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# Synthesis, Crystal Structure, and Biological Activity of Two Complexes Based on 5-Hydroxy-4′-Methoxyisoflavone-3′-Sulfonate[1]

**J. Shi[a], * and Z. T. Zhang[b]**

[a]*Shaanxi Key Laboratory of Catalysis, School of Chemical and Environmental Sciences, Shaanxi University of Technology, Hanzhong, 723001 P.R. China*

[b]*Key Laboratory of the Ministry of Education for Medicinal Resources and Natural Pharmaceutical Chemistry, National Engineering Laboratory for Resource Development of Endangered Crude Drugs in Northwest of China, and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062 P.R. China*

**e-mail: 446269824@qq.com*

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**Abstract**—Two metal complexes $[Mn(H_2O)_6(C_{16}H_{11}O_7S)_2] \cdot 2H_2O$ (**I**) and $Al(H_2O)_3(C_{16}H_{11}O_7S) \cdot 2H_2O$ (**II**) were synthesized by reaction of the sodium 5-hydroxy-4'-methoxyisoflavone-3'-sulfonate ($C_{16}H_{11}O_7SNa$) with $MnSO_4 \cdot 4H_2O$ or $Al(NO_3)_2 \cdot 6H_2O$, respectively. Complex **I** and **II** were characterized by the single crystal X-ray diffraction (CIF files CCDC nos. 1563980 (**I**), 1563981 (**II**)), IR spectroscopy, thermogravimetric and elemental analysis. For complex **I**, the coordination number of Mn(II) is 6 and the coordinated atoms are all oxygen atoms from six $H_2O$ molecules. For complex **II**, the coordination number of Al(III) is 4, and coordinated atoms come not only from three water molecules but also the sulfo-group. Furthermore, **I** and **II** have hydrogen bonding and π···π stacking supramolecular interactions. Hydrogen bonding forms a hydrophilic region, π···π stacking forms a hydrophobic region. The sulfo-group is a vital bridge between the hydrophilic region and the hydrophobic region, which improves the water-soluble ability and prompts the versatile assembly of pallidiflorin with metal ion. In addition, the preliminary biological test showed that **I**, **II** had antimicrobial activities.

*Keywords:* sodium 5-hydroxy-4'-methoxyisoflavone-3'-sulfonate, complex, hydrogen bond, π–π stacking, single crystal X-ray diffraction, antimicrobial activity

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## INTRODUCTION

Owing to wide range of biological activities, such as antioxidant [1], anticancer [2, 3], antiosteoporotic and anti-hyperkinesias [4, 5], isoflavonoids are well known in the literature. In view of poor bioavailability and high dose for its poor solubility of flavonoids, the structure modification was employed to improve the solubility of parent isoflavonoids and explored new drugs [6–11]. Some flavonoid sulfates were synthesized and their biological activities were studied, the results showed that the flavonoid sulfates possess better water-solubility and biological activities compared with their parent flavonoids [12–15]. Our research group have synthesized a serial of water-soluble derivatives of flavonoids and studied their crystal structures, for example, $[Ni(H_2O)_6(C_{17}H_{13}O_4SO_3)_2] \cdot 8H_2O$ [16], $[Ba(H_2O)_4(C_{15}H_9O_4SO_3)_2] \cdot 4H_2O$, $[Ba(H_2O)_4(C_{16}H_{11}O_4SO_3)_2] \cdot 8H_2O$, $[Ba(H_2O)_7(C_{17}H_{13}O_5SO_3)_2] \cdot 2H_2O$ and $[Ba(H_2O)_7(C_{17}H_{13}O_6O_3)] \cdot 3H_2O$ [17], $[M(H_2O)_6(C_{17}H_{12}O_6BrSO_3)_2] \cdot H_2O$ (M = Co, Zn, Fe, Ni, Mg, Cd) [18]. We found that electrostatic interactions, hydrogen bonding and π···π interactions were very common in those flavonoid sulfates, but coordination action was hardly found between the flavone skeleton and metal ion [19–22]. However, it is well-known that metal-organic complex are rapidly increasing in number in recently years because of their wide potential applications in photochemical areas, molecular magnetism, heterogeneous catalysis and so on. In the present paper, two complexes were prepared by the self-assembly of 5-hydroxy-4'-methoxy-isoflavone-3'-sulfonate ($C_{16}H_{11}O_7S$) with Mn(II) and Al(III). The structure of $[Mn(H_2O)_6(C_{16}H_{11}O_7S)_2] \cdot 2H_2O$ (**I**) contained two ($C_{16}H_{11}O_4SO_3^-$) anions, six coordination water and two lattice water molecules. The coordination interaction only happened between metal ion and coordination water. Compared with **I**, $[Al(C_{16}H_{11}O_7S)(H_2O)_3] \cdot 2H_2O$ (**II**) is an aluminum complex of sul-

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fonate pallidiflorin. The coordinated oxygen atoms come from sulfo-group of ligand and three coordinated $H_2O$ molecules. The antimicrobial abilities of prepared **I** and **II** were evaluated against *Staphylococcus aureus* and *Escherichia coli*.

## EXPERIMENTAL

**Materials and measurements.** All the reagents and solvents were commercially available and used as received. The melting points were taken on X-5 melting point apparatus and uncorrected. The infrared spectra were recorded on a Nicollet 170SX FTIR spectrophotometer with KBr pellets in the 4000–500 $cm^{-1}$ region. The crystal diffraction data were collected on a Bruker Smart-1000 CCD diffractometer. The elemental analysis were carried out with a Perkin-Elmer 240C elemental analyzer.

