Chinese Journal of Chemistry, **2004**, *22*, 971—977 **Article**

Syntheses and Crystal Structures of $[Na(H_2O)](C_{17}H_{13}O_6SO_3)\cdot 2H_2O$ and $[Ni(H_2O)_6](C_{17}H_{13}O_6SO_3)_2\cdot 4H_2O$†

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Two hydrates of sodium 5,7-dihydroxy-6,4'-dimethoxyisoflavone-3'-sulfonate ($[Na(H_2O)](C_{17}H_{13}O_6SO_3)\cdot 2H_2O$, **1**) and nickel 5,7-dihydroxy-6,4'-dimethoxyisoflavone-3'-sulfonate ($[Ni(H_2O)_6](C_{17}H_{13}O_6SO_3)_2\cdot 4H_2O$, **2**) were synthesized and characterized by IR, ^{1}H NMR and X-ray diffraction analyses. The hydrate **1** crystallizes in the monoclinic system, space group $P2(1)$ with a=0.8201(9) nm, b=0.8030(8) nm, c=1.5361(16) nm, β=102.052(12)°, V=0.9893(18) nm^3, D_c=1.579 g/cm^3, Z=2, μ=0.252 nm^{-1}, $F(000)$=488, R=0.0353, wR=0.0873. The hydrate **2** belongs to triclinic system, space group P-1 with a=0.7411(3) nm, b=0.8333(3) nm, c=1.7448(7) nm, α=86.361(6)°, β=86.389(5)°, γ=88.999(3)°, V=1.0731(7) nm^3, D_c=1.587 g/cm^3, Z=1, μ=0.649 mm^{-1}, $F(000)$=534. In the structure of **1**, the sodium cation is coordinated by six oxygen atoms and two adjacent ones are bridged by three oxygen atoms to form an octahedron chain. The C—H···π hydrogen bonds exist between two isoflavone molecules in the structure of **2**. Meanwhile, hydrogen bonds in two compounds, link themselves to assemble two three-dimensional network structures, respectively.

Keywords irisolidon, sodium 5,7-dihydroxy-6,4'-dimethoxyisoflavone-3'-sulfonate, nickel 5,7-dihydroxy-6,4'-dimethoxyisoflavone-3'-sulfonate, crystal structure, C—H···π, hydrogen bond

Introduction

Flavonoids exist widely in edible plants, and have pharmacological activity. They played a major role in the successful medical treatments at ancient times, and their uses have been persevered up to now.[1-3] Flavonoid sulfates were found in a large number of plant species. They occupy an important position in the field of natural products chemistry since they provide structures consisted of organic and inorganic components. The pharmacological assay revealed that flavonoid sulfates have enhancements of antioxidant activity and aldose reductase inhibitory activity as compared with the corresponding parent flavonoids.[4-8] We synthesized the derivatives of daidzein, sodium 4',7-dihydroxyisoflavone-3'-sulfonate[9] and sodium 4'-hydroxy-7-methoxyisoflavone-3'-sulfonate,[10] and studied their crystal structures and biological activities. The results showed that the flavonoid sulfates possess better biological activity than their parent flavonoids. Kakkalide is one of the principal components of *Pueraia lobata*, and has been widely used to treat diabetes mellitus, lingering intoxication and the injury to liver.[11,12] Irisolidone (5,7-dihydroxy-6,4'-dimethoxyisoflavone) is the aglycon of kakkalide. The biological activities of flavonoids result from the hydroxyl groups and the C(2)=C(3) double bond[13]. In this paper, a sulfo-group was only added on the C-3' position of irisolidon skeleton and the active groups did not changed, which increased the water-solubility of irisolidon and so improved the biological activity.

Experimental

Syntheses of 1 and 2

Irisolidon was isolated from the flower of *Pueraia lobata* (Willd) and identified by IR and ^{1}H NMR. Other chemicals were of analytical reagent grade and used directly without further purification. The infrared spectra were recorded as KBr pellets on a Nicolet 170SX FT-IR spectrometer. The ^{1}H NMR spectra were recorded on a Bruker Am-300 spectrometer with TMS as internal standard and DMSO-d_6 as solvent. Elemental analyses were determined using a PE-2400 elemental analyzer.

