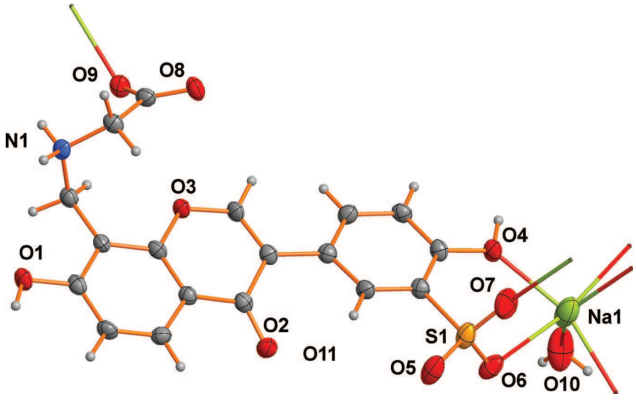
Hai-Lin Chen, Hong-Fang Lai, Yong-Ling Qin*, Yue-Ning Guo, Ting Chen and Xiao-Yuan Huang

Synthesis and crystal structure poly[aqua(μ$_3$-2-(((7-hydroxy-3-(4-hydroxy-3-sulfonatophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)ammonio) acetate-κ^4*O*,*O*′:*O*″:*O*‴) sodium] monohydrate, $C_{18}H_{18}NNaO_{11}S$



https://doi.org/10.1515/ncrs-2017-0321
Received October 18, 2017; accepted January 30, 2018; available online February 16, 2018

Abstract

$C_{18}H_{18}NNa_aO_{11}S$, triclinic, $P\bar{1}$ (no. 2), $a = 8.2627(12)$ Å, $b = 8.6490(11)$ Å, $c = 14.1791(17)$ Å, $\alpha = 82.883(10)°$, $\beta = 76.954(12)°$, $\gamma = 69.729(12)°$, $V = 924.8(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0574$, $wR_{ref}(F^2) = 0.1609$, $T = 293(2)$ K.

CCDC no.: 1820731

A part of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Formaldehyde solution (10 mL, 37%) and sodium 2-hydroxy-5-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)benzenesulfonate (3.56 g, 0.01 mol) were added to ethanol (200 mL, 99.9%) and stirred for 0.5 h at 333 K. The saturated solution of *L*-threonine (1.89 g, 0.016 mol) was added. Then, water was added until a transparent solution was obtained. After

***Corresponding author: Yong-Ling Qin,** College of Chemistry and Biological Engineering, Hechi University, Yizhou, Guangxi 546300, China; and Guangxi Colleges Universities Key Laboratary of Exploitation and Utilization of Microbial and Botanical Resources, Yizhou, Guangxi 546300, China, e-mail: qin0718@163.com
Hai-Lin Chen, Hong-Fang Lai, Yue-Ning Guo, Ting Chen and Xiao-Yuan Huang: College of Chemistry and Biological Engineering, Hechi University, Yizhou, Guangxi 546300, China

Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.37 × 0.27 × 0.17 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.27 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5987, 3262, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2465
$N(param)_{refined}$:	289
Programs:	Bruker programs [1], SHELX [2], Diamond [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2056(4)	0.2321(4)	−0.1916(2)	0.0314(7)
C2	0.1629(4)	0.1657(4)	−0.0986(2)	0.0327(7)
H2	0.1271	0.0733	−0.0901	0.039*
C3	0.1730(4)	0.2348(4)	−0.0200(2)	0.0313(7)
H3	0.1464	0.1878	0.0417	0.038*
C4	0.2233(4)	0.3769(4)	−0.0309(2)	0.0281(7)
C5	0.2574(4)	0.4440(4)	−0.1239(2)	0.0293(7)
C6	0.2547(4)	0.3737(4)	−0.2066(2)	0.0288(7)
C7	0.2501(4)	0.4455(4)	0.0501(2)	0.0302(7)
C8	0.2790(4)	0.6048(4)	0.0304(2)	0.0288(7)
C9	0.3002(5)	0.6615(4)	−0.0620(2)	0.0324(8)
H9	0.3162	0.7640	−0.0742	0.039*
C10	0.2876(4)	0.6996(4)	0.1086(2)	0.0290(7)
C11	0.2199(4)	0.6691(4)	0.2055(2)	0.0303(7)
H11	0.1681	0.5871	0.2217	0.036*
C12	0.2273(4)	0.7568(4)	0.2783(2)	0.0293(7)
C13	0.3028(4)	0.8809(4)	0.2561(2)	0.0310(7)
C14	0.3663(4)	0.9156(4)	0.1600(2)	0.0304(7)
H14	0.4148	1.0000	0.1439	0.037*
C15	0.3589(4)	0.8278(4)	0.0883(2)	0.0328(8)
H15	0.4024	0.8541	0.0242	0.039*
C16	0.3160(4)	0.4370(4)	−0.3060(2)	0.0314(7)
H16A	0.3810	0.3440	−0.3464	0.038*
H16B	0.3963	0.4947	−0.3025	0.038*
C17	0.0575(4)	0.6997(4)	−0.2990(2)	0.0317(7)
H17A	0.0085	0.6660	−0.2342	0.038*
H17B	−0.0394	0.7592	−0.3315	0.038*
C18	0.1581(5)	0.8136(4)	−0.2920(2)	0.0342(8)
N1	0.1710(4)	0.5506(3)	−0.35277(18)	0.0304(6)
H1A	0.2232	0.5811	−0.4105	0.046*
H1B	0.0975	0.4974	−0.3590	0.046*
Na1	0.3016(3)	0.9243(2)	0.49647(11)	0.0682(6)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.2065(3)	0.1620(3)	−0.27089(16)	0.0390(6)
H1	0.1654	0.0841	−0.2496	0.058*
O2	0.2538(4)	0.3675(3)	0.12934(16)	0.0437(7)
O3	0.3007(3)	0.5852(3)	−0.13928(15)	0.0341(6)
O4	0.3125(3)	0.9639(3)	0.32874(15)	0.0385(6)
H13	0.3376	1.0486	0.3023	0.058*
O5	0.0753(4)	0.5740(4)	0.39625(17)	0.0579(8)
O6	0.2752(4)	0.6683(3)	0.45350(16)	0.0478(7)
O7	−0.0077(4)	0.8583(4)	0.43419(19)	0.0629(8)
O8	0.0913(3)	0.9146(3)	−0.22695(17)	0.0426(6)
O9	0.2993(3)	0.7982(3)	−0.35233(16)	0.0364(6)
O10	0.6423(5)	0.8129(5)	0.4942(2)	0.0921(12)
H10A	0.7461	0.7497	0.4734	0.138*
H10B	0.6254	0.8004	0.5556	0.138*
O11	0.4328(5)	0.2036(4)	0.2745(3)	0.0867(13)
H11A	0.5155	0.2115	0.2979	0.130*
H11B	0.4008	0.2820	0.2330	0.130*
S1	0.13460(13)	0.71108(11)	0.39952(6)	0.0381(3)

9 h, the mixture was filtered, and the residue was collected. The residue was dried at 383 K for 3 h. And the title product was obtained. Colorless block crystals were obtained by vapor diffusion of ethanol into a water solution of the title product for 4 days. NMR spectra were recorded on a Bruker AVANCE III instrument. The NMR data represent the complex in solution, which may result in a mixture of the protonated ligand and mono to oligonuclear complexes. **^{1}H-NMR** (500 MHz, D_2O) δ: 8.12 (s, 1H, H9), 7.92 (d, $J = 8.9$ Hz, 1H, H3), 7.75 (s, 1H, H11), 7.35 (d, $J = 8.5$ Hz, 1H, H15), 6.99 (d, $J = 8.9$ Hz, 1H, H2), 6.93 (d, $J = 8.5$ Hz, 1H, H14), 4.44 (s, 2H, H16A, H16B), 3.64 (s, 2H, H17A, H17B). **^{13}C-NMR** (125 MHz, D_2O) δ: 177.61 (C7), 171.15 (C18), 163.01 (C1), 156.38 (C5), 154.25 (C13), 153.22 (C9), 133.68 (C15), 128.32 (C12), 128.06 (C3), 127.64 (C11), 122.92 (C10), 122.54 (C8), 117.28 (C4), 115.84 (C14), 115.47 (C2), 104.64 (C6), 48.53 (C17), 39.34 (C16). **IR spectra** (potassium bromide pellet) were recorded on a Nicolet 6700. IR (ν/cm^{-1}): 3494, 3025, 2872, 2804, 1629, 1586, 1512, 1451, 1397, 1360, 1339, 1323, 1303, 1278, 1245, 1206, 1179, 1098, 1081, 1052, 1026, 960, 898, 868, 846, 820, 798, 779, 736, 643, 568, 543, 491, 455.

Experimental details

Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C). The oxygen-bound and nitrogen-bond H atoms were located on a difference Fourier map.

