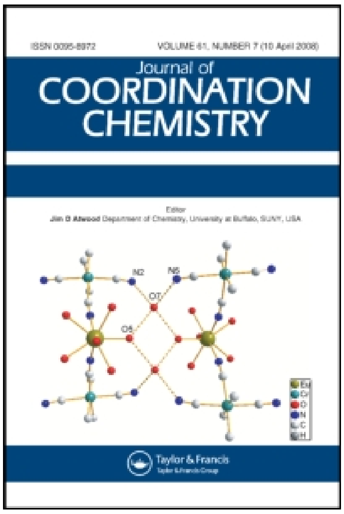

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Self-assembly and crystal structure of a three-dimensional copper(II) complex

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Self-assembly and crystal structure of a three-dimensional copper(II) complex

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A copper(II) complex of a sulfonate derivative of chrysin, 5,7-bihydroxyflavone-6-sulfonate, $Cu(C_{15}H_8O_7S)(3H_2O)$, has been prepared. The complex was characterized by elemental analysis, spectroscopic measurements and single-crystal X-ray diffraction studies. It crystallizes in the monoclinic space group $C2/c$, with $a = 16.036(18)$, $b = 6.944(8)$, $c = 28.03(3)$ Å, $\beta = 94.463(17)^\circ$, $V = 3112(6)$ Å^3, $Z = 8$. In the complex, Cu(II) is five-coordinate and all donors are oxygen atoms. Hydrogen bonds and π–π stacking interactions in the crystal lead to the formation of a three-dimensional supramolecular motif.

Keywords: Chrysin; Copper; Hydrogen bonding; π–π Stacking; Crystal structure

1. Introduction

Flavonoids, 2-phenylbenzo-γ-pyrones, are a broad class of polyphenolic secondary metabolites abundant in vascular plants and in various foods such as apples, soy, onions and tea [1]. They possess a number of pharmacological properties, including anti-oxidant, anti-cancer, anti-viral and anti-inflammatory behaviour [2]. Chrysin, a widely distributed flavone, has been reported to display anti-oxidant [3], anti-virus [1], anti-diabetogenic [4] and anti-anxiolytic effects [5]. Furthermore, chrysin has demonstrated anti-cancer activities [6, 7]. Chrysin and its sulfonate derivatives are able to coordinate metal ions [8–12]. In this article, we report a copper(II) complex of a chrysin sulfonate, $Cu(C_{15}H_8O_7S)(3H_2O)$. In the solid state, hydrogen bonds and π–π stacking interactions lead to the formation of a three-dimensional supramolecular motif.

2. Experimental

Chrysin was purchased from the Nantong Litian Chemicals Company of Jiangsu Province. Other chemicals of analytical reagent grade were used directly without

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Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{15}H_{14}CuO_{10}S_1$
Formula weight	449.86
Crystal size (mm^3)	$0.47 \times 0.23 \times 0.09$
Crystal system	Monoclinic
Space group	$C2/c$
Z	8
Unit cell dimensions (Å, °)	
a	16.036(18)
b	6.944(8)
c	28.03(3)
β	94.463(17)
Volume (Å^3)	3112(6)
Density (g cm^{-3})	1.920
Absorption coefficient (mm^{-1})	1.599
$F(000)$	1832
Limiting indices	$-18 \le h \le 17$, $-8 \le k \le 8$, $-29 \le l \le 33$
θ range for data collection (°)	2.55–25.01
Completeness to $\theta = 25.01°$	96.0%
Data/restraints/parameters	2644/9/263
Goodness-of-fit on F^2	1.014
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0672$, $wR_2 = 0.1623$
R indices (all data)	$R_1 = 0.1043$, $wR_2 = 0.1747$
Largest diff. peak and hole (e Å^{-3})	1.031 and −0.716

further purification. IR spectra (KBr discs) were measured as on a Nicolet 170SX FT-IR spectrophotometer in the range 4000–500 cm^{-1}, and ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer with TMS as internal reference and DMSO-d$_6$ as solvent. Elemental analyses were performed with a VarioEL III instrument.