As shown in Scheme 1, irisolidon (5.0 g) was slowly added to the stirred concentrated sulfuric acid (10 mL). The mixture was heated at 60 ℃ for half an hour and cooled to room temperature. Then, the mixture was added to a saturated NaCl solution (40 mL) and a yellow precipitate began to appear. After 3 h, the precipitate was filtered and washed with saturated NaCl solution until the pH value of the filtrate was 7. The pre-

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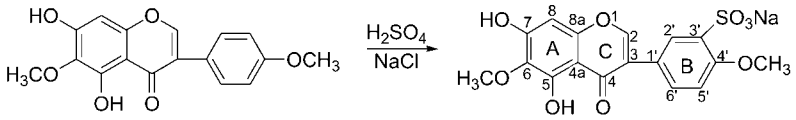
Scheme 1



cipitate was recrystallized from water to afford compound **1** (6.3 g) in good yield (83%). Yellow single crystals suitable for X-ray diffraction were grown in ethanol-water (*V*∶*V*, 1∶1) solution by slow evaporation. m.p. 318 ℃(decomposed). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 3.76 (s, 3H, C_6-OCH_3), 3.81 (s, 3H, $C_{4'}$-OCH_3), 6.55 (s, 1H, H-C_8), 7.06 (d, J=8.6 Hz, 1H, H-$C_{5'}$), 7.49 (dd, J=2.2, 8.6 Hz, 1H, H-$C_{6'}$), 7.90 (d, J=2.2 Hz, 1H, H-$C_{2'}$), 8.37 (s, 1H, H-C_2), 10.87 (s, 1H, C_7-OH), 13.03 (s, 1H, C_5-OH); IR (KBr) ν: 3452, 3069, 2946, 2844, 1654, 1626, 1579, 1496, 1464, 1367, 1337, 1262, 1189, 1156, 1097, 1071, 1033, 1001 cm^{-1}. Anal. calcd for $C_{17}H_{19}NaO_{12}S$: C 43.40, H 4.04; found C 43.35, H 4.01.

1 (2.0 g) was dissolved in water (20 mL), and mixed with saturated $Ni(NO_3)_2$·$6H_2O$ solution (5 mL). The crystals of **2** were obtained after 24 h and recrystallized from water in good yield (78%). Green plate single crystals suitable for single crystal X-ray diffraction were grown in ethanol-water (*V*∶*V*, 1∶1) solution by slow evaporation. m.p. 282 ℃ (decomposed). IR (KBr) ν: 3381, 2842, 1655, 1578, 1496, 1462, 1367, 1338, 1282, 1154, 1097, 1026 cm^{-1}.

X-ray crystal structure determination

In the determination of the structures of the crystals **1** and **2**, X-ray determination data were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ=0.071073 nm) using ω-2θ scan technique. The structures were solved by direct method and refined on F^2 by full matrix least-squares with the Bruker's SHELXL-97[14] program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. The crystals used for the diffraction study showed no decomposition during data collection. The crystals data, experimental details, and refinement results are summarized in Table 1. The structures of **1** and **2** are shown in Figures 1 and 2, respectively. The fractional non-hydrogen atomic coordinates and equivalent isotropic displacement parameters of **1** and **2** are shown in Tables 2 and 3, respectively. The selected bond lengths and angles of **1** and **2** are given in Table 4.

Results and discussion

As shown in Figures 1 and 2, both **1** and **2** contain a sulfonate of isoflavone anion $C_{17}H_{13}O_6SO_3^-$, which consists of a benzopyranone moiety, a phenyl moiety and a sulfonate monoanion. The bond lengths and bond angles of isoflavone skeleton of **1** and **2** are in agreement with that of monomethoxy-daidzein,[10] respectively. The atoms of benzopyranone moiety of two compounds are nearly coplanar. The dihedral angle between ring A and ring C of **1** is 0.24°, and that of **2** is 3.32°. To avoid steric hindrance, the two rigid ring systems, phenyl ring and benzopyranone moiety of **1** and **2** are roated by 40.3° and 37.6° with respect to each other, respectively. The methoxy group at C-4' is slightly twisted out of phenyl ring with the torsion angle C(17)-O(6)-C(13)-C(14)=10.26° in the structure of **1** and with the torsion angle C(17)-O(6)-C(13)-C(14)=5.16° in the structure of **2**, whereas the methoxy group at C-6 is nearly oriented out of the benzopyranone moiety, as indicated by the torsion angle C(16)-O(4)-C(6)-C(7)=72.14° in the structure of **1** and by the torsion angle C(16)-O(4)-C(6)-C(7)=90.41° in structure of **2**, which is due to the disubstitution on C(5) and C(7) positions in the ring A of the isoflavone moiety. The S—O distances of **1** are consistent with the length of S=O in some degree, and the bond lengths of S—O(7) and S—O(8) are slightly longer than that of S—O(9), owing to the coordination of O(7) and O(8) with sodium cation. And the close S—O distances and angles of **2** indicated that the negative charge is delocalized over three oxygen atoms.

