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Synthesis and crystal structure of *trans*-tetraaqua-bis(3-(((7-hydroxy-3-(4-hydroxy-3-sulfonatophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)ammonio)propanoato- κO)zinc(II) tetrahydrate, $C_{38}H_{48}N_2O_{26}S_2Zn$

<https://doi.org/10.1515/ncrs-2018-0250>

Received July 18, 2018; accepted November 18, 2018; available online December 22, 2018

Abstract

$C_{38}H_{48}N_2O_{26}S_2Zn$, monoclinic, $P2_1/c$ (no. 14), $a = 15.7219(7)$ Å, $b = 8.0394(4)$ Å, $c = 17.1968(8)$ Å, $\beta = 92.210(4)^\circ$, $V = 2171.97(18)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0395$, $wR_{ref}(F^2) = 0.0951$, $T = 293(2)$ K.

CCDC no.: 1879642

The 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

The educt sodium 5-(8-(((2-carboxyethyl)amino)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate

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Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.40 × 0.10 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.76 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{max} , completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	8830, 3813, 0.031
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2937
$N(param)_{refined}$:	313
Programs:	Bruker programs [1], SHELX [2, 3]

was synthesized *via* a Mannich reaction. In a typical experiment a 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%) and stirred for 0.5 h at 328 K. Then, the saturated solution of 3-aminopropionic acid (1.336 g, 0.015 mol) was added to the reaction mixture. Then, hot water was added until a transparent solution was obtained. After 24 h reaction time, the mixture was filtered, and the residue was collected. Then the residue was dried at 383 K. Sodium 5-(8-(((2-carboxyethyl)amino)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate (0.874 g) was obtained. NMR spectra were recorded on a Bruker AVANCE III HD instrument. ¹H-NMR (400 MHz, DMSO-*d*₆) δ : 10.61 (s, 1H, H13), 8.37 (s, 1H, H9), 8.07

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	1.000000	0.000000	0.500000	0.02915(15)
S1	0.22333(5)	0.53926(9)	0.20695(4)	0.02665(19)
N1	0.89627(14)	0.4397(3)	0.39539(14)	0.0290(6)
H1A	0.872895	0.356788	0.360936	0.044*
H1B	0.909195	0.366288	0.437436	0.044*
O1	0.81607(13)	0.4478(3)	0.56448(12)	0.0393(6)
H1	0.812103	0.428794	0.612815	0.059*
O2	0.46416(14)	0.3251(3)	0.38305(14)	0.0530(7)
O3	0.68781(13)	0.5283(3)	0.31862(12)	0.0355(5)
O4	0.27956(13)	0.4169(3)	0.05569(12)	0.0426(6)
H13	0.300359	0.391576	0.012364	0.064*
O5	0.17162(13)	0.3915(3)	0.20238(13)	0.0405(6)
O6	0.22958(13)	0.6102(3)	0.28481(12)	0.0374(5)
O7	0.19513(14)	0.6621(3)	0.14980(12)	0.0411(6)
O8	1.02329(13)	0.2369(2)	0.45895(12)	0.0337(5)
O9	1.13537(13)	0.1783(3)	0.38890(13)	0.0396(6)
O10	0.98447(14)	−0.0842(3)	0.38270(12)	0.0410(6)
H10A	0.940233	−0.069369	0.353534	0.062*
H10B	1.023722	−0.073889	0.350414	0.062*
O11	0.87349(13)	0.0691(3)	0.50467(13)	0.0381(5)
H11A	0.850268	−0.005392	0.531796	0.057*
H11B	0.843768	0.066668	0.462326	0.057*
O12	0.31241(14)	0.3285(3)	0.91059(13)	0.0506(6)
H12A	0.354258	0.265109	0.901917	0.076*
H12B	0.271478	0.269969	0.891927	0.076*
O13	0.12753(16)	0.9099(3)	0.28461(14)	0.0560(7)
H13A	0.148019	0.992954	0.309553	0.084*
H13B	0.163609	0.837765	0.300643	0.084*
C1	0.74705(19)	0.4302(4)	0.51697(17)	0.0294(7)
C2	0.6729(2)	0.3550(4)	0.54189(19)	0.0415(8)
H2	0.670727	0.313741	0.592289	0.050*
C3	0.6040(2)	0.3424(4)	0.49243(19)	0.0429(9)
H3	0.554518	0.293994	0.509898	0.052*
C4	0.60531(19)	0.3999(4)	0.41630(17)	0.0306(7)
C5	0.68042(18)	0.4706(3)	0.39292(17)	0.0263(7)
C6	0.75214(18)	0.4889(3)	0.44191(17)	0.0261(6)
C7	0.53140(19)	0.3868(4)	0.36301(18)	0.0331(7)
C8	0.54401(19)	0.4511(4)	0.28476(18)	0.0315(7)
C9	0.61941(19)	0.5171(4)	0.26920(19)	0.0359(8)
H9	0.625303	0.559500	0.219378	0.043*
C10	0.47498(19)	0.4443(4)	0.22402(18)	0.0324(7)
C11	0.39245(18)	0.4888(4)	0.24024(18)	0.0297(7)
H11	0.380490	0.524063	0.290154	0.036*
C12	0.32762(18)	0.4822(3)	0.18397(17)	0.0260(7)
C13	0.34441(18)	0.4289(4)	0.10891(17)	0.0312(7)
C14	0.4271(2)	0.3883(5)	0.09246(19)	0.0449(9)
H14	0.439548	0.355447	0.042316	0.054*
C15	0.4910(2)	0.3955(4)	0.14875(19)	0.0436(9)
H15	0.546173	0.367178	0.136203	0.052*
C16	0.83206(18)	0.5683(3)	0.41536(17)	0.0272(7)
H16A	0.818968	0.636909	0.370060	0.033*
H16B	0.855644	0.639647	0.456264	0.033*
C17	0.97687(18)	0.5093(4)	0.36714(19)	0.0314(7)
H17A	1.005671	0.570749	0.408956	0.038*
H17B	0.963986	0.586377	0.324918	0.038*
C18	1.03512(19)	0.3753(4)	0.33912(17)	0.0337(7)
H18A	1.004805	0.312375	0.298699	0.040*
H18B	1.083284	0.428152	0.315597	0.040*
C19	1.06836(19)	0.2559(4)	0.40006(18)	0.0314(7)