2.1. *Synthesis*

Chrysin (2.0 g) was added to concentrated sulfuric acid (10 cm^3) with stirring. The mixture was heated at 80° for 12 h, cooled at room temperature and poured into a saturated aqueous solution of sodium chloride (100 cm^3). After 2 h, the yellow precipitate that had formed was filtered off and washed with saturated sodium chloride solution until the pH of the filtrate was 7. It was then dissolved in water (100 cm^3), and mixed with a saturated $CuSO_4$ solution (10 cm^3) to give a green precipitate appeared. The precipitate was filtered off, washed with boiling water (50 cm^3) and recrystallized from 5% aqueous DMSO. Yield: 42.4%. Anal. Calcd for $C_{15}H_{14}CuO_{10}S_1$ (%): C, 40.05; H, 3.11. Found: C, 40.43; H, 3.54. IR (cm^{-1}): 3358(br, w), 2284(br, w), 1634(s), 1597(s), 1543(s), 1449(s), 1377(s), 1171(br, w), 1149(s), 1026(s), 923, 771, 587. ^{1}H NMR (ppm): 7.46(1H, s, H–C3), 6.73(1H, s, H–C8), 7.79(3H, m, H–C2′, C4′, C6′), 8.08(2H, q, H–C3′, C5′), 13.69(1H, s, HO–C7).

2.2. *X-ray structure*

Green prismatic crystals of the complex suitable for single-crystal X-ray diffraction were obtained from aqueous DMSO solution after 2 weeks. Crystallographic data for the complex are summarized in table 1. Intensity data were collected on a Bruker Smart-1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Cu(1)–O(3)	1.894(4)	O(3)–Cu(1)–O(2)	94.63(17)
Cu(1)–O(2)	1.906(4)	O(3)–Cu(1)–O(9)	89.41(18)
Cu(1)–O(9)	1.950(4)	O(2)–Cu(1)–O(9)	165.6(2)
Cu(1)–O(10)	1.976(5)	O(3)–Cu(1)–O(10)	178.24(18)
Cu(1)–O(8)	2.320(5)	O(2)–Cu(1)–O(10)	86.97(18)
O(2)–C(3)	1.247(7)	O(9)–Cu(1)–O(10)	88.86(19)
O(3)–C(5)	1.285(7)	O(3)–Cu(1)–O(8)	94.46(16)
O(5)–S(1)	1.459(4)	O(2)–Cu(1)–O(8)	95.24(18)
O(6)–S(1)	1.442(4)	O(9)–Cu(1)–O(8)	98.2(2)
O(10)–Cu(1)–O(8)	86.10(18)	C(3)–O(2)–Cu(1)	125.4(3)
C(5)–O(3)–Cu(1)	126.5(3)	Cu(1)–O(8)–H(18)	114(6)
Cu(1)–O(8)–H(17)	107(6)	Cu(1)–O(9)–H(19)	115(5)
Cu(1)–O(9)–H(20)	135(5)	Cu(1)–O(10)–H(21)	108(5)
Cu(1)–O(10)–H(22)	137(6)	O(6)–S(1)–O(5)	113.7(3)
O(6)–S(1)–O(7)	109.8(2)	O(5)–S(1)–O(7)	111.1(2)
O(6)–S(1)–C(6)	106.3(2)	O(5)–S(1)–C(6)	108.7(3)

($\lambda = 0.71073$ Å) by the ω scan mode. A total of 5757 reflections was collected at 298(2) K to give 2644 independent reflections ($R_{\text{int}} = 0.1152$). The structure was solved by direct methods (SHELXL-97) and 263 parameters refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. Hydrogen atoms were treated using a riding model. The final R indices [$I > 2\sigma(I)$] were $R_1 = 0.0672$, $wR_2 = 0.1623$. A summary of crystal data and refinement details is given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

