Journal of Chemical Crystallography, Vol. 36, No. 8, August 2006 (© 2006)
DOI: 10.1007/s10870-006-9074-8

Synthesis and crystal structure of $[Ni(H_2O)_6](C_{19}H_{17}O_9S)_2 \cdot 2H_2O$

Zun-Ting Zhang,[(1)]* Xue-Ling Zhang,[(1)] and Yun He Zhang[(1)]

Received September 29, 2005; accepted January 17, 2006
Published Online July 6, 2006

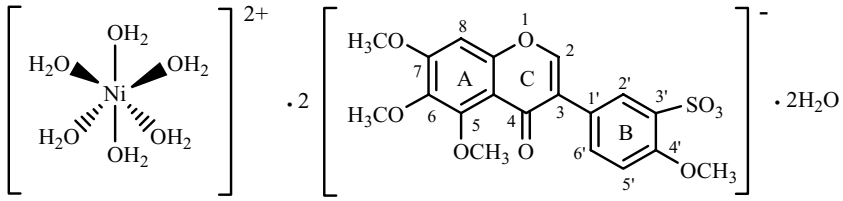
A water soluble flavonoid sulfate, $[Ni(H_2O)_6](C_{19}H_{17}O_9S)_2 \cdot 2H_2O$ was synthesized and its structure was determined by single-crystal X-ray diffraction analysis. The crystal of it belongs to triclinic crystal system, space group *P*–1. The results show that the title compound consists of $[Ni(H_2O)_6]^{2+}$, $C_{19}H_{17}O_6SO_3^-$ and H_2O. Ni(II) is located on the symmetry center and octahedrally coordinated by six water molecules. A variety of hydrogen bonds among $[Ni(H_2O)_6]^{2+}$, $C_{19}H_{17}O_6SO_3^-$ and the lattice water molecules build a hydrophilic region. Aromatic π–π stacking interactions assemble isoflavone skeletons into a column and the columns form a hydrophobic region of the title compound. The sulfo-groups bridge the hydrophilic regions and the hydrophobic regions as well as the inorganic components and organic components. Hydrogen bonds, $\pi \cdots \pi$ stacking interactions and the electrostatic interactions between cation $[Ni(H_2O)_6]^{2+}$ and anion sulfonate $C_{19}H_{17}O_6SO_3^-$ lead the moieties to a three-dimensional structure.

KEY WORDS: $[Ni(H_2O)_6](C_{19}H_{17}O_9S)_2 \cdot 2H_2O$; crystal structure; π–π stacking; hydrogen bond.

Introduction

Flavonoids and related compounds are known to exhibit a wide range of interesting biological activities.[1,2] Besides the extensive biological activities of flavonoids, this class of compounds exhibits antidiabetic[3–5] and aldose reductase inhibitory activity.[6] Because the solubility of flavonoid is poor, its biological utilization rate is low. Thus, it is necessary to synthesize a water soluble derivative of flavonoid in order to study its possible biological effects. Our previous works[7–9] found the solubility of flavonoid sulfates is better and the pharmacological assay of them has revealed an enhancement of antioxidant activity as compared with the parent flavonoids. Flavonoid sulfate occupies an important position in the field of natural products chemistry since they provide a structural link between organic and inorganic components in nature.[10] Irisolidone (5,7-dihydroxy-6,4′-dimethoxyisoflavone), a kind of flavonoid, had the most potent inhibitory activity against *Helicobacter pylori* (HP)[11] and reduced the ethanol-induced mortality as well as serum alanine aminotransferase (ALT) and aspartate aminotransferase (AST) activities.[12–14] In this paper, irisolidone as leading compound, a water soluble flavonoid sulfate $[Ni(H_2O)_6](C_{19}H_{17}O_9S)_2 \cdot 2H_2O$ (Scheme 1) was synthesized. Its structure was elucidated by ^1H NMR, IR spectroscopic techniques and X-ray single crystal diffraction.

[(1)] School of Chemistry and Materials Science, ShaanXi Normal University, Xi'An 710062 People's Republic of China.
* To whom correspondence should be addressed; e-mail: zhangzt@snnu.edu.cn.