**Synthesis of complex I.** Sodium 5-hydroxy-4'-methoxyisoflavone-3'-sulfonate ($C_{16}H_{11}O_7SNa$) was obtained firstly according to a published procedure [23]. Furthermore, $C_{16}H_{11}O_7SNa$ (0.37 g) and $MnSO_4 \cdot 4H_2O$ (0.36 g) was added to water (20 mL) and heated to dissolve and cooled at room temperature, **I** was obtained and recrystallized from methanol and water mixture (v : v = 10 : 1) at room temperature.

For $C_{32}H_{38}O_{22}S_2Mn$ ($M$ = 893.68)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 43.01 | H, 4.29 | O, 39.39 |
| Found, % | C, 43.11 | H, 4.35 | O, 39.26 |

IR (KBr; ν, $cm^{-1}$): 3089, 2846, 1627, 1445, 1370, 1123, 1005, 1036, 958.

**Synthesis of complex II** was carried out by the same procedure as used for the preparation of **I** except $Al(NO_3)_2 \cdot 6H_2O$ (0.41 g) was used instead $MnSO_4 \cdot 4H_2O$ and was recrystallized from methanol at room temperature.

For $C_{16}H_{19}O_{12}SAl$ ($M$ = 462.37)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 41.56 | H, 4.14 | O, 41.52 |
| Found, % | C, 41.38 | H, 4.25 | O, 41.41 |

IR (KBr; ν, $cm^{-1}$): 3045, 2813, 1633, 1465, 1343, 1023, 1009, 1016, 949.

**X-ray crystallography.** Single-crystal X-ray data for complexes **I**, **II** were performed on a Bruker Smart-1000 CCD diffractometer at 296(2) K. The diffractometer was equipped with graphite-monochromated Mo$K_\alpha$ radiation (λ = 0.71073 Å). All data sets were corrected for absorption by the ψ–ω method. All structures were solved by the direct method and refined by full matrix least-squares fitting on $F^2$ by SHELX-97. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms on carbon atoms were calculated theoretically. Crystal data and structural refinement parameters for **I** and **II** are summarized in Table 1. Selected bond distances and angles for structures **I** and **II** are listed in Table 2. Geometric parameters of hydrogen bond for **I** and **II** are given in Table 3.

Supplementary material for complexes has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1563980 (**I**), 1563981 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc. camac. uk).

**Antibacterial activity.** The antibacterial activities of complexes **I**, **II** against *Staphylococcus aureus* and *Escherichia coli* were screened. The Oxford cup method was employed and LB agar was prepared in the sterilized flasks. The bacteria solution (0.5 mL) was plated on LB agar. The solutions of **I**, **II** (6.25, 12.5, 25, 50, 100 ppm) were prepared in $H_2O$ for evaluating the biological activity. Under strict aseptic operations, the Oxford cup was placed on the surface of the LB agar. Vertically, and **I**, **II** solutions (0.1 mL) with different concentration were added in the Oxford cups, respectively. The experimental plates were incubated for 24 h at 37°C and the zone of inhibition was measured. Every test was performed in triplicate.

## RESULTS AND DISCUSSION

Single-crystal X-ray diffraction analysis are performed for the **I**, **II** crystals to determine their structures. The molecular structures of **I**, **II** are illustrated in Fig. 1. The investigations revealed that **I** has a complex cation $[Mn(H_2O)_6]^{2+}$, two ($C_{16}H_{11}O_4SO_3^-$) anions and two lattice water molecules. The coordination number of Mn(II) is 6 and the coordinated atoms are all oxygen atoms of six $H_2O$ molecules (O(8), O(8)*, O(9), O(9)*, O(10), O(10)*). Mn(II) lies on an inversion centre and forms a slightly distorted octahedral complex cation, the distances of Mn–O are 2.138, 2.157 and 2.181 Å. The crystal structure of **II** (Fig. 1) is an aluminum complex of sulfonate pallidiflorin. The complex consists of a 5-hydroxy-4'-methoxyisoflavone-3'-sulfonate, Al(III), three coordinated water and two lattice water molecules. The coordination number of Al(III) is 4 and coordinated atoms comes from three coordination waters (O(8), O(9), O(10)) and 3'-sulfonate group (O(7)). The distances of Al–O are 2.403, 2.358, 2.432 Å and 2.374 in order, which are agreement with that of reported Al and O [24].

In crystal structure of **I** and **II**, the ($C_{16}H_{11}O_4SO_3^-$) anion possesses isoflavone skeleton including in a benzopyranone moiety, benzene ring, hydroxyl, methoxyl and sulfo-group. The atoms of benzopyranone moiety composed of ring A (C(4)–C(9)) and ring C (O(1)/C(1)–C(4)/C(9)) are planar with dihedral angles of 2.0° (**I**) and 2.4° (**II**). To avoid steric conflicts, phenyl ring B (C(10)–C(15)) and benzopyranone moieties are rotated with angles of 48.0° (**I**)