A perspective view of the complex and the numbering of the atoms are shown in figure 1. The complex consists of 5-hydroxyl-7-hydroxyflavone-6-sulfonate with the 5-hydroxyl group deprotonated, a Cu(II) ion and three water molecules. Bond lengths and angles in the flavone ligand are in agreement with those reported elsewhere [13]. The benzopyranone moiety consists of ring A(C4–C9) and ring C(O1/C1–C4/C9), which are planar with a dihedral angle of 1.3°. Rings B and C are rotated by 2.4°, which shows that the flavone skeleton is nearly coplanar. In addition, atoms of the benzopyranone moiety and the Cu(II) ion are almost coplanar, with a mean deviation from the least-squares plane of 0.0692 Å. The coordination number of Cu(II) is 5 and the coordinating atoms are all oxygen (carbonyl, hydroxyl and H_2O). The flavone derivative acts as a bidentate and coordination is completed by three water molecules. The range of Cu–O bond lengths is 1.894(4) to 2.320(5) Å, which is close normal [14]. O(4)–H(4)$\cdots$O(7) constitutes an intramolecular hydrogen bond between the 7-hydroxyl and sulfonate groups of the flavone ligand; the H(4)–O(7) distance is 1.84 Å.

Aromatic stacking interactions exist in the crystal. The benzopyranone moiety forms a π_{10}^{11} conjugated system in the flavone skeleton. As shown in figure 2, C_gAC, C_gA and C_gB are the centres of gravity of the benzopyranone, rings A and B of the molecule at (x, y, z), respectively. The molecule arranged in an antiparallel fashion with an adjacent molecule

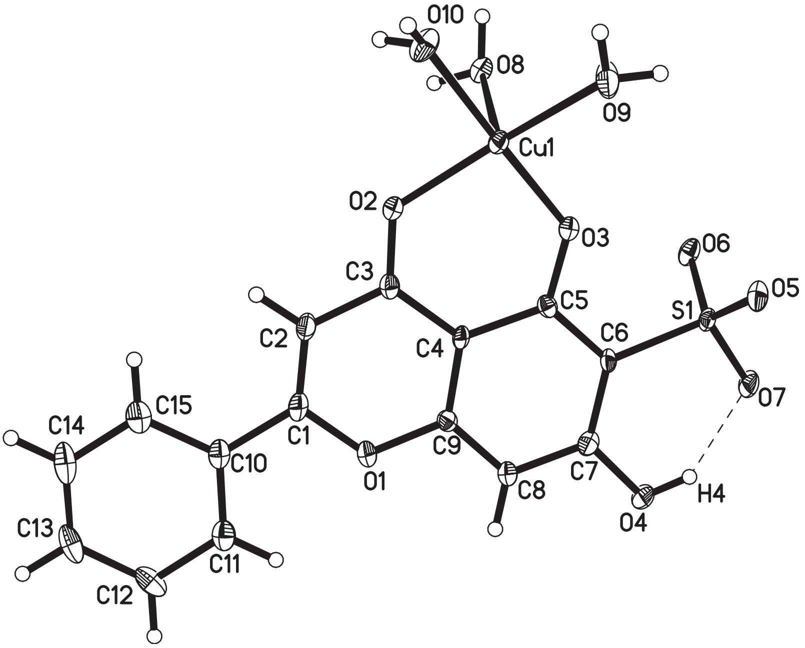

Figure 1. Molecular structure of the complex.