Discussion

In the past decades, amino acids have been found to participate as the amine component in the Mannich reaction [4–9]. It is an important method for synthesizing derivatives of natural amino acids with retention of the asymmetric centers. The goal of our work was to synthesize amino-acid derivatives of daidzein to obtain substances which retain the amine and carboxylic acid.

To extend this research, we used sodium 2-hydroxy-5-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)benzenesulfonate to react with L-threonine and got a new unexpected complex. The studies on the bioactivity of the title compound are presently ongoing. The asymmetric unit of the title structure contains one sodium ion, one ligand, one coordinated water molecule and one uncoordinated water molecule (*cf*. the figure). The sodium ion is six-coordination and resides in a distorted octahedral environment defined by four oxygen atoms from three ligands, and other two oxygen atoms from two coordinated water molecules. Two coordinated water molecules were shared with another sodium ion. Four oxygen atoms (O4, O6, O9A, O10A) are at the equatorial plane of this octahedron, and the rest two oxygen atoms are at the axle of the octahedron. The sodium ions are linked with the neighboring sodium ions through the bridging of oxygen atoms, and forming four-member rings and eight-member rings. The bond lengths are Na1—O10 = 2.634(5) Å, Na1—O7A = 2.572(4) Å, Na1—O10A = 2.496(3) Å, Na1—O6 = 2.459(3) Å, Na1—O4 = 2.346(2) Å, Na1—O9A = 2.281(3) Å, respectively, which is in the normal range [10]. The nitrogen atom N1 is protonated. The sodium coordination polymer is extended to a 2D layer structure along the *ac* plane. The 2D layers form 3D framework structure by hydrogen bonds. It is obvious that the hydrogen bonds play important roles in the self-assembly and enhance stability of the resultant structure.

Acknowledgements: This work was financially supported by the Foundation of Guangxi Colleges Universities Key Laboratary of Exploitation and Utilization of Microbial and Botanical Resources (No. 2016HL004), the Education Department of Guangxi Zhuang Autonomous Region of China (No. KY2016LX290), the Foundation of Hechi University (No. XJ2016QN023) and the Education Department of Guangxi Zhuang Autonomous Region of China (No. KY2015ZD104).

References

1. Bruker. APEX2, SAINT and SADABS. Brucker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Brandenburg, K.: DIAMOND. Visual crystal structure information system. Version 3.2i. Crystal Impact, Bonn, Germany (2012).

4. Garazd, M. M.; Garazd, Y. L.; Ogorodniichuk, A. S.; Shilin, V. V.; Turov, A. V.; Khilya, V. P.: Mannich reaction in the series of 7-hydroxy-3-phenoxychromones and their derivatives. Chem. Nat. Compd. **34** (1998) 442–447.
5. Frasinyuk, M. S.; Mrug, G. P.; Fedoryak, O. D.; Bondarenko, S. P.: Synthesis of amino-acid derivatives of formononetin and cladrin. Chem. Nat. Compd. **48** (2012) 570–573.
6. Gorbulenko, N. V.; Tkachuk, T. M.; Shokol, T. V.; Semeniuchenko, V. V.; Turov, A. V.; Khilya, V. P.: 2-[6-Alkyl-3-hetaryl-4-oxo-9,10-dihydro-4*H*,8*H*-chromeno-[8,7-e][1,3]oxazin-9-ψl]acetic acids. Chem. Heterocycl. Compd. **43** (2007) 569–575.
7. Gradre, J. N.; Shetty, N. K.; Raote, P. S.: Synthesis and antibacterial activity of mannich bases of 4-[2-(2-furyl)vinyl]-7-hydroxy coumarin. Indian J. Heterocycl. Chem. **5** (1996) 207–210.
8. Hassan, H. M.; Shedid, S. A. M.: Synthesis and antimicrobial activity of some new Mannich bases, *N*-(2-hydroxy-1-naphthyl)amino acid, methyl ester and hydrazide derivatives. J. Serb. Chem. Soc. **63** (1998) 125–130.
9. Gadre, J. N.; Mulay, M.; Vaze, C.: Synthesis of Mannich bases of 4-(4-methoxy phenyl)-1-aryl-3*H*-pyridine-2,6-dione and 2-aryl-4*H*-isoquinoline-1,3-dione under microwave irradiation using solid support. Indian J. Heterocycl. Chem. **13** (2004) 335–338.
10. Dong, J.; Su, F.; Song, Z.; Li, H.; Ren, Y.; Ren, J.: Crystal structure of the coordination polymer of sodium with hydrazone derivant of acetoacetanilide. Chinese J. Struct. Chem. **35** (2016) 521–528.