**Table 1.** Crystallographic data and structure refinement for complexes for **I** and **II**

| Parameter | Value | |
|---|---|---|
| | **I** | **II** |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 8.2261(12) | 8.1979(9) |
| $b$, Å | 33.917(5) | 37.531(4) |
| $c$, Å | 7.5129(11) | 7.2908(9) |
| β, deg | 116.839(2) | 116.007(2) |
| Volume, Å$^3$ | 1870.3(5) | 2016.1(4) |
| $Z$ | 2 | 4 |
| $\rho_{calcd}$, mg/m$^3$ | 1.729 | 1.530 |
| μ, mm$^{-1}$ | 0.572 | 0.267 |
| $F$(000) | 1006 | 968 |
| Reflections collected | 9300 | 9402 |
| Independent reflections | 3314 | 3558 |
| Reflections with $I > 2\sigma(I)$ | 2979 | 2929 |
| GOOF | 1.052 | 1.151 |
| $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.0320$, $wR_2 = 0.0821$ | $R_1 = 0.0521$, $wR_2 = 0.1572$ |
| $R$ indices (all data) | $R_1 = 0.0367$, $wR_2 = 0.0879$ | $R_1 = 0.0651$, $wR_2 = 0.1760$ |
| $\Delta\rho_{max}/\Delta\rho_{min}$, e Å$^{-3}$ | 0.268/−0.319 | 0.463/−0.487 |

**Table 2.** Selected bond distances (Å) and angles (deg) for structures **I** and **II**

| Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|
| | **I** | | |
| Mn(1)–O(8) | 2.1377(18) | S(1)–O(8) | 1.4449(16) |
| Mn(1)–O(9) | 2.1569(16) | S(1)–O(9) | 1.4492(16) |
| Mn(1)–O(10) | 2.1813(19) | S(1)–O(10) | 1.4564(16) |
| | | S(1)–C(14) | 1.7808(19) |
| | **II** | | |
| Al(1)–O(9) | 2.358(3) | S(1)–O(5) | 1.446(2) |
| Al(1)–O(7) | 2.375(3) | S(1)–O(6) | 1.454(3) |
| Al(1)–O(8) | 2.404(3) | S(1)–O(7) | 1.455(2) |
| | | S(1)–C(12) | 1.774(3) |
| **Angle** | **ω, deg** | **Angle** | **ω, deg** |
| | **I** | | |
| O(8)Mn(1)O(9) | 92.43(7) | O(8)S(1)O(10) | 113.42(11) |
| O(8)Mn(1)O(10) | 87.15(8) | O(8)S(1)O(9) | 112.70(10) |
| O(9)Mn(1)O(10) | 87.72(8) | O(10)S(1)O(9) | 111.01(10) |
| Mn(1)O(8)H(1*A*) | 120.6(1) | O(8)S(1)C(14) | 105.77(9) |
| Mn(1)O(8)H(1*B*) | 130.3(2) | O(10)S(1)C(14) | 106.70(9) |
| Mn(1)O(9)H(2*A*) | 109.4(5) | O(9)S(1)C(14) | 106.68(9) |
| Mn(1)O(9)H(2*B*) | 121.2(8) | | |
| Mn(1)O(10)H(3*A*) | 128.7(8) | | |
| Mn(1)O(10)H(3*B*) | 121.9(9) | | |
| | **II** | | |
| O(9)Al(1)O(7) | 101.53(10) | C(13)O(4)C(16) | 117.1(3) |
| O(9)Al(1)O(8) | 167.68(11) | S(1)O(7)Al(1) | 128.97(13) |
| O(7)Al(1)O(8) | 87.32(9) | Al(1)O(8)H(8*B*) | 123(4) |
| O(5)S(1)O(6) | 112.88(16) | Al(1)O(9)H(9*B*) | 122(4) |
| O(5)S(1)O(7) | 112.55(15) | O(2)C(7)C(8) | 122.8(3) |
| O(6)S(1)O(7) | 111.68(15) | O(2)C(7)C(6) | 121.2(3) |
| O(5)S(1)C(12) | 106.02(14) | O(3)C(9)C(8) | 125.7(3) |
| O(6)S(1)C(12) | 106.78(15) | O(3)C(9)H(9) | 117.2 |
| O(7)S(1)C(12) | 106.36(13) | O(4)C(13)C(14) | 123.5(3) |
| C(1)O(1)H(10) | 109.5 | O(4)C(13)C(12) | 116.8(3) |
| C(9)O(3)C(5) | 118.6(2) | | |

