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Synthesis and crystal structure of poly[aqua{ μ_3 -(1*S*,2*S*)-1-((7-hydroxy-3-(4-hydroxy-3-sulfonatophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)pyrrolidin-1-ium-2-carboxylato- $\kappa^4 O,O':O'':O'''$ }sodium(I)] monohydrate, $C_{21}H_{22}NNaO_{11}S$

Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.20 × 0.10 × 0.05 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	2.20 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	74.9°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13168, 4270, 0.079
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3213
$N(\text{param})_{\text{refined}}$:	316
Programs:	Bruker programs [1], SHELX [2], DIAMOND [3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.6665(7)	−0.2130(4)	0.84143(17)	0.0225(10)
H1A	0.723374	−0.197502	0.870923	0.034*
Na1	0.8487(4)	−0.2187(2)	0.99654(9)	0.0337(6)
O1	0.7099(6)	−0.0158(4)	0.73116(16)	0.0341(11)
H1	0.751418	0.015677	0.702807	0.051*
O2	0.9044(6)	0.3827(4)	0.91518(16)	0.0340(10)
O3	0.6452(6)	0.0523(3)	0.91771(15)	0.0259(9)
O4	0.7660(6)	0.4068(4)	1.18321(14)	0.0310(10)
H4	0.721610	0.477742	1.187061	0.047*
O5	0.7275(6)	0.6888(4)	1.07381(18)	0.0346(11)
O6	0.4498(5)	0.6064(4)	1.08094(16)	0.0287(9)
O7	0.6287(6)	0.6164(4)	1.16061(15)	0.0346(10)
O8	0.6289(6)	−0.2768(4)	0.94353(16)	0.0394(11)
O9	0.4352(5)	−0.4221(4)	0.92970(16)	0.0284(10)
O10	0.8242(6)	0.0295(4)	0.63554(16)	0.0352(11)
H10A	0.910825	−0.010585	0.625994	0.053*
H10B	0.746625	0.039005	0.612354	0.053*
O11	0.9966(7)	−0.3923(5)	0.9655(2)	0.0516(14)
H11A	1.052672	−0.370132	0.937754	0.077*
H11B	0.942553	−0.457012	0.955593	0.077*
S1	0.6193(2)	0.60198(12)	1.10116(5)	0.0247(3)
C1	0.7381(8)	0.0603(5)	0.7736(2)	0.0262(13)
C2	0.8226(8)	0.1753(5)	0.7693(2)	0.0265(13)
H2	0.858530	0.204573	0.734604	0.032*
C3	0.8533(8)	0.2456(5)	0.8153(2)	0.0279(13)
H3	0.914219	0.321684	0.812000	0.033*
C4	0.7972(8)	0.2080(5)	0.8669(2)	0.0235(12)
C5	0.7075(8)	0.0960(5)	0.8697(2)	0.0237(12)
C6	0.6757(8)	0.0194(5)	0.8242(2)	0.0230(12)
C7	0.8228(8)	0.2829(5)	0.9164(2)	0.0238(12)

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Abstract

$C_{21}H_{22}NNaO_{11}S$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.0489(4)$ Å, $b = 10.6418(5)$ Å, $c = 24.4850(10)$ Å, $V = 2097.26(17)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0513$, $wR_{\text{ref}}(F^2) = 0.1350$, $T = 150(2)$ K.

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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

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 (100 mL, 99%) and stirred for 0.5 h at 333 K. Then, the saturated solution of *L*-Proline (6.0 g, 0.052 mol) was added to the reaction

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C8	0.7529(8)	0.2310(5)	0.9660(2)	0.0258(13)
C9	0.6691(8)	0.1203(5)	0.9631(2)	0.0255(12)
H9	0.6234(18)	0.0884(8)	0.9960(87)	0.031*
C10	0.7647(8)	0.2890(5)	1.0208(2)	0.0241(12)
C11	0.7005(7)	0.4058(5)	1.0337(2)	0.0229(11)
H11	0.6563(96)	0.4574(43)	1.0055(59)	0.028*
C12	0.6997(8)	0.4491(5)	1.0880(2)	0.0255(12)
C13	0.7630(8)	0.3739(5)	1.1298(2)	0.0267(13)
C14	0.8324(9)	0.2577(5)	1.1162(2)	0.0302(14)
H14	0.8798(88)	0.2067(45)	1.1440(14)	0.036*
C15	0.8327(8)	0.2166(5)	1.0634(2)	0.0276(13)
H15	0.8800(69)	0.1371(3)	1.0551(16)	0.033*
C16	0.5708(8)	−0.0957(5)	0.8290(2)	0.0285(13)
H16A	0.5095(70)	−0.1078(29)	0.7943(76)	0.034*
H16B	0.4877(21)	−0.0823(3)	0.8582(92)	0.034*
C17	0.5557(8)	−0.3249(5)	0.8522(2)	0.0249(13)
H17	0.4360(29)	−0.3042(33)	0.8369(50)	0.037*
C18	0.6431(9)	−0.4362(6)	0.8239(3)	0.0355(15)
H18A	0.6446(61)	−0.5110(24)	0.8479(39)	0.043*
H18B	0.5865(93)	−0.4581(19)	0.7893(307)	0.043*
C19	0.8184(9)	−0.3887(6)	0.8133(2)	0.0319(14)
H19A	0.8889(01)	−0.3966(40)	0.8462(10)	0.038*
H19B	0.8710(99)	−0.4347(21)	0.7826(74)	0.038*
C20	0.7889(8)	−0.2529(5)	0.7988(2)	0.0278(13)
H20A	0.8928(15)	−0.2033(73)	0.8011(58)	0.033*
H20B	0.7418(82)	−0.2444(33)	0.7615(93)	0.033*
C21	0.5391(8)	−0.3428(5)	0.9139(2)	0.0262(13)

