we report its crystal structure here.



(I)

Compound (I) consists of an $[Ni(H_2O)_6]^{2+}$ cation, two 4′,7-dimethoxyisoflavone-3′-sulfonate anions and eight lattice water molecules (Fig. 1). The Ni^{II} atom lies on an inversion centre and is coordinated by six water molecules which form a slightly distorted octahedron, in which the average Ni—O bond length is 2.0541 Å. In the 4′,7-dimethoxyisoflavone-3′-sulfonate anion, the bond lengths and angles of the isoflavone skeleton are similar to those in both magnesium 7-methoxy-4′-hydroxyisoflavone-3′-sulfonate (Zhang *et al.*, 2003) and cobalt 7-methoxy-4′-hydroxyisoflavone-3′-sulfonate (Zhang *et al.*, 2002). The atoms in the benzopyranone moiety are nearly coplanar, as the dihedral angle between rings *A* (C4–C9) and *C* (C1–C4/C9/O1) is only 1.6°. To avoid steric conflict, the two rigid ring systems, namely benzene ring *B* (C10–C15) and the benzopyranone moiety, are rotated by 56.5° with respect to each other. The methoxy group at atom C7 is nearly coplanar

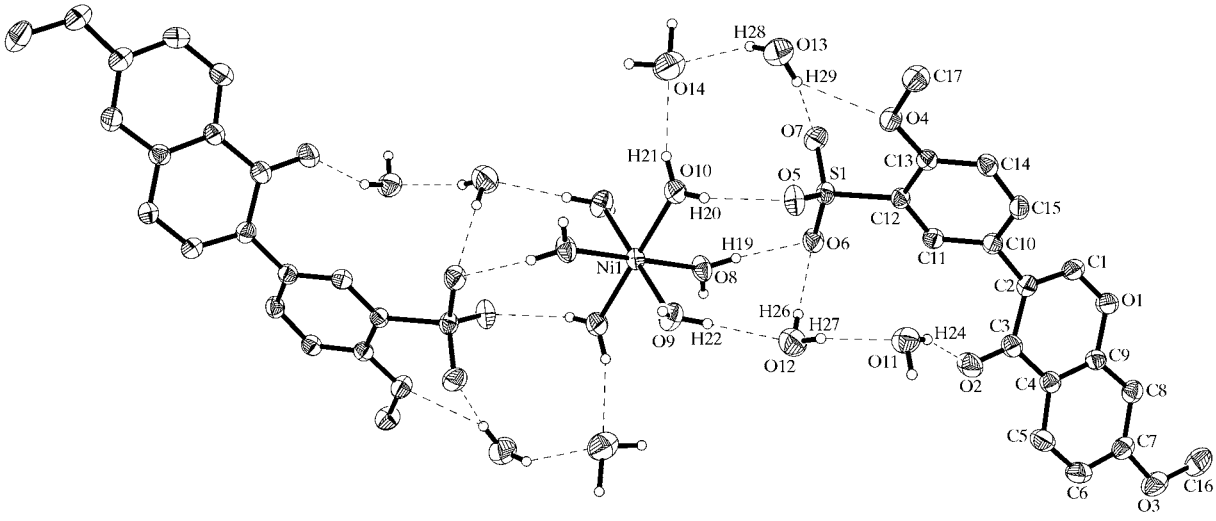


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Thin dashed lines indicate the O—H···O hydrogen bonds. For clarity, all the H atoms of the isoflavone skeletons have been omitted.

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with the benzopyranone moiety, as indicated by the C16—O3—C7—C8 torsion angle of 2.7°. The methoxy group at atom C13 is also nearly coplanar with the attached ring, the C17—O4—C13—C14 torsion angle being 1.7°.

The sulfonate ($-SO_3$), carbonyl (–C═O) and methoxy ($-OCH_3$) substituents of the isoflavone units, the eight lattice water molecules and the six coordinated water molecules are linked by hydrogen bonds (Table 1 and Fig. 1). Atoms H20 and H19 from the coordinated water molecules, as donors, form hydrogen bonds with two O atoms (O5 and O6) of the sulfonate group of the isoflavone skeleton, which can be observed for the hydrogen bonds O10—H20···O5 and O8—H19···O6. Two hydrogen-bond chains exist between the isoflavone skeleton and the coordinated water molecules, bridged by the lattice water molecules O11 and O12, and O13 and O14, respectively. Each chain contains three hydrogen bonds, *viz*. O11—H24···O2, O12—H27···O11 and O9—H22···O12, and O13—H29···O4, O13—H28···O14 and O10—H21···O14. The hydrogen bonds O12—H26···O6 and O13—H29···O7 exist between the O atoms (O6 and O7) of the sulfonate group of the isoflavone skeleton and the lattice water molecules O12 and O13, respectively. In the hydrogen bonds O13—H29···O7 and O13—H29···O4, atom H29, as donor, forms one three-centred hydrogen bond with atoms O7 and O4. Atom O6 acts as acceptor for atoms H19 and H26 to form another three-centred hydrogen bond, which includes the hydrogen bonds O8—H19···O6 and O12—H26···O6. The lattice water molecules O12 and O13 are involved in the formation of three hydrogen bonds. All these hydrogen bonds not only link the isoflavone skeletons, coordinated water molecules and lattice water molecules together, but also play very important roles in the formation, stability and crystallization of (I).