**Table 3.** Geometric parameters of hydrogen bond for **I** and **II***

| D–H···A | Distance, Å | | | Angle D–H···A, deg |
|---|---|---|---|---|
| | D–H | H···A | D–A | |
| | | **I** | | |
| O(3)–H(3)···O(2) | 0.82 | 1.86 | 2.590(3) | 148 |
| O(8)–H(8*B*)···O(5) | 0.78(4) | 2.04(4) | 2.812(3) | 170(4) |
| O(9)–H(9*B*)···O(6) | 0.83(4) | 2.04(4) | 2.854(3) | 167(3) |
| O(11)–H(11*B*)···O(2) | 0.93(4) | 1.93(4) | 2.864(3) | 175 |
| C(11)–H(11)···O(5) | 0.93 | 2.44 | 2.853(3) | 107 |
| C(1)–H(1)···O(3)$^{i}$ | 0.93 | 2.41 | 3.305(3) | 160 |
| C(15)–H(15)···O(3)$^{i}$ | 0.93 | 2.71 | 3.249(4) | 118 |
| C(11)–H(11*A*)···O(7)$^{ii}$ | 0.83 | 2.08 | 2.827(4) | 159(4) |
| C(8)–H(8)···O(5)$^{iii}$ | 0.93 | 2.63 | 3.558(3) | 178 |
| O(8)–H(8*A*)···O(11)$^{iv}$ | 0.92(3) | 1.77(3) | 2.667(4) | 165(3) |
| O(9)$^{i}$–H(9*A*)$^{i}$···O(6) | 0.82 | 2.02 | 2.787(3) | 155 |
| O(10)–H(10*B*)···O(4)$^{ii}$ | 0.76(4) | 2.26(4) | 3.006(3) | 168(4) |
| C(16)–H(16*B*)···O(6)$^{v}$ | 0.96 | 2.65 | 3.477(4) | 145 |
| O(10)–H(10*A*)···O(7)$^{vi}$ | 0.79(4) | 2.13(4) | 2.896(3) | 167(4) |
| | | **II** | | |
| O(3)–H(3)···O(2) | 0.82(4) | 1.86(4) | 2.58(8) | 146(5) |
| O(12)–H(12*B*)···O(2) | 0.82(4) | 2.16(4) | 2.97(8) | 173(5) |
| O(11)–H(11*A*)···O(8) | 0.92(6) | 1.93(6) | 2.83(7) | 172(4) |
| O(11)–H(11*B*)···O(6) | 0.82(4) | 2.10(4) | 2.91(5) | 175(3) |
| O(9)–H(9*B*)···O(5)$^{iii}$ | 0.81(4) | 2.10(4) | 2.84(3) | 153(4) |
| O(10)–H(10*B*)···O(11)$^{iv}$ | 0.83(3) | 1.97(4) | 2.79(2) | 177(5) |
| O(12)–H(12*A*)···O(6)$^{i}$ | 0.82(3) | 2.03(4) | 2.81(5) | 160(4) |
| O(8)–H(8)···O(7)$^{ii}$ | 0.82(4) | 2.07(4) | 2.87(3) | 169(4) |
| O(8)–H(8)···O(9)$^{ii}$ | 0.81(5) | 2.99(7) | 2.95(1) | 78(9) |
| C(1)–H(1)···O(3)$^{v}$ | 0.93(4) | 2.46(4) | 3.34(4) | 159 |
| C(11)–H(11)···O(5) | 0.93 | 2.43 | 2.84(4) | 107(1) |
| C(15)–H(15)···O(3)$^{v}$ | 0.93 | 2.62 | 3.20(3) | 121(1) |

* Symmetry codes: $^{i}$ $x-1, y, z$; $^{ii}$ $x, y, 1-z$; $^{iii}$ $x, 1/2-y, 1-z$; $^{iv}$ $1+x, y, 1+z$; $^{v}$ $-x, -y, 1-z$; $^{vi}$ $-x, -y, -z$ (**I**); $^{i}$ $x, 1/2-y, z-1$; $^{ii}$ $1+x, y, z$; $^{iii}$ $x, y, z-1$, $^{iv}$ $1-x, -y, 2-z$; $^{v}$ $x-1, y, z-1$; $^{vi}$ $-x, -y, 1-z$ (**II**).

