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Tetraaqua(7-hydroxy-5-oxidoflavone-6-sulfonato-κ^2O^4,O^5)nickel(II) dimethylformamide solvate monohydrate

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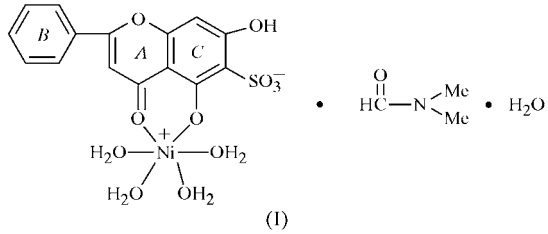
In the title compound, $[Ni(C_{15}H_8O_7S)(H_2O)_4]\cdot C_3H_7NO\cdot H_2O$, the Ni^{II} cation is chelated by a 7-hydroxy-5-oxidoflavone-6-sulfonate ligand through one oxide and one carbonyl O atom, and the sixfold coordination is completed by four aqua ligands. Individual molecules are linked into hydrogen-bonded dimers by way of five pairs of O—H···O hydrogen bonds. These dimers, in turn, determine a three-dimensional supramolecular arrangement through a variety of interdimeric interactions, such as O—H···O, C—H···O and π–π stacking.

Comment

Flavonoids (2-phenylbenzo-γ-pyrones) are a broad class of polyphenolic secondary metabolites abundant in vascular plants and in a variety of edible vegetables, such as apples, soy, onions and tea (Zheng *et al.*, 2003). They possess a number of pharmacological properties, including anti-oxidant, anti-cancer, antiviral and anti-inflammatory (Bertrand & Oliver, 1999). Chrysin, a naturally occurring and widely distributed flavone, has been reported to have many different biological activities, such as anti-oxidant (Chan *et al.*, 2000), antivirus (Zheng *et al.*, 2003), antidiabetogenic (Sternsdorf *et al.*, 1997) and anti-anxiolytic (Shin *et al.*, 1999). Furthermore, chrysin has demonstrated anticancer activities (Liu *et al.*, 1992; Hebtemariam, 1997). Owing to the particularities of their carbonyl and hydroxyl groups, chrysin and chrysinsulfonate are able to coordinate with some metal ions (Puse & Nikta, 1997, 2000; Puse *et al.*, 2001, 2003; Zhang *et al.*, 2004*b*). We report here the crystal structure of a nickel(II) complex of chrysin-6-sulfonate, namely tetraaqua(7-hydroxy-5-oxidoflavone-6-sulfonato-κ^2O^4,O^5)nickel(II) dimethylformamide solvate monohydrate, (I).



(I)

The title compound consists of an Ni^{II} center sixfold coordinated by a chelating 7-hydroxy-5-oxidoflavone-6-sulfonate ligand plus four coordinated water molecules, and the structure is stabilized by dimethylformamide and water solvent molecules (Fig. 1). The ligand possesses a flavone skeleton, and the bond lengths and angles are in agreement with those reported for flavone (Waller *et al.*, 2003). The benzopyranone system consists of ring *A* (atoms C1–C6) and ring *C* (O7/C5–C9), which are planar [the mean deviation from the least-squares planes is 0.050 (2) Å] and subtend a dihedral angle of 5.4 (1)°. The planes of rings *B* (C10–C15) and *C*, in turn, make