The isoflavone skeletons are arranged in an antiparallel fashion and π–π stacking interactions exist between their rings *A* (C4–C9), linking the isoflavone skeletons into a column along the *b* axis (Fig. 2). Rings *A* of the isoflavone skeleton stack with those of neighbouring isoflavone skeletons, with $Cg\cdots Cg\# = 3.644$ (2) Å and $Cg\cdots Cg^* = 3.773$ (2) Å, where *Cg* is the centroid of ring *A* at (*x*, *y*, *z*), and *Cg*# and *Cg** are the centroids of rings *A* of the neighbouring isoflavone skeletons at $(2-x, 2-y, 2-z)$ and $(2-x, 1-y, 2-z)$, respectively. The corresponding interplanar spacings are 3.540 (2) and 3.567 (2) Å. Both of the ring-centroid distances lie in the normal range of 3.3–3.8 Å (Janiak, 2000), indicative of π–π stacking interactions.

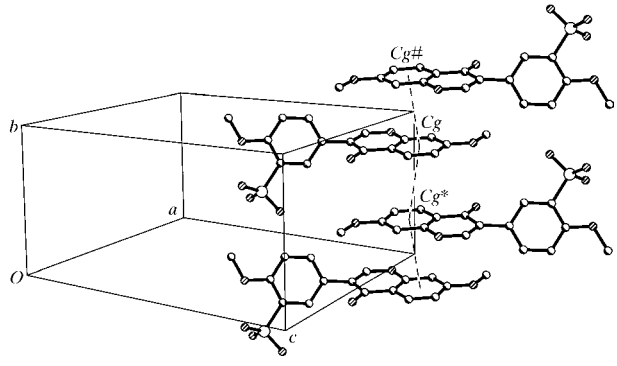

Figure 2
The π–π stacking interactions in (I). For clarity, all the H atoms of the isoflavone skeletons have been omitted. Atoms labelled with a hash (#) or an asterisk (*) are at the symmetry positions $(2-x, 2-y, 2-z)$ and $(2-x, 1-y, 2-z)$, respectively.

Finally, it is noteworthy that compound (I) has a special packing motif (Fig. 3). The coordinated water molecules, sulfonate group and carbonyl group are all hydrophilic. The distance between them is short and the areas which are surrounded by them are filled with the lattice water molecules. Therefore, there are hydrogen-bond networks in these areas. Apart from the hydrogen bonds involved in Fig. 1, the hydrogen bond O8—H18···O11^{i} exists between the coordinated and lattice water molecules, O9—H23···O5^{ii} exists between the sulfonate group of the isoflavone skeleton and the coordinated water molecule, and O11—H25···O13^{iii}, O14—H30···O13^{iv} and O14—H31···O12^{v} are all hydrogen bonds between the lattice water molecules (Table 1). By contrast, there are no hydrophilic groups or hydrogen bonds in the hydrophobic areas formed by the isoflavone moieties. In these hydrophobic areas, the isoflavone skeletons are arranged in an antiparallel fashion, and π–π stacking interactions exist between them. The sulfonate group is an important bridge as a structural link between the hydrophilic and hydrophobic regions. The hydrogen bonds, π–π stacking interactions and electrostatic interactions between the cation $[Ni(H_2O)_6]^{2+}$ cation and the 4′,7-dimethoxyisoflavone-3′-sulfonate anion lead to the formation of a three-dimensional supramolecular structure.