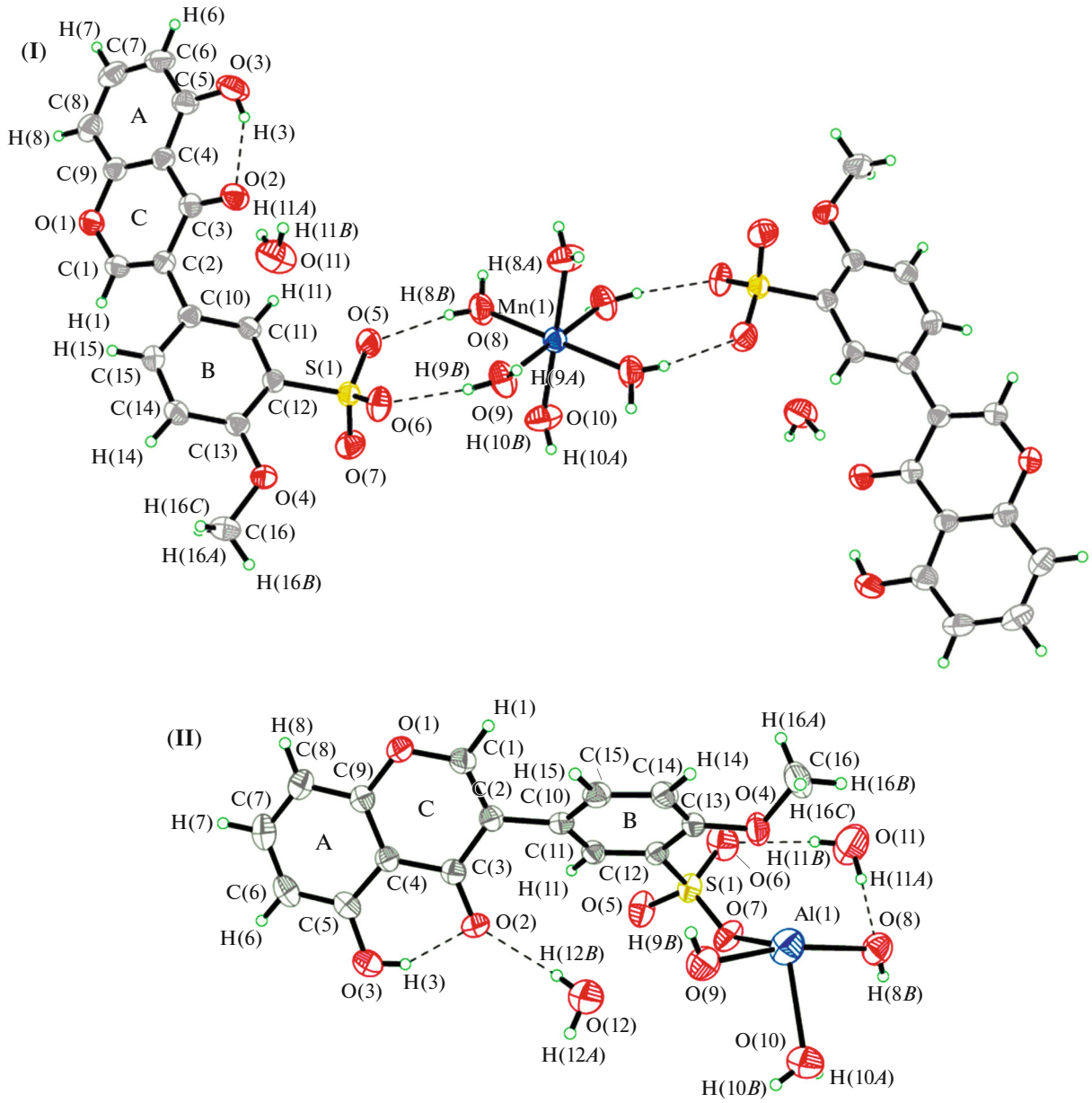


**Fig. 1.** Molecular structure of **I**, **II**. A: the center of the ring A (C(4)–C(9)); B: the center of ring B (C(10)–C(15)); C: the center of ring C (O(1)/C(1)–C(4)/C(9).

and 47.1° (**II**). In addition, the 5-hydroxyl group in **I**, **II** skeleton easily formed O(3)–H(3)···O(2) strong intramolecular hydrogen (bonds O···O are ~2.58 Å, angles OHO ~148°), which formed a typical S(6) ring in the asymmetric unit. And the methoxyl groups at C(13) are nearly coplanar with its attached ring B, indicative of the small torsion angles of 160.0° (**I**) and 155.9° (**II**).

In crystal structure of **I**, **II**, the lattice water molecules, coordinated water molecules, sulfo-group and isoflavone skeleton take part in the hydrogen bond network and produce a variety of hydrogen bondings, which can be classified into four types. Take **I** as an example, the isoflavone closely linked with the complex cation $[M(H_2O)_6]^{2+}$ *via* the influence of O(8)–H(8*B*)···O(5) and O(9)–H(9*B*)···O(6). Two hydrogen bondings exist in sulfo-group and coordination water molecule (Fig. 2). Furthermore, neighboring asymmetric units of **I** are connected together with two H-bonds ((O(10)–H(10*B*)···O(4)$^{ii}$ and O(9)$^{i}$–H(9*A*)$^{i}$···O(6), symmetry code: $^{i}$ $x-1, y, z$, $^{ii}$ $1+x, y, 1+z$)) and formed a two-dimensional chain structure.

In the **II** crystal structure, three hydrogen bonds, O(11)–H(11*A*)···O(8), O(11)–H(11*B*)···O(6) and O(12)–H(12*B*)···O(2) exist in the asymmetric unit and strengthen the connection between the ligand and