In the structure of **1** (see Figure 3), the sodium cation [Na(1)] is coordinated by six oxygen atoms, *i.e.* O(10) from the water ligand, O(5) from the hydroxy group at C-7, O(4) from methoxy group at C-6, the other two [O(7), O(8)] from the sulfate monoanion and O(7A) from the sulfate monoanion of another molecule, which accords with the rule of the optimal coordinated number. Two adjacent sodium ions separated by 0.4303 nm are bridged by O(7) or O(7A) to form an octahedron chain running in *b*-axis. The isoflavone skeletons are outstretched to form a molecular column along *b*-axis. In the molecular column, the skeletons of isoflavone are arranged in an anti-parallel fashion. The dihedral angles of benzopyranone moiety, and the benzopyranone moiety and phenyl ring of adjacent isoflavone skeleton are 23.3° and 6.1°, respectively. The chains together with the columns are linked to form a sheet viewed along *a*-axis. Furthermore, a planar three-center (C—H)$_2$···O hydrogen bond is formed by two C—H···O intermolecular hydrogen bonds, in which atom O(3) acts as an acceptor, and the two donors are C(15), via atom H(15) and C(1), via atom H(9). The combination of the three-center (C—H)$_2$···O hydrogen bond generates a $R_2^1(7)$ring (Figure 4(a)), which propagates itself via intermolecular (C—H)$_2$···O hydrogen bonds and links the sheets to assemble a three-dimensional network structure. The unit cell packing diagram of **1** is shown in

Table 1 Crystal data and structure refinement for **1** and **2**

	Compound **1**	Compound **2**
Empirical formula	$C_{17}H_{19}NaO_{12}S$	$C_{34}H_{46}NiO_{28}S_2$
Formula weight	470.37	1025.54
Crystal size	0.43 mm×0.34 mm×0.17 mm	0.48 mm×0.37 mm×0.11 mm
Temperature	298(2) K	298(2) K
Crystal system	Monoclinic	Triclinic
Space group	*P*2(1)	*P*-1
Unit cell dimensions	a=0.8201(9) nm	a=0.7411(3) nm
	b=0.8030(8) nm	b=0.8333(3) nm
	c=1.5361(16) nm	c=1.7448(7) nm
Volume, Z	0.9893(18) nm^3, 4	1.0731(7) nm^3, 1
Density (calculated)	1.579 g/cm^3	1.587 g/cm^3
Absorption coefficient	0.252 mm^{-1}	0.649 mm^{-1}
θ range for data collection	2.54° to 25.03°	2.34° to 25.02°
Limiting indices	$-8\leqslant h\leqslant 8, -9\leqslant k\leqslant 9, -18\leqslant l\leqslant 18$	$-9\leqslant h\leqslant 9, -9\leqslant k\leqslant 7, -12\leqslant l\leqslant$
20Reflections collected/unique	5050/2597 [R(int)=0.0241]	5576/3701 [R(int)=0.0324]
Max. and min. transmission	0.9584 and 0.8995	0.9320 and 0.7459
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2597/12/307	3701/23/352
Goodness-of-fit on F^2	1.017	0.971
Final R indices [$I>2\sigma(I)$]	R_1=0.0353, wR_2=0.0873	R_1=0.0614, wR_2=0.161
R indices (all data)	R_1=0.0402, wR_2=0.0905	R_1=0.0871, wR_2=0.1795
Largest diff. peak and hole	200 and −328 e•nm^{-3}	832 and −7318 e•nm^{-3}

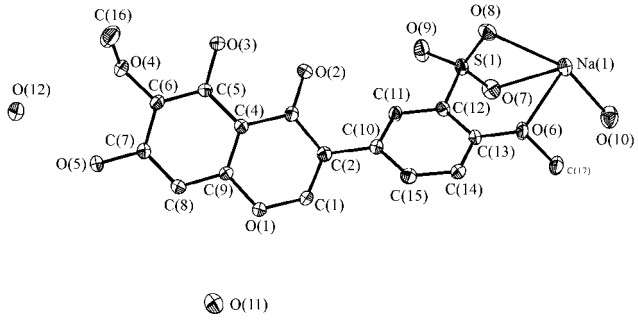


Figure 1 Molecular structure of **1**.