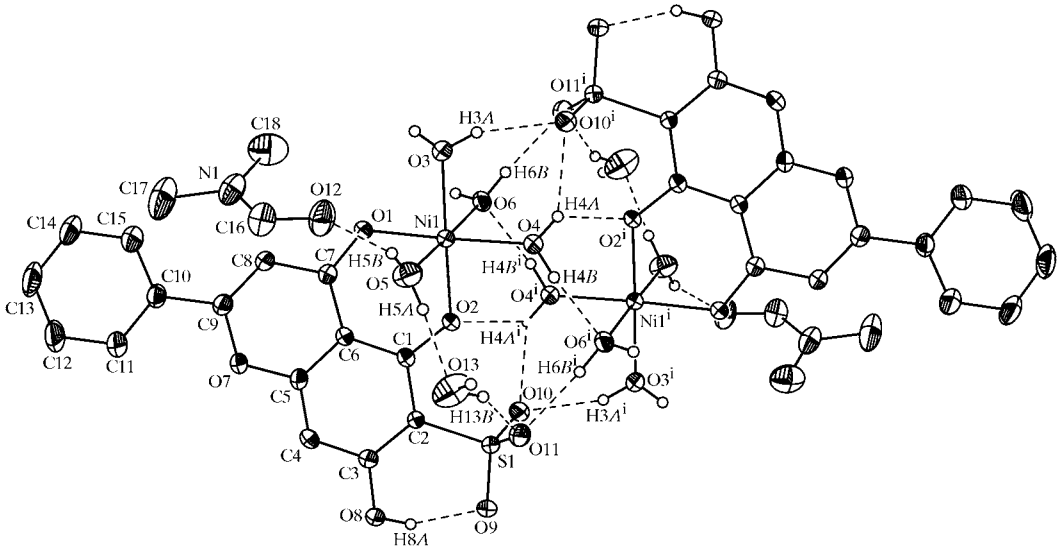


Figure 1
Part of the crystal structure of (I), showing the numbering scheme, the hydrogen-bonded dimer and the intermolecular interactions. Displacement ellipsoids are drawn at the 30% probability level. For clarity, some H atoms have been omitted. Thin dashed lines indicate the hydrogen-bonding interactions. See Table 2 for symmetry code.

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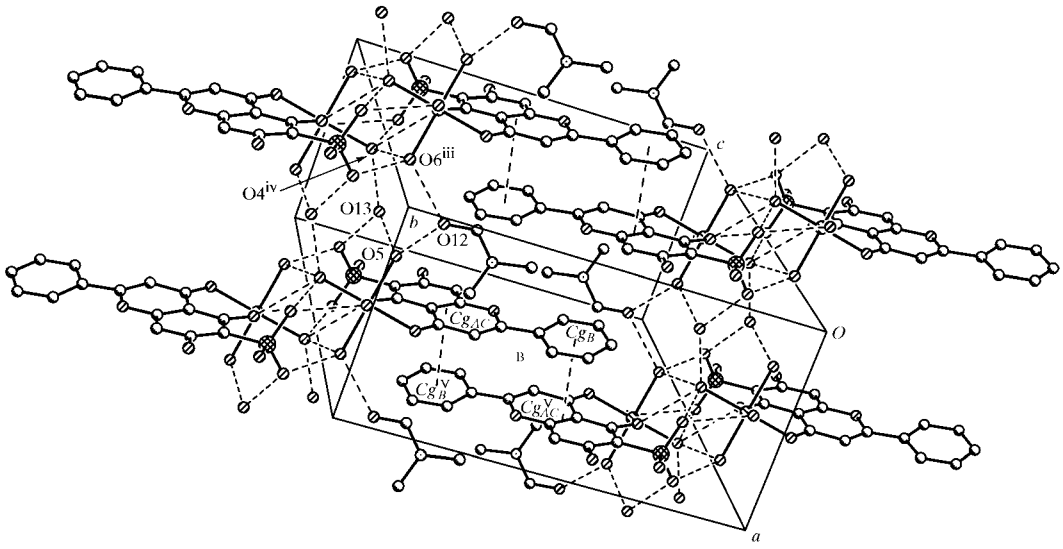

Figure 2
A view of the packing of (I), showing some of the hydrogen bonds, the π–π stacking interactions and the $R_5^5(10)$ synthon. For clarity, H atoms have been omitted. Thin dashed lines indicate hydrogen-bonding and π–π stacking interactions. Cg_{AC} and Cg_B are the centroids of the C1–C9/O7 ring system and the C10–C15 ring, respectively. [Symmetry code: (v) $-x+2, -y+1, -z+1$; for (iii) and (iv), see Table 2.]