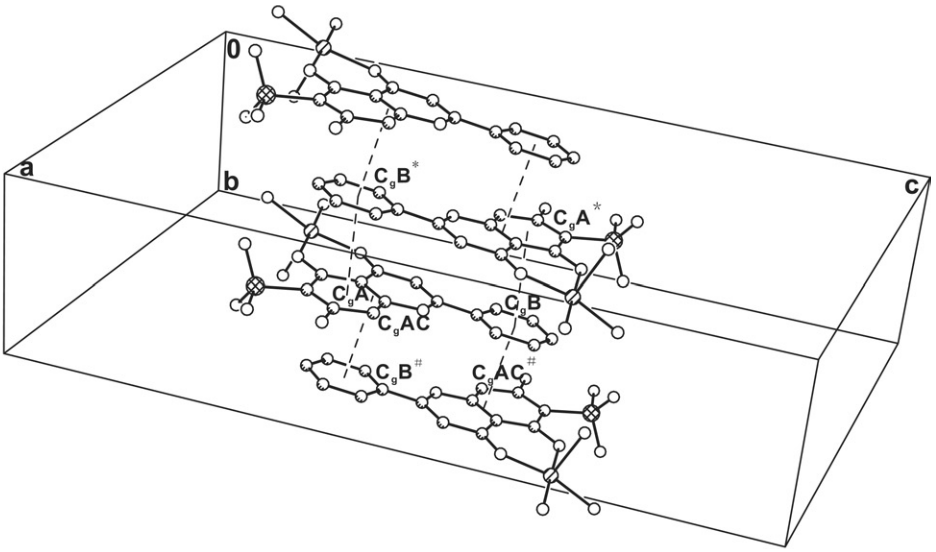

Figure 2. π–π stacking in the complex along the *b* axis.

with $C_gAC - C_gB^\# = 3.452$ and $C_gAC^\# - C_gB = 3.452$, where $C_gAC^\#$ and $C_gB^\#$ are the centres of gravity of the benzopyranone and ring B at $(1.5 - x,\ 1.5 - y,\ 1 - z)$. Meanwhile, the molecule is also antiparallel to another adjacent molecule with the $C_gA - C_gB^* = 3.357$ and $C_gB - C_gA^* = 3.357$, where C_gA^* and C_gB^* are at

Table 3. Hydrogen bond data for the complex.

D–H···A	δ(D–H)	δ(H···A)	δ(D···A)	∠(DHA)
O(8)–H(4)···O(7)	0.82	1.84	2.558	144.88
O(8)–H(17)···O(7)	0.84	2.07	2.8782	160.70
O(8)–H(18)···O(5)	0.85	1.84	2.6901	178.41
O(9)–H(19)···O(6)	0.85	1.90	2.7354	171.80
O(9)–H(20)···O(8)	0.85	1.84	2.7113	151.43
O(10)–H(21)···O(5)	0.84	2.05	2.8400	158.46
O(10)–H(22)···O(6)	0.84	1.94	2.7729	169.80