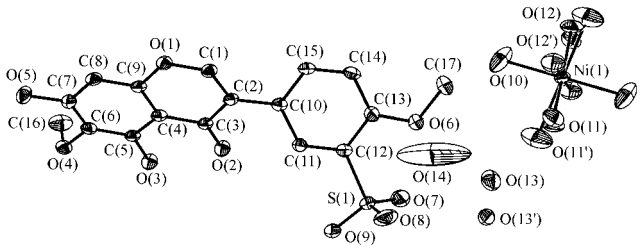


Figure 2 Molecular structure of **2**.

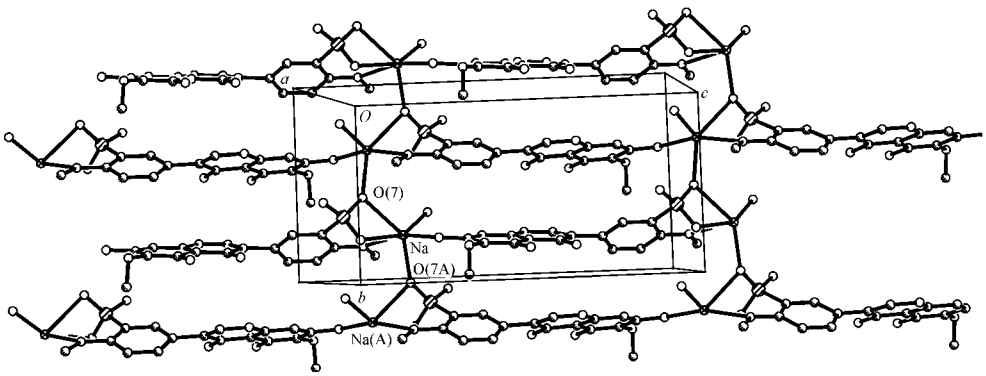


Figure 3 The sheet of **1** looking down *a*-axis.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($10\times nm^2$) for **1**

Atom	*x*	*y*	*z*	U_{eq}
Na(1)	5056(2)	2070(2)	−497(1)	41(1)
O(1)	6325(2)	2093(3)	5996(1)	44(1)
O(2)	2409(2)	3110(3)	3962(1)	44(1)
O(3)	494(3)	3229(4)	5078(1)	48(1)
O(4)	198(2)	3005(3)	6832(1)	41(1)
O(5)	2992(3)	2382(4)	8117(1)	44(1)
O(6)	6833(2)	2572(3)	1014(1)	42(1)
O(7)	4499(3)	−147(3)	609(2)	50(1)
O(8)	2972(3)	2362(3)	457(1)	44(1)
O(9)	2305(3)	204(4)	1424(2)	60(1)
O(10)	7110(4)	678(4)	−955(2)	61(1)
O(11)	8677(3)	222(4)	7579(2)	62(1)
O(12)	513(4)	3113(5)	8880(2)	74(1)
S(1)	3570(1)	989(1)	1053(1)	34(1)
C(1)	6500(4)	2162(5)	5139(2)	40(1)
C(2)	5288(3)	2477(4)	4431(2)	32(1)
C(3)	3623(4)	2776(4)	4578(2)	31(1)
C(4)	3433(3)	2671(4)	5489(2)	32(1)
C(5)	1864(3)	2932(4)	5720(2)	32(1)
C(6)	1721(3)	2839(4)	6592(2)	33(1)
C(7)	3122(4)	2502(4)	7260(2)	33(1)
C(8)	4663(4)	2271(5)	7057(2)	38(1)
C(9)	4775(3)	2352(4)	6176(2)	31(1)
C(10)	−467(5)	4636(6)	6762(3)	59(1)
C(11)	5667(3)	2547(4)	3531(2)	31(1)
C(12)	4617(4)	1847(4)	2796(2)	31(1)
C(13)	5012(4)	1869(4)	1961(2)	30(1)
C(14)	6495(4)	2583(4)	1847(2)	30(1)
C(15)	7555(4)	3296(4)	2580(2)	35(1)
C(16)	7130(4)	3282(5)	3403(2)	36(1)
C(17)	8460(4)	3074(6)	924(2)	51(1)