Scheme 1.

Experimental

The chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification. The infrared spectrum was recorded as KBr pellets on a Nicollet 170SX FT-IR spectrophotometer. The melting point was determined using X4 melting point instrument (the thermometer had not been emended). The ^{1}H NMR spectrum was recorded on a Bruker AM-300 spectrometer with TMS as internal reference and DMSO-d_6 as solvent. The crystal structure was determined with a Bruker Smart-1000 CCD Diffractometer instrument.

Irisolidone (2.0 g) was dissolved into acetone (60 mL) and KOH (2 mL, 0.3%). Dimethyl sulfate (2 mL) was added dropwise to the solution with vigorous stirring. The mixture was stirred at room temperature for 8 h. The solution was poured into water (60 mL), pale yellow precipitation appeared which was filtered and washed with water until the pH of the filtrate was 7. The resulting solid residue (1.8 g) was slowly added to the concentrated sulfuric acid (9 mL), the mixture was stirred at 40°C for 30 min and poured into the saturated NaCl solution (40 mL) to obtain another yellow precipitate. After 2 h, the precipitate was filtered and washed with saturated NaCl solution until the pH value of the filtrate was 7. It was dissolved in water (20 mL), mixed with saturated $NiCl_2{\cdot}6H_2O$ solution (10 mL). Crystals of the title compound were obtained after one week at room temperature, which were recrystallized from ethanol-water (V:V = 1:1) solution to give green prismatic crystals, m.p.: 584 K (decomposed). IR (KBr) ν: 3447, 1645, 1598, 1489, 1258, 1191, 1091, 828, 631, 550, 489 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ: 3.77 (s, 3H, CH_3O–C_6), 3.79 (s, 6H, CH_3O–C_7 and CH_3O–$C_{4'}$), 3.93 (s, 3H, CH_3O–C_5), 7.00 (s, 1H, H–C_8), 7.03 (d, 1H, $J = 5.4$ Hz, H–$C_{5'}$), 7.44 (dd, 1H, $J = 8.5$ Hz, $J = 2.0$ Hz, H–$C_{6'}$), 7.84 (d, 1H, $J = 2.0$ Hz, H–$C_{2'}$), 8.25 (s, 1H, H–C_2).

A single crystal with dimensions of 0.39 mm × 0.36 mm × 0.17 mm was chosen for

Table 1. Crystal Data and Structure Refinement for the Title Compound

CCDC no	284891
Empirical formula	C_{38} H_{50} Ni O_{26} S_2
Formula weight	1045.61
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*–1
Unit cell dimensions	
a (Å)	8.3518(16)
b (Å)	11.402(2)
c (Å)	13.432(3)
α	66.676(3)°
β	80.337(3)°
γ	73.289(3)°
Volume (Å^3)	1122.8(4)
Z, Calculated density (mg m^{-3})	1, 1.546
Absorption coefficient (mm^{-1})	0.619
F(000)	546
Crystal size (mm)	0.39 × 0.36 × 0.17
θ range for data collection (°)	2.01–28.41
Limiting indices	$-11 \le h \le 10$, $-14 \le k \le 9$, $-17 \le l \le 17$
Reflections collected/unique	7368/5197 [$R_{int} = 0.0142$]
Absorption correction	Semi empirical from equivalents
Max. and min. transmission	0.9021 and 0.7944
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5197/12/339
Goodness Of fit on F^2	1.007
Final *R* indices [$I > 2\sigma$ (*I*)]	$R_1 = 0.0383$, $wR_2 = 0.0984$
R indices (all data)	$R_1 = 0.0535$, $wR_2 = 0.1097$
Largest diff. peak and hole (eA^{-3})	0.492 and −0.359

X-ray diffraction (XRD) studies. The data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart-1000 CCD diffractometer at room temperature. The structure was solved by direct methods and refined on F^2 by full matrix least-squares with the Bruker's SHELXL-97 program.[15] 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 refinement converged to final $R = 0.0383$, $wR = 0.0984$. Data collection detail and structure determination results are summarized in Table 1. Selected bond lengths and angles are presented in Table 2.