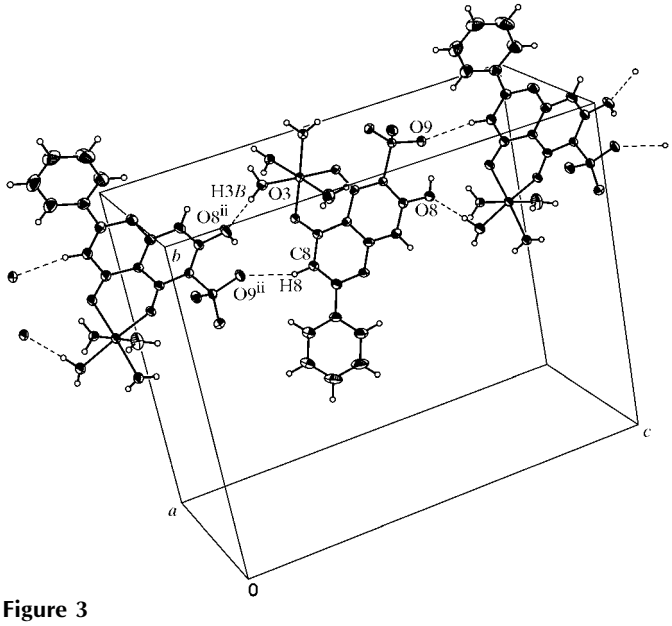

Figure 3
A complementary packing view of (I), showing the remaining hydrogen bonds and the resulting supramolecular $R_2^2(12)$ synthon. Thin dashed lines indicate the hydrogen bonding. [Symmetry code (ii), see Table 2.]

an angle of 8.3 (1)°, which shows that the flavone skeleton deviates only slightly from planarity; the overall mean deviation from the least-squares planes is 0.098 (3) Å. The Ni^{II} cation is coordinated by six O atoms (O1–O6) from the carbonyl and hydroxy groups of the chelating 7-hydroxy-5-oxidoflavone-6-sulfonate ligand and from four coordinated water molecules, defining a slightly distorted octahedron. The range of the Ni—O bond lengths is 1.9995 (17)–2.1149 (19) Å (Table 1) and can be considered as normal (Chen & Wen, 2004).

The S—O distances and angles in (I) have similar values, suggesting that the negative charge is delocalized over the three sulfonate O atoms, thus giving some shared double-bond character to the whole group (Zhang *et al.*, 2004*a*). The S1—O9 bond is slightly longer than the S1—O10 and S1—O11 bonds, owing to the intramolecular O8—H8*A*···O9 hydrogen bond between the 7-hydroxy and sulfonate groups in the ligand (first entry in Table 2, and Fig. 1).

There are three hydrogen bonds linking the main molecule and the water and dimethylformamide solvent molecules into a group (entries 2–4 in Table 2, and Fig. 1), and these groups, in turn, are connected into well defined hydrogen-bonded dimers by way of five pairs of $(O—H)_{aqua}\cdots O$ hydrogen bonds (entries 5–9 in Table 2, and Fig. 1).

Finally, a neat three-dimensional supramolecular structure arises from a variety of interdimeric interactions, the most relevant of which are the hydrogen bonds presented in Table 2 as entries 10–13, and a stacking contact between the *AC* ring system and ring *B*, with a centroid–centroid distance [$Cg_{AC}\cdots Cg_B(-x+2, -y+1, -z+1$; Fig. 2] of 3.708 (2) Å and a mean slippage angle of 15 (2)°.

In the process, some interesting hydrogen-bonded structures build up, such as the $R_5^5(10)$ synthon (Etter, 1990) determined by atoms O12, O5, O13, $O4^{iv}$ and $O6^{iii}$ and shown in Fig. 2, and the $R_2^2(12)$ motif defined by the 10th and 11th hydrogen bonds in Table 2 and shown in Fig. 3.