Figure 5, in which the lattice water molecules and the atoms of isoflavone form many hydrogen bonds, playing an important role in the structure of **1**. A supramolecule of three-dimensional network structure of **1** was formed by the coordination of sodium cation and oxygen atoms, the O—H···O hydrogen bonds and the electrostatic interaction of between the cation $[Na(H_2O)]^+$ and the anion sulfonate $C_{17}H_{13}O_6SO_3^-$.

In the crystal structure of **2**, Ni^{2+} cation is located at the symmetry center and coordinated by six water molecules. In the $[Ni(H_2O)_6]^{2+}$, a distorted octahedral complex cation, the average Ni—O bond length is 0.204 nm. The isoflavone skeletons are arranged in an

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($10\times nm^2$) for **2**

Atom	*x*	*y*	*z*	U_{eq}
Ni(1)	0	0	5000	38(1)
O(1)	8665(4)	5777(3)	−924(2)	36(1)
O(2)	6888(5)	8585(4)	808(2)	45(1)
O(3)	7540(5)	11102(3)	−106(2)	45(1)
O(4)	8887(4)	12324(3)	−1531(2)	41(1)
O(5)	10240(5)	10252(4)	−2581(2)	53(1)
O(6)	5690(5)	2337(4)	3152(2)	55(1)
O(7)	5893(6)	5363(5)	3879(2)	67(1)
O(8)	8848(6)	4251(5)	3642(2)	74(1)
O(9)	8189(5)	6967(4)	3200(2)	56(1)
O(10)	4(10)	1252(6)	3957(2)	110(2)
O(11)	2668(10)	61(9)	5110(5)	63(2)
O(12)	282(12)	−2052(8)	4431(5)	63(2)
O(13)	4901(8)	2592(6)	4892(3)	68(1)
O(11')	1862(15)	1702(14)	5268(7)	120(4)
O(12')	2035(11)	−1339(10)	4481(5)	69(2)
O(13')	6340(20)	3000(20)	5132(10)	44(4)
O(14)	2020(20)	5450(30)	4118(13)	447(16)
S(1)	7487(2)	5372(1)	3368(1)	42(1)
C(1)	8047(6)	5141(5)	−233(2)	35(1)
C(2)	7442(5)	5962(5)	372(2)	31(1)
C(3)	7440(5)	7719(5)	279(2)	30(1)
C(4)	8094(5)	8395(5)	−466(2)	31(1)
C(5)	8147(6)	10075(5)	−638(2)	33(1)
C(6)	8823(6)	10684(5)	−1350(3)	35(1)
C(7)	9513(6)	9648(5)	−1890(2)	37(1)
C(8)	9444(6)	7989(5)	−1747(2)	36(1)
C(9)	8733(5)	7415(5)	−1049(2)	30(1)
C(10)	6859(5)	5074(5)	1102(2)	32(1)
C(11)	7264(5)	5586(5)	1815(2)	34(1)
C(12)	6848(5)	4681(5)	2482(2)	35(1)
C(13)	6002(6)	3175(5)	2473(3)	39(1)
C(14)	5550(6)	2687(5)	1769(3)	38(1)
C(15)	5958(6)	3611(5)	1104(2)	36(1)
C(16)	7312(9)	12924(7)	−1883(4)	69(2)
C(17)	4956(10)	750(7)	3138(4)	72(2)

anti-parallel fashion and every a pair of them exists fourC—H···π hydrogen bonds, C(14)—H(14)···C*g*1*, C(15)—H(15)···C*g*2*, C(14*)—H(14*)···C*g*1 and C(15*)—H(15*)···C*g*2, where *Cg*1 and *Cg*2 are the centre of gravity of the ring A and ring C of isoflavone, respectively (Figure 6). The adjacent pairs of isoflavone