Results and discussion

The title compound consists of a complex cation $[Ni(H_2O)_6]^{2+}$, two anions of isoflavone sulfonate $C_{19}H_{17}O_6SO_3^-$ and two lattice water molecules (Fig. 1). Ni(II) lies on an inversion center and is coordinated by six water molecules which form a slightly distorted octahedron, in which the average bond length of Ni–O is 2.055 Å. The anion $C_{19}H_{17}O_6SO_3^-$ is composed of a benzopyranone moiety, including rings A (C4–C9) and C (O1/C9/C1–C4), a phenyl moiety B (C10–C15), four methoxyl groups and a sulfo-group. The atoms of benzopyranone moiety are nearly coplanar, the dihedral angle between ring A (C4–C9) and ring

Table 2. Selected Bond Lengths (Å) and Angles (°) for the Title Compound

Ni(1)–O(12)	2.0351(16)	Ni(1)–O(10)	2.0572(15)
Ni(1)–O(11)	2.0744(16)	O(1)–C(1)	1.343(2)
O(1)–C(9)	1.375(2)	O(2)–C(3)	1.235(2)
O(3)–C(5)	1.376(2)	O(4)–C(6)	1.373(3)
O(5)–C(7)	1.345(3)	O(6)–C(13)	1.351(2)
O(7)–S(1)	1.4458(15)	O(9)–S(1)	1.4585(17)
O(10)–H(21)	0.826(16)	O(11)–H(23)	0.858(16)
O(11)–H(24)	0.833(16)	O(12)–H(25)	0.860(16)
O(13)–H(27)	0.900(14)	S(1)–C(12)	1.777(2)
C(1)–C(2)	1.346(3)	C(1)–H(1)	0.9300
C(2)–C(3)	1.466(3)	C(4)–C(9)	1.397(3)
C(5)–C(6)	1.382(3)	C(6)–C(7)	1.413(3)
C(8)–H(8)	0.9300	C(10)–C(11)	1.392(3)
C(12)–C(13)	1.403(3)	C(16)–H(16A)	0.9600
O(12)–Ni(1)–O(12)	180.0	O(12)–Ni(1)–O(10)	90.69(6)
O(12)–Ni(1)–O(11)	92.79(7)	O(12)–Ni(1)–O(11)	87.21(7)
O(10)–Ni(1)–O(11)	88.77(7)	O(10)–Ni(1)–O(11)	91.23(7)
O(11)–Ni(1)–O(11)	180.00(9)	C(1)–O(1)–C(9)	118.43(16)
C(5)–O(3)–C(16)	114.83(18)	C(13)–O(6)–C(19)	117.99(19)
Ni(1)–O(10)–H(21)	115(2)	H(21)–O(10)–H(22)	107(2)
Ni(1)–O(11)–H(23)	118.6(18)	H(23)–O(11)–H(24)	104.0(19)
Ni(1)–O(12)–H(26)	126(2)	H(27)–O(13)–H(28)	87.6(17)
O(7)–S(1)–O(8)	112.72(10)	O(7)–S(1)–C(12)	108.40(9)
O(1)–C(1)–C(2)	125.84(19)	C(1)–C(2)–C(3)	118.57(18)
C(9)–C(4)–C(5)	115.90(18)	C(6)–C(5)–C(4)	120.89(19)
O(4)–C(6)–C(5)	120.4(2)	C(5)–C(6)–C(7)	120.5(2)
O(5)–C(7)–C(8)	124.4(2)	C(8)–C(7)–C(6)	119.99(19)
C(9)–C(8)–H(8)	120.9	O(1)–C(9)–C(8)	114.12(17)
C(8)–C(9)–C(4)	124.47(19)	C(11)–C(10)–C(15)	117.34(19)
C(15)–C(10)–C(2)	121.03(19)	C(12)–C(11)–C(10)	121.38(19)
C(10)–C(11)–H(11)	119.3	C(11)–C(12)–C(13)	120.39(19)
C(11)–C(12)–S(1)	118.27(16)	O(6)–C(13)–C(14)	124.7(2)
C(15)–C(14)–C(13)	120.7(2)	C(15)–C(14)–H(14)	119.6
O(3)–C(16)–H(16A)	109.5	H(16A)–C(16)–H(16B)	109.5