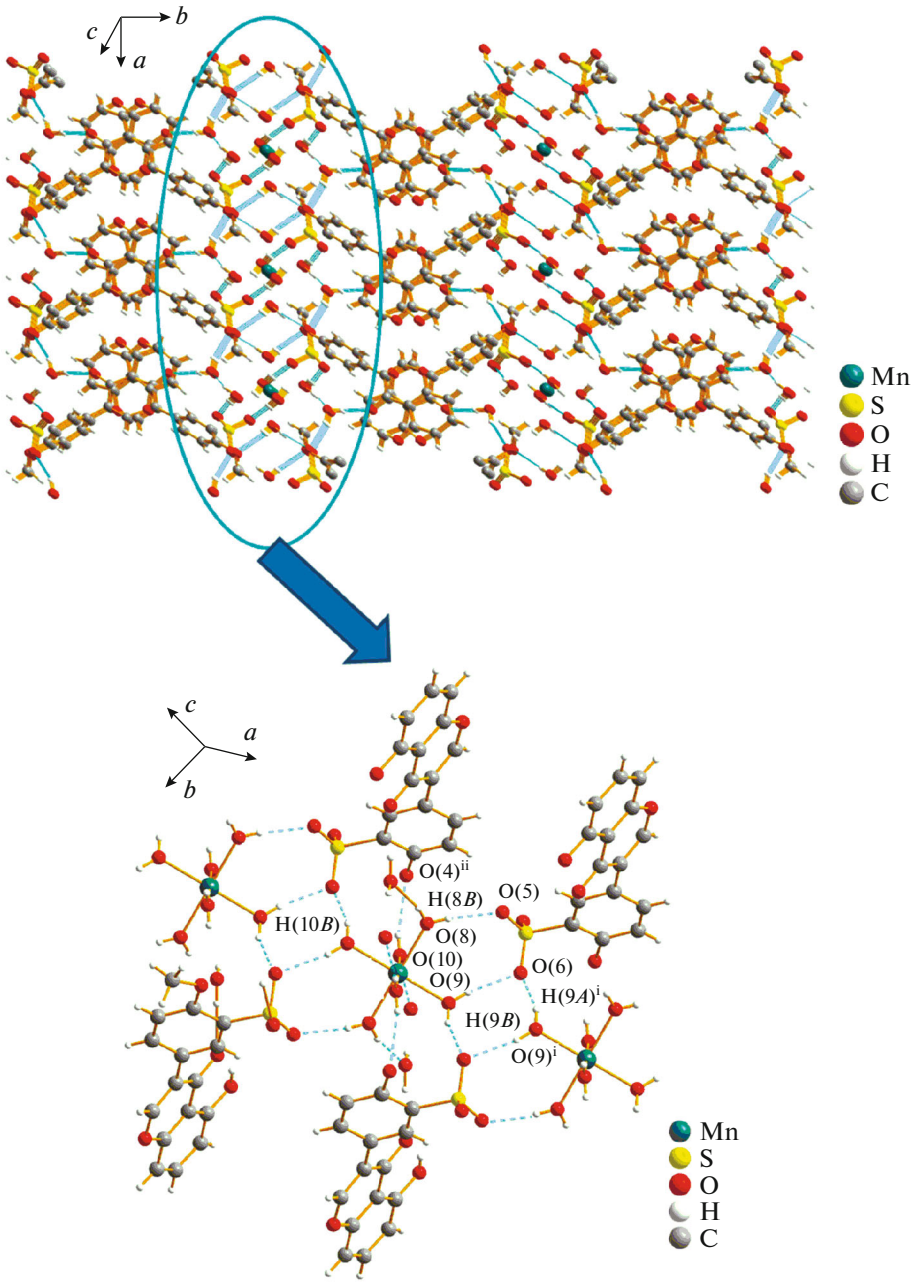


**Fig. 2.** Packing view of complex **I**, showing the hydrogen bonds (dashed lines).

coordination or lattice water (bonds H···O are 1.93, 2.10 and 2.16 Å). Furthermore, O(12)–H(12*A*)···O(6)$^{i}$ and O(8)–H(8)···O(7)$^{ii}$ exist in adjacent asymmetric unit and link neighboring molecules into chain structure (Fig. 3). Hydrogen bond O(12)–H(12*A*)···O(6)$^{i}$ exists in the sulfo-group and lattice $H_2O$ molecule, the bond H···O is 2.00 Å, and O(8)–H(8)···O(7)$^{ii}$ existed in the sulfo-group and coordination water molecule, the bond length is 2.07 Å, symmetry codes: $^{i}$ $x$, $1/2 - y$, $z - 1$, $^{ii}$ $1 + x$, $y$, $z$.

As a result of the larger angles between phenyl ring B (C(10)–C(15)) and benzopyranone moieties in **I** and **II**, the adjacent isoflavone skeletons were forced to arranged in an antiparellel fashion. The benzopyranone moiety forms a $\pi_{10}^{12}$ conjugation system in the flavone skeleton of **I**, **II** (Fig. 4). CgAC is the center of the benzopyranone. CgC is the center ring C in the **I**, **II** complexes at ($x$, $y$, $z$) and CgAC$^{i}$ is the center of the benzopyranone from adjacent molecule with the CgAC$^{i}$–CgC = 3.560 Å (**I**), 3.452 Å (**II**) (symmetry code: $^{i}$ $x$, $0.5 - y$, $z + 0.5$). The adjacent isoflavone