Table 4 Bond lengths (nm) and angles (°) for **1** and **2**

1		**2**	
O(1)—C(1)	0.1355(4)	O(1)—C(1)	0.1343(5)
O(2)—C(3)	0.1252(4)	O(2)—C(3)	0.1251(5)
O(4)—C(6)	0.1381(4)	O(4)—C(6)	0.1384(5)
O(4)—C(16)	0.1414(5)	O(4)—C(16)	0.1422(6)
O(5)—C(7)	0.1345(4)	O(5)—C(7)	0.1359(5)
O(6)—C(17)	0.1428(4)	O(6)—C(17)	0.1441(6)
O(7)—S(1)	0.1447(3)	O(7)—S(1)	0.1434(4)
O(8)—S(1)	0.1451(3)	O(8)—S(1)	0.1446(4)
O(9)—S(1)	0.1430(3)	O(9)—S(1)	0.1442(4)
C(1)—C(2)	0.1335(4)	C(1)—C(2)	0.1343(6)
C(2)—C(10)	0.1480(4)	C(2)—C(10)	0.1477(6)
C(4)—C(9)	0.1381(4)	C(4)—C(9)	0.1398(6)
C(6)—C(7)	0.1398(4)	C(6)—C(7)	0.1386(6)
C(7)—C(8)	0.1376(4)	C(7)—C(8)	0.1391(6)
C(12)—C(13)	0.1388(4)	C(12)—C(13)	0.1415(6)
C(14)—C(15)	0.1380(4)	C(14)—C(15)	0.1372(6)
Na(1)—O(10)	0.2253(3)	Ni(1)—O(11)	0.2000(7)
Na(1)—O(7)#1	0.2277(4)	Ni(1)—O(11)#1	0.2000(7)
Na(1)—O(8)	0.2484(3)	Ni(1)—O(10)	0.2039(4)
Na(1)—O(6)	0.2503(3)	Ni(1)—O(10)#1	0.2039(4)
Na(1)—O(7)	0.2567(3)	Ni(1)—O(12')	0.2058(7)
Na(1)—S(1)	3.019(3)	Ni(1)—O(11')	0.2090(10)
O(10)-Na(1)-O(7)#1	108.74(13)	O(5)#2-Na(1)-S(1)	113.37(10)
O(10)-Na(1)-O(8)	151.94(11)	O(8)-Na(1)-S(1)	28.51(6)
O(10)-Na(1)-O(6)	92.35(12)	O(7)-Na(1)-S(1)	28.58(6)
O(11)-Ni(1)-O(10)	96.7(3)	O(10)#1-Ni(1)-O(11')	94.9(4)
O(7)#1-Na(1)-O(7)	141.66(9)	O(12')-Ni(1)-O(11')	90.8(4)
O(5)#2-Na(1)-O(7)	117.49(10)	O(11)-O(11')-Ni(1)	65.1(5)
O(9)-S(1)-O(7)	113.99(19)	O(7)-S(1)-O(9)	112.4(2)
O(7)-S(1)-O(8)	108.92(16)	O(7)-S(1)-O(8)	111.8(3)
O(9)-S(1)-O(8)	114.11(18)	O(9)-S(1)-O(8)	112.2(3)
O(7)-S(1)-C(12)	106.90(15)	O(7)-S(1)-C(12)	107.0(2)
C(2)-C(1)-O(1)	126.0(3)	O(1)-C(1)-C(2)	126.3(4)
C(1)-C(2)-C(3)	118.0(3)	C(1)-C(2)-C(3)	117.8(4)
C(1)-C(2)-C(10)	120.2(3)	C(1)-C(2)-C(10)	119.4(4)
C(3)-C(2)-C(10)	121.8(2)	C(3)-C(2)-C(10)	122.8(4)
O(2)-C(3)-C(4)	121.1(3)	O(2)-C(3)-C(4)	121.9(4)
O(2)-C(3)-C(2)	122.9(3)	O(2)-C(3)-C(2)	122.4(4)
C(4)-C(3)-C(2)	116.0(2)	C(4)-C(3)-C(2)	115.7(3)
C(9)-C(4)-C(5)	117.1(2)	C(9)-C(4)-C(5)	117.0(4)
C(9)-C(4)-C(3)	121.5(3)	C(9)-C(4)-C(3)	121.4(4)
C(5)-C(4)-C(3)	121.4(2)	C(5)-C(4)-C(3)	121.6(4)
O(3)-C(5)-C(6)	119.7(3)	O(3)-C(5)-C(6)	119.3(4)
C(5)-C(6)-O(4)	121.5(2)	C(5)-C(6)-O(4)	121.3(4)
C(5)-C(6)-C(7)	120.2(3)	C(5)-C(6)-C(7)	119.9(4)
O(4)-C(6)-C(7)	118.3(3)	O(4)-C(6)-C(7)	118.8(4)
O(5)-C(7)-C(8)	118.5(2)	O(5)-C(7)-C(8)	118.8(4)