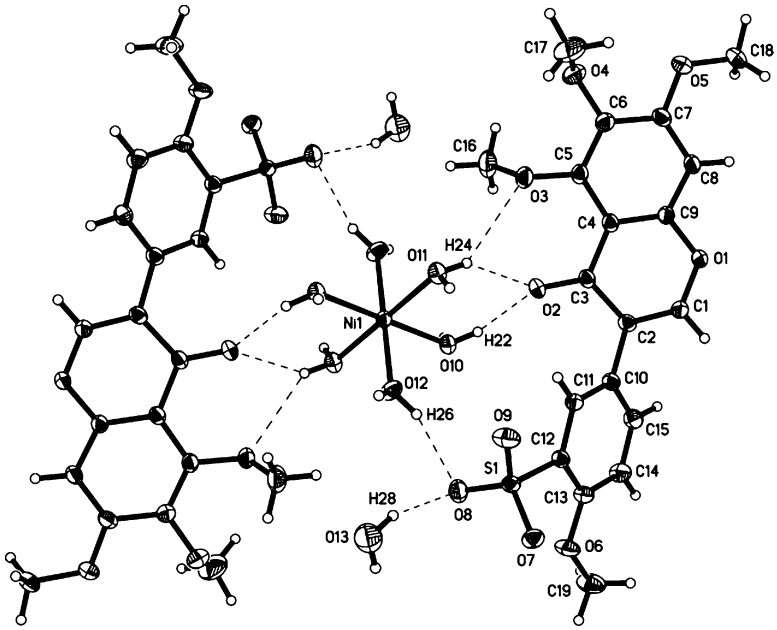


Fig. 1. Molecular structure of the title compound showing 30% probability displacement ellipsoids. Thin dashed lines indicate O–H···O hydrogen bonds.

C (O1/C9/C1–C4) is 4.8° To avoid steric conflicts, the two rigid ring systems, phenyl ring B (C10–C15) and benzopyranone moiety are rotated by 37.1° with respect to each other. The methoxyl groups at atom C7 and C13 are nearly coplanar with their attached rings, as indicated by the torsion angle C8–C7–O5–C18 = 8.5° and C14–C13–O6–C19 = 1.7°. The methoxyl groups at atom C5 and C6 are almost vertical with the benzopyranone moiety, indicative of the torsion angle C4–C5–O3–C16 = −105.6° and C5–C6–O4–C17 = 90.6° The similar S–O bond lengths and bond angles involving O7, O8, and O9 show that the negative charge is delocalized over the three oxygen atoms.[10] As shown in Fig. 1, the sulfo-group(–SO_3), methoxyl group, carbonyl group, two lattice water molecules and six coordinated water molecules are linked by the O–H···O hydrogen bonds (The typical hydrogen bond lengths and angles are given in Table 3). The carbonyl oxygen atom accepts protons from the coordinated water molecules to form tricenterd hydrogen bond, O2 acts as an acceptor, *via* H22 and H24 to O10 and O11, which can be observed for O10–H22···O2, O11–H24···O2. The combination of them generates a $R_2^2(6)$ ring. The oxygen atom of sulfo-group also forms tricenterd hydrogen bond with lattice water molecule and coordinated water molecule, which can be observed for O12–H26···O8, O13–H28···O8. The methoxyl group and the coordinated water molecule are linked by the hydrogen bond O11–H24···O3.

Table 3. Typical Hydrogen Bond Lengths (Å) and Angles (°) for the Title Compound

D–H···A	D–H	H···A	D···A	D–H···A
O10–H21···O7@	0.826	1.928	2.754	176.69
O10–H22···O2	0.833	1.921	2.737	165.93
O11–H23···O13#	0.858	1.846	2.700	173.08
O11–H24···O2	0.833	2.117	2.848	146.25
O11–H24···O3	0.833	2.536	3.234	142.09
O12–H25···O9#	0.860	1.902	2.754	170.87
O12–H26···O8	0.824	2.066	2.857	160.74
O13–H27···O5&	0.900	2.638	3.537	176.64
O13–H28···O8	0.924	2.034	2.927	162.16
C8–H8···O7$	0.930	2.477	3.381	164.18

Symmetry code: @ $x-1, y, z$; # $-x+1, -y+1, -z+1$; & $x+1, y-1, z+1$; \$ $1-x, 1-y, -z$.