(d, $J = 8.9$ Hz, 1H, H3), 7.69 (d, $J = 2.3$ Hz, 1H, H11), 7.40 (dd, $J = 8.5, 2.3$ Hz, 1H, H15), 7.10 (d, $J = 8.9$ Hz, 1H, H2), 6.86 (d, $J = 8.5$ Hz, 1H, H14), 4.33 (s, 2H, H16A, H16B), 3.21 (t, $J = 6.9$ Hz, 2H, H17A, H17B), 2.68 (t, $J = 6.9$ Hz, 2H, H18A, H18B). **¹³C-NMR** (100 MHz, DMSO-*d*₆) δ : 174.54 (C7), 172.02 (C19), 161.58 (C1), 155.85 (C5), 153.36 (C13), 152.77 (C9), 131.47 (C15), 130.71 (C12), 128.14 (C3), 127.68 (C11), 123.28 (C10), 121.96 (C8), 116.48 (C4), 116.35 (C14), 114.42 (C2), 105.57 (C6), 42.90 (C17), 39.10 (C16), 30.36 (C18). **IR** (potassium bromide pellet) were recorded on a Nicolet 6700. IR (ν/cm^{-1}): 3565, 3428, 3090, 1707, 1632, 1605, 1510, 1452, 1400, 1383, 1329, 1300, 1274, 1213, 1172, 1107, 1071, 1093, 1040, 1025, 832, 811, 793, 741, 728, 645, 620, 534. ESI-MS: m/z 434.17[M-Na]⁺. Zincacetate dihydrate (0.0550 g, 0.25 mmol) and the aforementioned sodium salt (0.0229 g, 0.05 mmol) were added to water (10 mL) and sonicated for 10 min. The mixture was heated for 9 h at 358 K. After filtration, a transparent solution was obtained. After 2 days, colorless needle crystals of the title compound were obtained.

Experimental details

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

Discussion

In the past decades, the synthesis of Mannich bases that contained amino acids has been widely studied [4–8]. We have already synthesized two amino-acid derivatives of sodium 2-hydroxy-5-(7-hydroxy-4-oxo-4H-chromen-3-yl) benzenesulfonate by the Mannich reaction and studied their coordination behavior with metal ions [9–11]. As a continuation, we synthesized a 3-aminopropanoic acid derivative, sodium 5-(8-(((2-carboxyethyl)amino)methyl)-7-hydroxy-4-oxo-4H-chromen-3-yl)-2-hydroxybenzenesulfonate. We used this compound to react with a zinc(II) acetate solution and got the title complex.

X-ray crystallographic analysis of a single crystal of the title Zn(II) complex reveals a mononuclear structure. There is one half of a Zn(II) ion, one organic ligand, two coordinated water molecules and two uncoordinated water molecules in the asymmetric unit of the title structure (*cf.* the figure, the asymmetric unit is labeled). Zn1, located at an inversion center, is six-coordinated with a distorted octahedral geometry by four coordinated water and two O atoms from two monodentate coordinating ligands. The Zn–O bond distances are in the range of 2.0686(19) Å and 2.133(2) Å. The carboxylate groups adopt *trans* conformations, with the

C19—C18—C17—N1 torsion angles to be -65.0° . The nitrogen atom N1 is protonated. Adjacent ligands have intramolecular N1—H1B $\cdots$ O8 hydrogen bond of length 2.094 Å. There exist some more O—H $\cdots$ O and N—H $\cdots$ O hydrogen bonds forming a three-dimensional framework. 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 Laboratory of Exploitation and Utilization of Microbial and Botanical Resources (No. 2018HL005), the Education Department of Guangxi Zhuang Autonomous Region of China (No. KY2016LX290), the Foundation of Hechi University (No. XJ2016QN023).

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