Experimental

Chrysin (2.0 g) was added with stirring to a concentrated sulfuric acid solution (10 ml) at 353 K over a period of 12 h. After cooling to room temperature, the resulting solution was poured into an aqueous solution of saturated sodium chloride (100 ml) and a yellow precipitate began to appear. After 2 h, the yellow precipitate was filtered off and washed with a saturated sodium chloride solution until the pH of the filtrate was 7. It was then dissolved in a buffer solution of NH_4Cl–$NH_3\cdot H_2O$ (pH = 10, 100 ml) and mixed with a saturated $NiSO_4$ solution (10 ml), at which point a green precipitate appeared,

which was filtered off and added to boiling water (50 ml) (some of the green precipitate could not be dissolved). The solution was filtered and (I) was obtained in 62.8% yield by recrystallization from a 95% dimethylformamide (*v*/*v*) solution. Analysis calculated for $C_{18}H_{25}NNiO_{13}S$: C 38.99, H 4.51, N 2.53%; found: C 38.76, H 4.54, N 2.45%. IR (KBr disk; cm^{-1}): 3365 (*br*, *v*), 1638 (*s*), 1599 (*s*), 1546 (*s*), 1450 (*s*), 1379 (*s*), 1168 (*br*, *v*), 1150 (*s*), 1029 (*s*), 926, 774, 590.

Crystal data

$[Ni(C_{15}H_8O_7S)(H_2O)_4]\cdot C_3H_7NO\cdot H_2O$
$M_r = 554.16$
Monoclinic, $P2_1/c$
$a = 7.876$ (2) Å
$b = 15.594$ (4) Å
$c = 19.136$ (5) Å
$\beta = 93.214$ (5)°
$V = 2346.6$ (10) Å^3
$Z = 4$
$D_x = 1.569$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.98$ mm^{-1}
$T = 298$ (2) K
Block, green
0.36 × 0.26 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.717$, $T_{max} = 0.898$
11820 measured reflections
4182 independent reflections
3060 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 25.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.084$
$S = 1.05$
4182 reflections
342 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.04P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O1	1.9995 (17)	Ni1—O5	2.059 (2)
Ni1—O2	2.0031 (16)	Ni1—O3	2.0796 (19)
Ni1—O4	2.0588 (19)	Ni1—O6	2.1149 (19)

All H atoms, except methyl H atoms, were found in difference maps. H atoms bonded to C atoms were placed in calculated positions (C—H = 0.93 and 0.96 Å) and refined as riding, allowing for free rotation of the rigid methyl groups; U_{iso}(H) values were constrained to be 1.2 or 1.5 times U_{eq}(C). The positions of O-bound H atoms were refined freely (hydroxy group) or with distance restraints (water molecules), with U_{iso}(H) values set at 0.08 Å^2.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; 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*.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8*A*···O9	0.77 (3)	1.81 (3)	2.522 (2)	153 (4)
O5—H5*B*···O12	0.806 (17)	2.14 (2)	2.900 (3)	159 (3)
O5—H5*A*···O13	0.834 (18)	1.839 (19)	2.663 (3)	169 (3)
O13—H13*B*···O11	0.877 (17)	2.011 (18)	2.870 (3)	166 (3)
O3—H3*A*···O10^{i}	0.856 (18)	1.96 (2)	2.775 (3)	158 (3)
O4—H4*A*···O10^{i}	0.815 (18)	2.05 (2)	2.767 (2)	147 (3)
O4—H4*A*···O2^{i}	0.815 (18)	2.29 (3)	2.854 (2)	127 (3)
O4—H4*B*···O6^{i}	0.826 (17)	1.923 (19)	2.734 (3)	167 (3)
O6—H6*B*···O11^{i}	0.862 (18)	1.902 (19)	2.754 (3)	170 (3)
O3—H3*B*···O8^{ii}	0.842 (18)	1.916 (18)	2.757 (3)	177 (3)
C8—H8···O9^{ii}	0.93	2.40	3.277 (3)	157
O6—H6*A*···O12^{iii}	0.824 (17)	1.85 (2)	2.652 (3)	163 (3)
O13—H13*A*···O4^{iv}	0.892 (15)	2.22 (2)	2.882 (3)	130 (2)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3016). Services for accessing these data are described at the back of the journal.

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