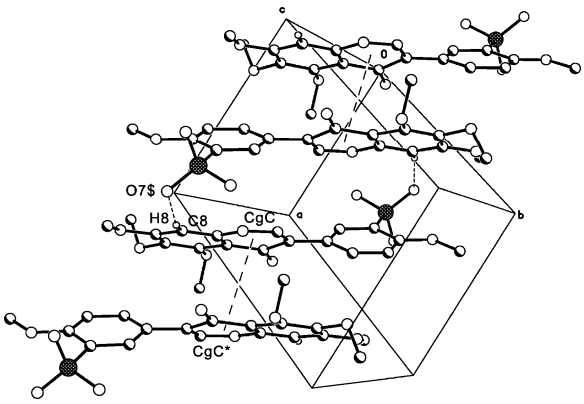


Fig. 2. Part of crystal structure of the title compound, showing π–π stacking interactions and hydrogen bonds. For clarity, some H atoms have been omitted. Symmetry code: $*\ -x, 1-y, -z$; \$ $1-x, 1-y, -z$.

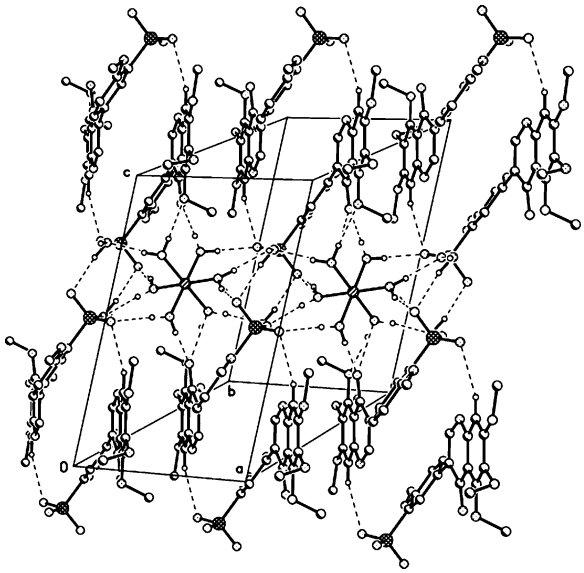


Fig. 3. Unit-cell packing diagram of the title compound.

These hydrogen bonds not only link the isoflavone skeletons, coordinated water molecules and lattice water molecules, but also play an important role in the formation, stability and crystallization of the title compound.

The isoflavone skeletons of title compound are stacked into a hydrophobic column as displayed in Fig. 2. Two adjacent molecules form a π–π interaction dimer by a completely antiparalleled manner between rings C with the interplanar distance of 3.485 Å, the offset distance of 1.021 Å and CgC–CgC* = 3.631 Å, where CgC and CgC* are the centroids of ring C of the adjacent isoflavone skeletons at (x, y, z) and ($-x$, $1-y$, $-z$), respectively. The ring-centroid distance lies in the normal range of 3.3–3.8 Å,[16] indicative of π–π stacking interactions. The dimmer interacts with the other *via* paired intermolecular hydrogen bonds C8–H8···O7 which form a R_2^2 (22) ring. For the hydrogen bond C8–H8···O7\$ [Symmetry code: \$ ($1-x$, $1-y$, $-z$)], atom O7 acted as hydrogen-bond acceptor, *via* atom H8 to C8, the distances of C8···O7 and H8···O7 are 3.381 Å and 2.447 Å, the bond angle C8–H8···O7 being 164.1° Combination of the aromatic π–π stacking interactions and the "soft" C–H···O hydrogen bonds generates the hydrophobic columns along a-axis.