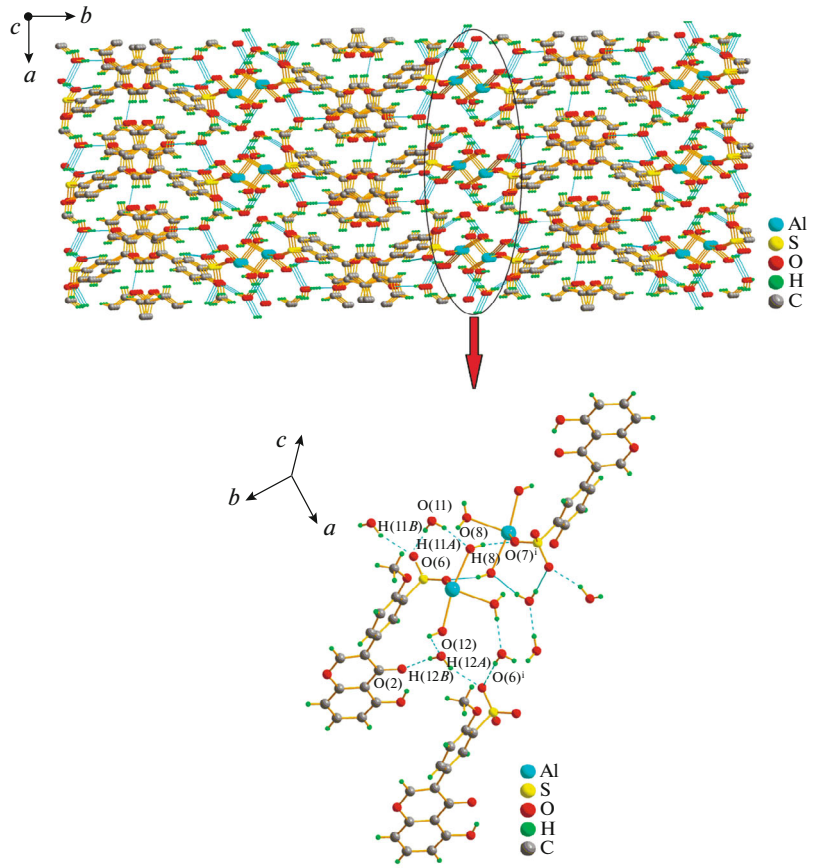


**Fig. 3.** Packing view of compound **II**, showing the hydrogen bonds (dashed lines).

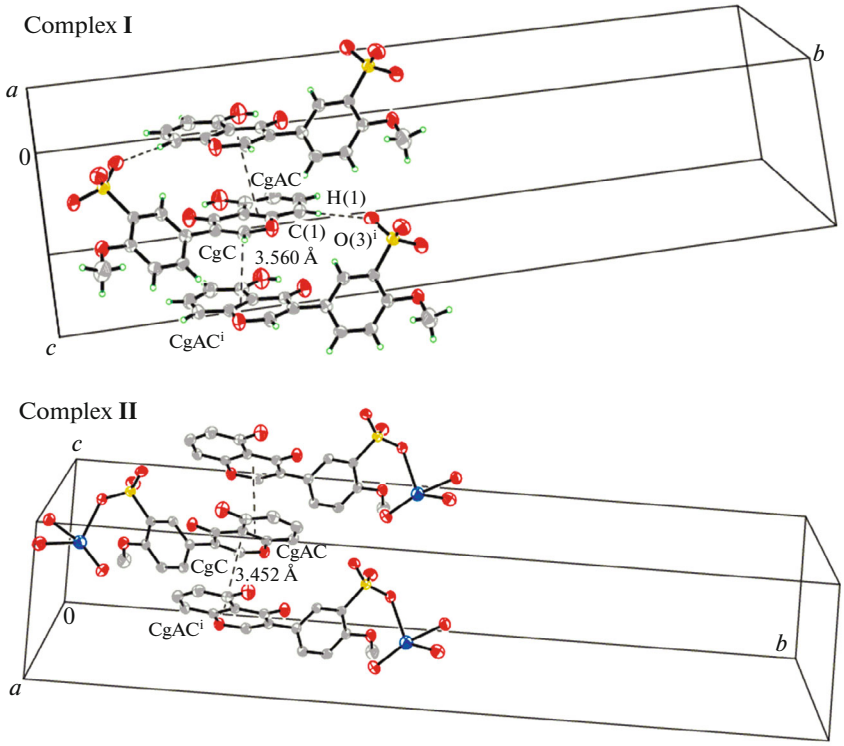


**Fig. 4.** π···π Interaction between two neighboring **I** (a) and **II** (b) molecules (H atoms are omitted for clarity).

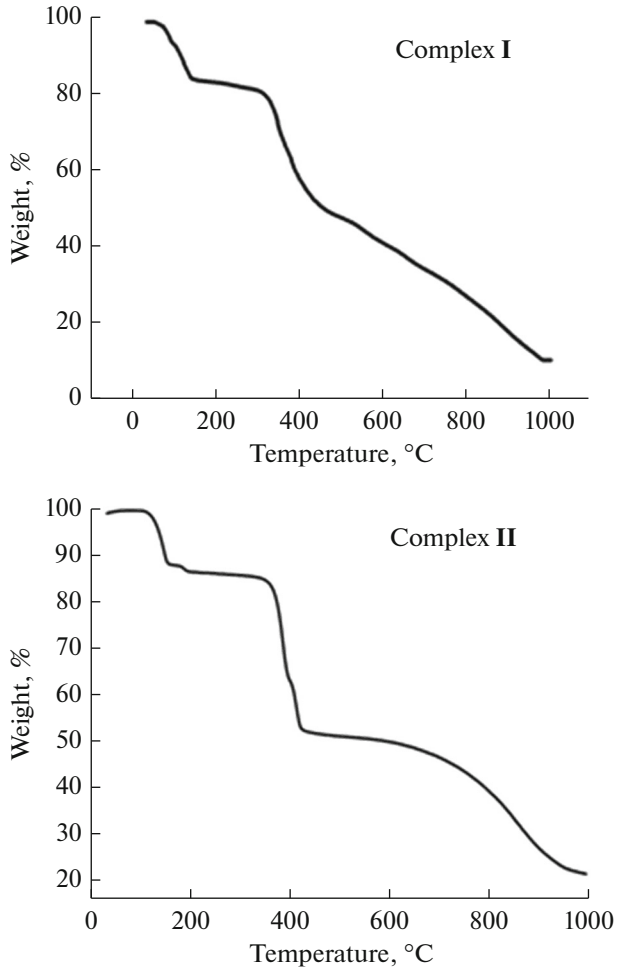


**Fig. 5.** The TG graph of complexes **I** and **II**.

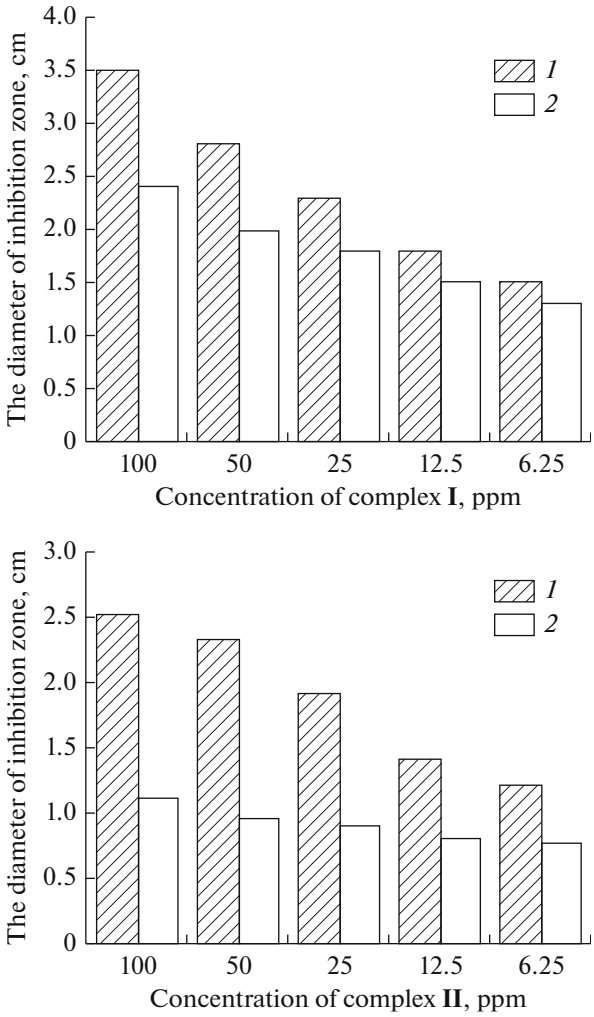


**Fig. 6.** Antimicrobial effect of **I**, **II** with different concentration (the antibacterial activity against *Staphylococcus aureus* (1), against *Escherichia coli* (2)).

skeletons are linked into a inversion dimers, the dimers stacked together to form columns along the *b* axis.