mixture. Then, water was added until a clear solution was immediately obtained. After 2 h reaction time, the mixture was filtered. The residue was washed with ethanol (50 mL, 99%) and collected. Then, the residue was dried at 383 K for 3 h. Sodium (1*S*,2*S*)-1-((7-hydroxy-3-(4-hydroxy-3-sulfonatophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)pyrrolidin-1-ium-2-carboxylate (2.427 g, 0.005 mol) was obtained. This product (0.1 g) and water (20 mL) were mixed and stirred at 353 K for 10 min. After filtration, a transparent solution was obtained. Colorless block-shaped crystals of the title compound were obtained by vapor diffusion of ethanol into a water solution of the title product for 2 days. NMR spectra were recorded on a Bruker-AVANCE III HD instrument. ¹H-NMR (500 MHz, D₂O) δ: 8.02 (s, 1H, H9), 7.81 (d, *J* = 8.9 Hz, 1H, H3), 7.74 (d, *J* = 1.8 Hz, 1H, H11), 7.24 (dd, *J* = 8.4, 1.8 Hz, 1H, H15), 6.91 (d, *J* = 8.9 Hz, 1H, H2), 6.90 (d, *J* = 8.4 Hz, 1H, H14), 4.46 (s, 2H, H16A, H16B), 4.00 (m, 1H, H17), 3.64 (m, 1H, H20A), 3.22 (m, 1H, H20B), 2.51 (m, 1H, H18A), 2.15 (m, 1H, H18B), 2.07 (m, 1H, H19A), 1.96 (m, 1H, H19B); ¹³C-NMR (125 MHz, D₂O) δ: 179.71 (C7), 176.46 (C21), 165.17 (C1), 158.91 (C13), 156.78 (C5), 156.10 (C9), 136.08 (C15), 131.50 (C11), 130.72 (C12), 130.62 (C3), 125.39 (C10), 125.15 (C8), 120.10 (C4), 118.78

(C14), 117.94 (C2), 107.06 (C6), 71.59 (C17), 60.34 (C20), 49.29 (C16), 31.81 (C18), 25.95 (C19). IR spectra (potassium bromide pellet) were recorded on a Nicolet 6700. IR (ν/cm^{−1}): 3754, 3466, 3040, 2365, 1624, 1586, 1561, 1508, 1491, 1440, 1368, 1292, 1243, 1218, 1164, 1092, 1041, 1020, 931, 904, 841, 799, 757, 720, 644, 543.

Experimental details

The 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 water H atoms and nitrogen-bound H atoms were located on a difference Fourier map and refined freely. The remaining oxygen-bound H atoms were idealized and refined using a riding model (AFIX 83 option of the SHELX program [2]). The absolute structure was established by refinement of the Flack parameter (0.040(23) from 1057 selected quotients) using the Parsons-Flack method [3].

Discussion

In the past decades, proline has been gradually recognized as a simple, commercial and cheap chiral catalyst for many asymmetric reactions, such as Aldol reaction, Mannich reaction, Diels-Alder reaction, Michael reaction [5–10]. *L*-Proline is a chiral molecule, with a carboxylic acid and an amine portion. Because chemical modification of natural biologically active compounds is a promising pathway to create substances which have significant physiological and biological activity, the goal of our work is to synthesize amino-acid derivatives of daidzein. To extend this research, we used sodium 2-hydroxy-5-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)benzenesulfonate to react with *L*-Proline by Mannich reaction and got the title compound. We speculate that *L*-Proline not only acts as a reactant but also acts as a catalyst in this reaction. The studies on the bioactivity of this chiral complex are presently ongoing.

The asymmetric unit of the title structure contains one sodium ion, one organic 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 five oxygen atoms (O8, O5B, O6C, O8A, O9A); A = 0.5 + *x*, −0.5 − *y*, 2 − *z*; B = *x*, −1 + *y*, *z* from four organic ligands and one oxygen atom (O11) from one coordinated water molecule. One oxygen atom (O8) is shared with another sodium ion. Four oxygen atoms (O8, O11, O8A, O9A) are at the equatorial plane of this octahedral, and the rest two oxygen atoms (O6C = 0.5 + *x*, 0.5 − *y*, 2 − *z*, O5B) are at the axle of the octahedron. The sodium ions are linked with the neighboring sodium ions through the bridging of oxygen atoms. The bond lengths are Na1–O8 = 2.280(4) Å, Na1–O11 = 2.326(6) Å,

Na1—O5B = 2.345(5) Å, Na1—O6C = 2.385(5) Å, Na1—O9A = 2.448(5) Å, Na1—O8A = 2.691(6) Å, respectively, which is in the normal range [11]. The nitrogen atom N1 is protonated. The sodium coordination polymer is extended to a two-dimensional layer along the *ab* plane. The two-dimensional layers form three-dimensional 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.

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