Continued

1		**2**	
O(5)-C(7)-C(6)	120.7(3)	O(5)-C(7)-C(6)	119.9(4)
C(8)-C(7)-C(6)	120.8(3)	C(6)-C(7)-C(8)	121.3(4)
C(7)-C(8)-C(9)	118.0(3)	C(9)-C(8)-C(7)	117.7(4)
O(1)-C(9)-C(8)	116.5(2)	C(8)-C(9)-O(1)	116.6(4)
C(15)-C(10)-C(2)	120.3(3)	C(15)-C(10)-C(2)	120.8(4)
C(10)-C(11)-C(12)	121.5(3)	C(12)-C(11)-C(10)	121.6(4)
O(6)-C(13)-C(12)	118.0(2)	O(6)-C(13)-C(12)	117.4(4)
O(6)-C(13)-C(14)	123.1(3)	O(6)-C(13)-C(14)	125.3(4)
C(12)-C(13)-C(14)	118.9(2)	C(14)-C(13)-C(12)	117.3(4)
C(14)-C(15)-C(10)	121.6(3)	C(14)-C(15)-C(10)	122.1(4)

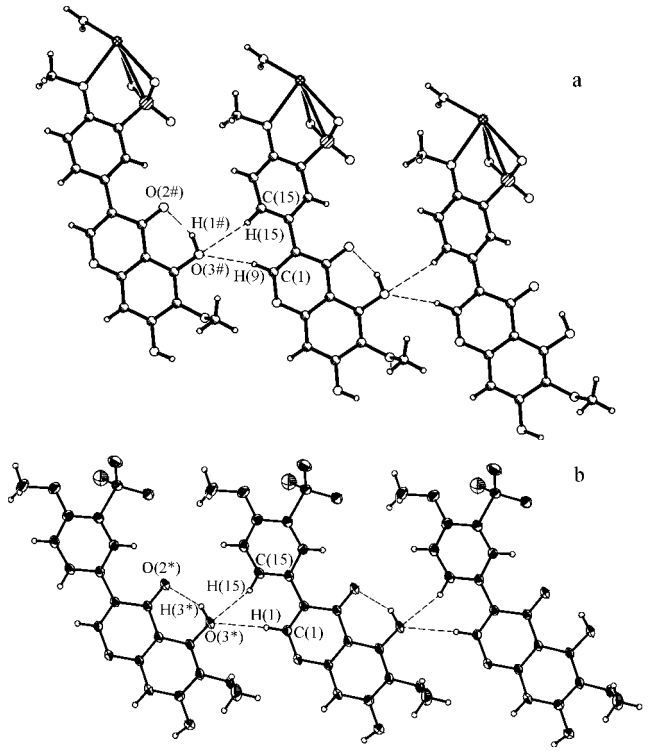


Figure 4 Intermolecular hydrogen bonding of **1** (a) and **2** (b). Symmetry code: # 1+*x*, *y*, *z*; * *x*, 1+*y*, *z*.

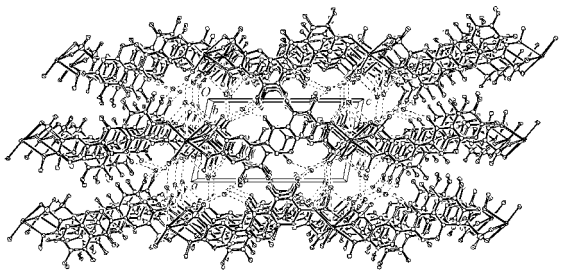


Figure 5 Unit cell packing diagram of **1**.

are tied by another two intermolecular C—H···π hydrogen bonds with C(8)—H(8)···*Cg*3$^{\#}$ and C(8$^{\#}$)—H(8$^{\#}$)···*Cg*3, where *Cg*3 is the center of gravity of the ring B. The C—H···π stacking makes the isoflavone to form a molecular column. The isoflavone anions in