To estimate the stability of the complex, thermal gravimetric measurements for **I** and **II** were carried out. As shown in Fig. 5, the TG curve of **I** shows a weight loss of 16.9% from 95 to 185°C, corresponding to the removal of eight water of $[Mn(H_2O)_6]^{2+} \cdot 2H_2O$ (calcd. 16.1%). The framework ($(C_{16}H_{11}O_4SO_3^-)$ anions) of **I** is stable up to 350°C and then the framework begins to collapse. The end product, estimated as $MnO_2$, has an observed mass of 10.1% compared with the calculated value of 9.8%.

The TG curve of **II** shows a weight loss of 8.0% from 110 to 145°C, corresponding to the removal of two lattice water molecule of each formula unit (calcd. 4.8%). Then the decompositions of three coordinated water molecules and the ligand were followed. The end product, estimated as $Al_3O_2$, has an observed mass of 22.4% compared with the calculated value of 22.1%. The thermal gravimetric analyses show that **I** is more stable than **II**.

As outlined in Fig. 6, **I** and **II** were tested the antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* in vitro. Both of them showed higher antibacterial activities, the results show that a significantly positive correlation was observed between the concentration of **I**, **II** and antimicrobial effect. It also pointed that they had stronger inhibitory against *S. aureus* than *E. coli*. Specifically, **I** was more active than **II** against two bacteria.

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## REFERENCES


1. Saija, A., Scalese, M., Lanza, M., et al., *Free Radical Biol. Med.*, 1995, vol. 19, p. 481.
2. Michihara, S., Tanaka, T., Uzawa, Y., et al., *J. Nutr. Sci. Vitaminol.*, 2012, vol. 58, no. 3, p. 202.
3. Batra, P. and Sharma, A.K., *3Biotech*, 2013, vol. 3, no. 6, p. 439.
4. Mavel, S., Dikic, B., Palakas, S., et al., *Bioorg. Med. Chem.*, 2006, vol. 14, no. 5, p. 1599.
5. Shukla, S., MacLennan, G.T., Flask, C.A., et al., *Cancer Res.*, 2007, vol. 67, no. 14, p. 6925.
6. Wang, S.F., Jiang, Q., Ye, Y.H., et al., *Bioorg. Med. Chem.*, 2005, vol. 13, p. 4880.
7. Lewis, P.T., Wahala, K., Hoikkala, A., et al., *Tetrahedron*, 2000, vol. 56, p. 7805.
8. Yan, X., Li, Y.M., Yu, J., et al., *Acta Chim. Sin.*, 2007, vol. 65, no. 17, p. 1845.
9. Houerou, C.L., Bennetau-Pelissero, C., Lamothe, V., et al., *Tetrahedron*, 2000, vol. 56, p. 295.
10. Bennetau-Pelissero, C., Houerou, C.L., Lamothe, V., et al., *J. Agric. Food Chem.*, 2000, vol. 48, p. 305.
11. Biasutto, L., Marotta, E., Marchi, U.D., et al., *J. Med. Chem.*, 2007, vol. 50, p. 241.
12. Liu, Q.G., Zhang, Z.T., and Xue, D., *Chem. J. Chin. Univ.*, 2003, vol. 24, p. 820.
13. Zhang, Z.T., Wang, Q.Y., and He, Y., *Chem. J. Chin. Univ.*, 2005, vol. 26, p. 2247.
14. Zhang, Z.T., Guo, Y.N., and Liu, Q.G., *Chin. J. Chem.*, 2004, vol. 22, p. 971.
15. He, Y., Zhang, Z.T., and Yang, H.B., *Nat. Prod. Res. Dev.*, 2002, vol. 14, p. 54.
16. Wang, Q.Y. and Zhang, Z.T., *Acta Crystfllogr., Sect C: Cryst. Struct. Commun.*, 2005, vol. 61, p. 215.
17. Zhang, Z.T., Wang, Q.Y., Li, W.W., et al., *CrystEngComm*, 2012, vol. 14, p. 5042.
18. Shi, J., Wang, Y.C., Wang, Q.Y., et al., *Inorg. Chim. Acta*, 2014, vol. 409, p. 259.
19. Zhang, Z.T., Guo, Y.N., and Liu, Q.G., *Sci. China*, 2004, vol. 47, p. 396.
20. Shi, J., Zhang, Z.T., and He, Y., *Acta Chim. Sin.*, 2006, vol. 64, p. 930.
21. Shi, J. and Zhang, Z.T., *Chin. J. Chem.*, 2012, vol. 30, p. 1057.
22. Zhang, Z.T., Shi, J., He, Y., et al., *Inorg. Chem. Commun.*, 2006, vol. 9, p. 579.
23. Ding, R., Wei, T., Wang, et al., *Z. Anorg. Allg. Chem.*, 2015, vol. 641, p. 1130.
24. Hung, Q.D., Li, C.L., Zhang, Y., et al., *Chem. J. Chin. Univ.*, 2014, vol. 35, p. 524.