In the crystal structure of title compound, the hydrogen bonds among sulfo-group, carbonyl, methoxyl group of the isoflavone skeleton, lattice water molecules and coordinated water molecules, the π–π stacking interactions of isoflavone skeletons and the electrostatic interactions between the cation and the anion assemble the moieties into supramolecule with a three-dimensional structure. It is interesting that the title compound has a special configuration (Fig. 3). A hydrophilic metal region is formed among lattice water molecules, coordinated water molecules, sulfo-group, methoxyl group and carbonyl *via* hydrogen bonds network. Apart from the hydrogen bonds involved in the molecular structure, the hydrogen bond O11–H23···O13# [Symmetry code: # ($-x+1$, $-y+1$, $-z+1$)] exists between the coordinated water and the lattice water molecule. O13–H27···O5& [Symmetry code: & ($x+1$, $y-1$, $z+1$)] occurs between the lattice water molecule and the sulfo-group. O10–H21···O7@ [Symmetry code: @ ($x-1$, y, z)] and O12–H25···O9# are all hydrogen bonds between the coordinated water molecules and the sulfo-group. Combination of the hydrogen bonds generates the hydrophilic region of the title compound. On the other side, a column is formed

via the π–π stacking interactions of isoflavone skeleton and a hydrophobic region is built by the columns. The sulfo-group bridges the hydrophobic and hydrophilic region, as well as organic and inorganic components in the crystal structure of title compound.

Supplementary material CCDC-284891 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

References

1. Agullo, G.; Gamet-Payrastre, L.; Manenti, S.; Viala, C.; Remesy, C.; Chap, H. & Payrastre, B. *Biochem. Pharmacol*. **1997**, *53,* 1649–1657.
2. Wang, I.K.; Lin-Shiau, S.Y.; Lin, J.K. *Eur. J. Cancer*. **1999**, *35,* 1517–1525.
3. Basnet, P.; Kadota, S.; Shimizu, M.; Xu, H. X.; Namba, T. *Chem. Pharm. Bull*. **1993**, *41,* 1790–1795.
4. Hii, C.S.T.; Howell, S.L. *J. Endocrinol*. **1985**, *107,* 1–8.
5. Ragunathan, V.; Sulochana, N. *J. Indian Chem. Soc*. **1994**, *71,* 705–706.
6. Aida, K.; Tawata, M.; Shindo, S.; Onaya, T.; Sasaki, H.; Yamaguchi, T. *Planta Med*. **1990**, *56,* 254–258.
7. Liu, Q.G.; Zhang, Z.T.; Xue, D. *Chem. J. Chin. Univ.* **2003**, *24,* 820.
8. Wang, Q.Y.; Zhang, Z.T. *Acta Cryst*. **2005**, *61,* 215–217.
9. Zhang, Z.T; Guo, Y.N.; Liu, Q.G. *Chin. J. Chem*. **2004**, *22,* 971–977.
10. Wang, X.B.; Zhang, Z.T.; Wang, Q.Y. *Struct. Chem*. **2005**, *16*(5), 461–468.
11. Kim, D.H.; Yu, K.H.; Bae, E.A.; Han, MJ. *Biol. Pharm. Bull.* **1998**, *21,* 628–630.
12. Han, Y.O.; Han, M.J.; Park, S.H.; Kim, D.H. *J. Pharmacol. Sci.* **2003**, *93,* 331–336.
13. Yamazaki, T.; Nakajima, Y.; Niho, Y.; Hosono, T.; Kurashige, T.; Kinjo, J.; Nohara, T. *J. Pharm. Pharmacol*. **1997**, *49*(8), 831–833.
14. Yamazaki, T.; Hosono, T.; Matsushita, Y.; Kawashima, K.; Someya, M.; Nakajima, Y.; Narui, K.; Hibi, Y.; Ishizaki, M.; Kinjo, J.; Nohara, T. *Int. J. Clin. Pharmacol. Res*. **2002**, *22*(1), 23–28.
15. Sheldrick, G.M., *SHELX-97, Program Package for Crystal Structure Solution and Refinement*; University of Göttingen: Germany, 1997.
16. Janiak, C. *J. Chem. Soc. Dalton Trans*. **2000**, 3885–3896.