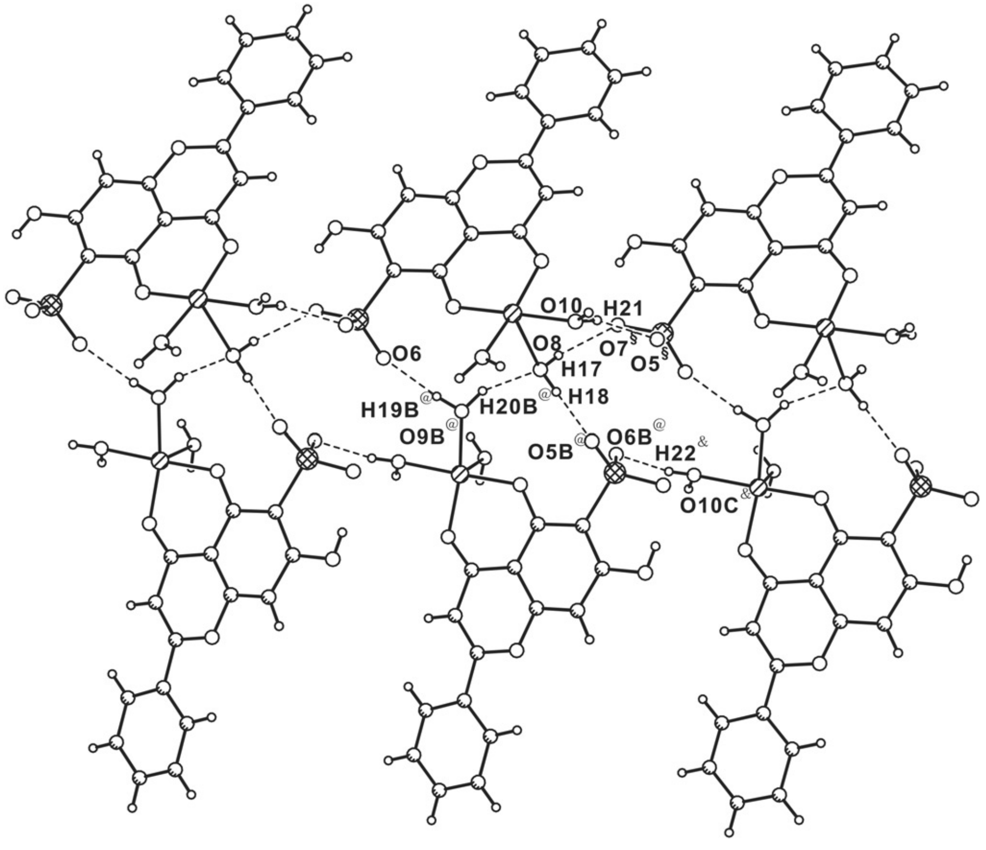

Figure 3. The hydrogen bond network linking molecules in the lattice.

$(1.5 - x, 0.5 - y, 1 - z)$. These centriod–centroid distances are in the usual range of π–π stacking interactions (3.30–3.80 Å) [15]. The aromatic stacking propagates along the *b* axis.

There are six different intermolecular hydrogen bonds in the crystal structure of the complex (table 3). O(8)–H(17)···O(7) and O(10)–H(21)···O(5) interactions link the molecules into a infinite saw-toothed chain. At the same time, another similar chain is formed by O(6)–H(22)···O(10). The two chains are connected by O(8)–H(18)···O(5), O(9)–H(19)···O(6) and O(9)–H(20)···O(8) to form a more complex chain extending

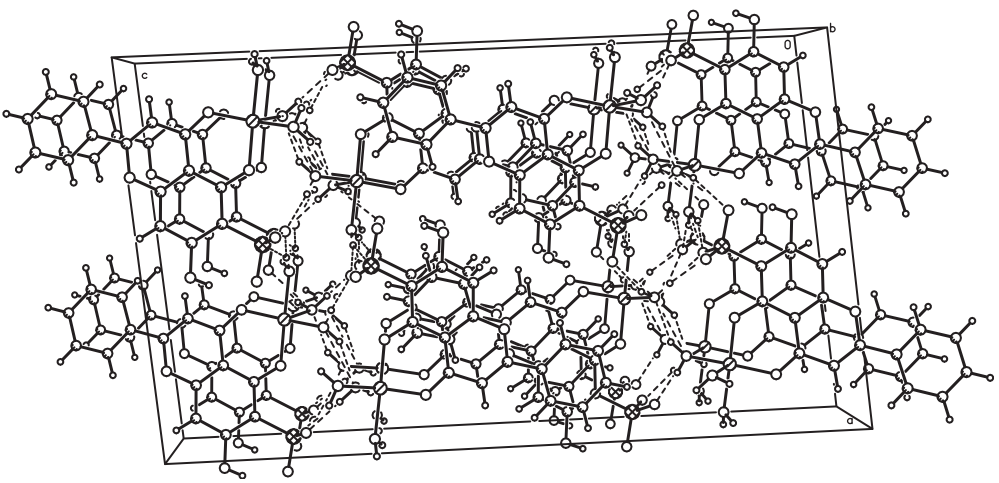

Figure 4. Packing of the complex in the lattice.

along [110] (figure 3). The hydrogen bonds and aromatic stacking interactions assemble the complex to a three-dimensional network (figure 4).

3.2. *Spectroscopy*

In the IR spectrum of the complex, the absorption peak of the carbonyl group appears at 1634 cm^{-1} and has an Einstein shift contrary to that of the free flavone ligand (1654 cm^{-1}), which indicates that the carbonyl is coordinated to Cu^{2+}. Strong absorption due to water is seen at 3358 cm^{-1}; rocking modes occur at 771 and 587 cm^{-1}, in agreements with its coordination [16]. Characteristic absorption peaks of sulfonate group appear at 1171, 1149 and 1026 cm^{-1} [17]. In ^{1}H NMR spectra, the peak of the 5-hydroxyl proton disappears in the complex, confirming that this group is coordinated to Cu^{2+} as O^-.

Supplementary material

Supplementary data have been deposited with the Cambridge Crystallographic Centre, CCDC No. 290370. These data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/deposit).

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