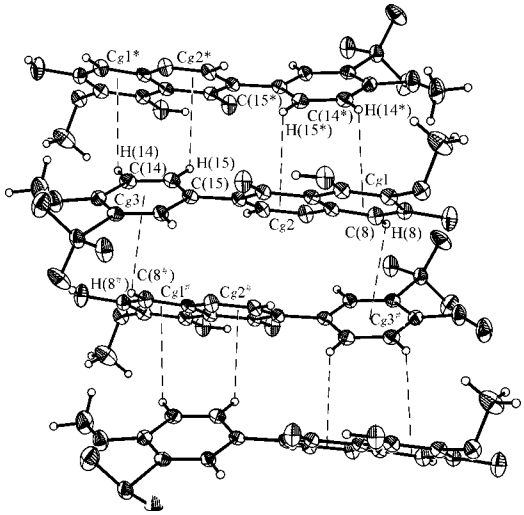


Figure 6 The C—H···π hydrogen bonds in column of isoflavone skeletons of **2**. Symmetry code: * 1−*x*, 1−*y*, −*z*; # 2−*x*, 1−*y* , −z.

columns are linked by C—H···O hydrogen bonds. The oxygen atoms of hydroxy and methoxy accept protons to form intermolecular hydrogen bonds, C(1)—H(1)···O(3*) and C(15)—H(15)···O(3*) (Figure 4(b)). The combination of them generates a R_2^1 (7) ring, which propagates itself via intermolecular C—H···O hydrogen bonds to build a layer. The columns together with the layers are tied to form a sheet.

Furthermore, in the structure of **2**, the sulfo-group, carbonyl, hydroxy of the isoflavone, four lattice water molecules and six coordination water molecules are linked by hydrogen bonds which are classified into four types. The first type is the hydrogen bonds between $[Ni(H_2O)_6]^{2+}$ and $C_{17}H_{13}O_6SO_3^-$, including two kinds of hydrogen bonds, which exist between coordination water molecules and sulfo-group; and coordination water molecules and 4'-hydroxy group. The second consists of $C_{17}H_{13}O_6SO_3^-$ and two lattice water molecules. The third type of hydrogen bonds exists between coordination water molecules and lattice water molecules. The hydrogen bonds between lattice water molecules are the fourth type of hydrogen bonds. It should be

pointed out that the interactions of hydrogen bonds and C—H···π play a very important role in the formation, stability and crystallization of **2**.

A supramolecule of three-dimensional network structure of **2** was formed by the above discussed hydrogen bonds and the C—H···π stacking interactions of isoflavone skeletons and the electrostatic interaction of between the cation $[Ni(H_2O)_6]^{2+}$ and the anion sulfonate $C_{17}H_{13}O_6SO_3^-$. It is interesting that the supramolecular compound has a special packing manner. In Figure 7, the distance of the hydrophilic groups, coordinated water molecules, sulfo-groups, carbonyl and hydroxyl of phenol, are short. The hydrophilic areas which are surrounded by them are filled with the lattice water molecules, therefore, there are hydrogen bonds network in them. On the contrary, there is not any hydrophilic group and hydrogen bond in the hydrophobic areas which are surrounded by isoflavone structures.

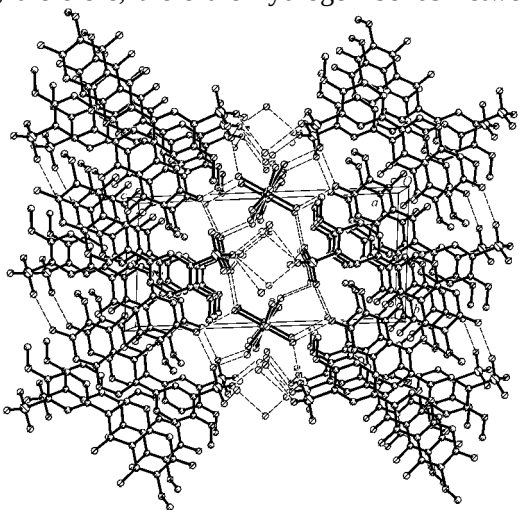


Figure 7 Unit cell packing diagram of **2**.

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