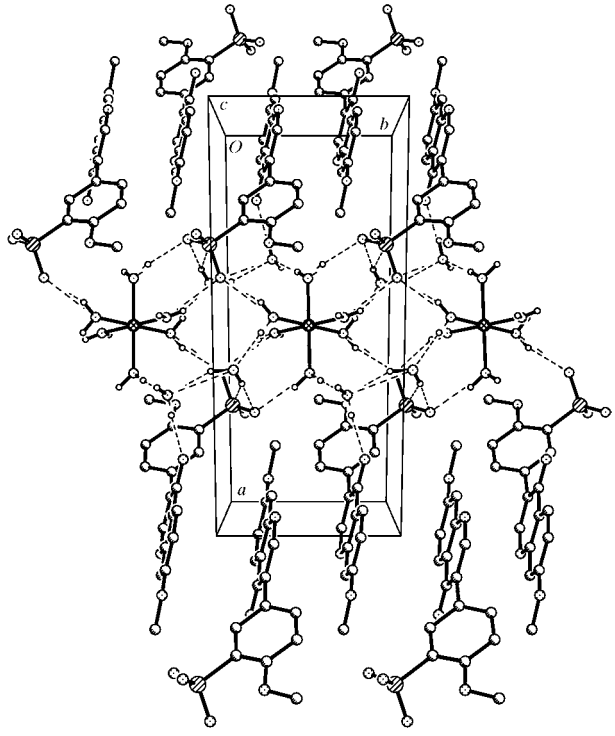

Figure 3
The unit-cell packing diagram of (I).

Experimental

Dimethyl sulfate (6 ml) was added dropwise to a solution of daidzein (4 g) in NaOH (50 ml, 5%) with vigorous stirring. The mixture was stirred at room temperature for 3 h and a precipitate appeared. This was collected by filtration and washed with water until the pH of the filtrate was 7, giving 4′,7-dimethoxyisoflavone (3.5 g), 2 g of which was added slowly to sulfuric acid (8 ml, 98%) and stirred at room temperature. After 1 h, the resulting solution was poured into a saturated NaCl solution (60 ml) and a white precipitate formed. This precipitate was collected by filtration and washed with saturated NaCl solution until the pH value of the filtrate was 7. Finally, the precipitate was recrystallized from water to afford sodium 4′,7-dimethoxyisoflavone-3′-sulfonate (2.7 g), 1 g of which was dissolved in water (10 ml) and then mixed with a saturated $NiSO_4{\cdot}7H_2O$ solution (5 ml). Crystals of the title compound were obtained after 24 h. Compound (I) was recrystallized from ethanol–water (1:3 *v*/*v*) after 3 d at room temperature, yielding crystals suitable for single-crystal X-ray analysis.

Crystal data

$[Ni(H_2O)_6](C_{17}H_{13}O_7S)_2{\cdot}8H_2O$
$M_r = 1033.60$
Monoclinic, $P2_1/c$
$a = 18.472\ (4)$ Å
$b = 7.3227\ (15)$ Å
$c = 18.247\ (4)$ Å
$\beta = 115.293\ (3)^\circ$
$V = 2231.4\ (8)$ Å^3
$Z = 2$
$D_x = 1.538$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5366 reflections
$\theta = 2.4$–27.9°
$\mu = 0.63$ mm^{-1}
$T = 298\ (2)$ K
Prismatic, green
0.56 × 0.15 × 0.13 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.721$, $T_{max} = 0.923$
11 337 measured reflections
3930 independent reflections
3164 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.0^\circ$
$h = -21 \rightarrow 16$
$k = -8 \rightarrow 8$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.092$
$S = 1.00$
3930 reflections
351 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 1.1606P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

H atoms bonded to O atoms were found in difference maps and refined as riding. H atoms bonded to C atoms were placed in calculated positions (C—H = 0.93–0.96 Å) and refined as riding, allowing for free rotation of the rigid methyl groups. U_{iso}(H) values were constrained to be $1.2U_{eq}$(C,O) or $1.5U_{eq}(C_{methyl})$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H18···O11^{i}	0.82 (3)	1.93 (3)	2.741 (3)	176 (3)
O8—H19···O6	0.88 (3)	1.97 (4)	2.836 (3)	167 (3)
O9—H22···O12	0.84 (4)	2.03 (4)	2.870 (3)	178 (4)
O9—H23···O5^{ii}	0.83 (4)	2.01 (4)	2.800 (3)	161 (3)
O10—H20···O5	0.77 (4)	2.09 (4)	2.824 (3)	159 (4)
O10—H21···O14	0.88 (4)	2.10 (4)	2.925 (3)	158 (4)
O11—H24···O2	0.82 (4)	2.03 (4)	2.827 (3)	162 (4)
O11—H25···O13^{iii}	0.88 (3)	1.90 (3)	2.781 (3)	179 (3)
O12—H26···O6	0.87 (4)	2.10 (4)	2.959 (3)	169 (4)
O12—H27···O11	0.93 (5)	2.02 (5)	2.880 (3)	153 (4)
O13—H28···O14	0.94 (4)	1.99 (4)	2.780 (4)	140 (3)
O13—H29···O7	0.90 (6)	2.21 (6)	3.061 (3)	156 (5)
O13—H29···O4	0.90 (6)	2.41 (5)	2.974 (3)	121 (4)
O14—H30···O13^{iv}	0.93 (2)	1.92 (2)	2.809 (4)	161 (4)
O14—H31···O12^{v}	0.94 (6)	1.87 (6)	2.808 (3)	179 (5)

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

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1372). Services for accessing these data are described at the back of the journal.

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