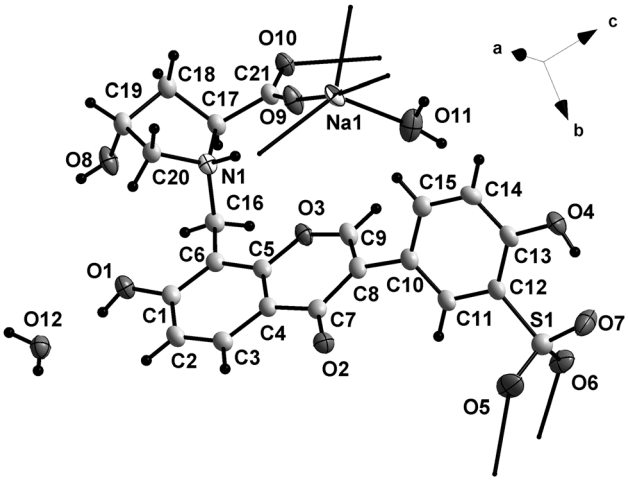
Hai-Lin Chen, Xiu-Xiang Huang*, Jian-Jing Lan, Dong-Mei Yao, Yan-Ping Wang and Qiu-Ping Liu

Synthesis and crystal structure of poly[aqua(μ$_4$-(1*R*,2*S*,4*R*)-4-hydroxy-1-((7-hydroxy-3-(4-hydroxy-3-sulfonatophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)pyrrolidin-1-ium-2-carboxylate-κ^4*O*:*O*′:*O*″:*O*‴)sodium(I)] monohydrate, $C_{21}H_{22}NNaO_{12}S$



https://doi.org/10.1515/ncrs-2022-0208
Received April 22, 2022; accepted May 19, 2022; published online June 8, 2022

Abstract

$C_{21}H_{22}NNaO_{12}S$, orthorhombic, $P2_12_12_1$ (no. 19), a = 7.6850(1) Å, b = 10.8030(1) Å, c = 25.9262(2) Å, V = 2152.42(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0309, $wR_{ref}(F^2)$ = 0.0818, T = 100.0(4) K.

CCDC no.: 2173634

***Corresponding author: Xiu-Xiang Huang**, School of Chemical and Biological Engineering, Hechi University, Yizhou District, Hechi, Guangxi, 546300, P. R. China, E-mail: 931636463@qq.com
Hai-Lin Chen, Jian-Jing Lan, Dong-Mei Yao, Yan-Ping Wang and Qiu-Ping Liu, School of Chemical and Biological Engineering, Hechi University, Yizhou District, Hechi, Guangxi, 546300, P. R. China, E-mail: 337092873@qq.com (H.-L. Chen), 170118546@qq.com (J.-J. Lan), dmyao47@163.com (D.-M. Yao), 329845837@qq.com (Y.-P. Wang), 2014154995@qq.comn (Q.$.$. Liu). https://orcid.org/0000-0001-9471-8109 (H.-L. Chen)

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.19 × 0.15 × 0.13 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	2.20 mm^{-1}
Diffractometer, scan mode:	ROD, Synergy Custom DW system, ω
θ_{max}, completeness:	75.8°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12,136, 4,386, 0.021
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4,356
$N(param)_{refined}$:	335
Programs:	CrysAlis^{PRO} [1], Diamond [2], SHELX [3, 4]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized *via* a Mannich reaction. Formaldehyde solution (10 mL, 37%), water (20 mL), *trans*-4-hydroxy-L-proline (1.97 g, 0.015 mol) 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 (150 mL, 99.5%) and stirred for 24 h at 338 K. Then the mixture was filtered and the residue was collected. Then the residue was dried at 373 K. Sodium 5-(8-(((2*S*,4*R*)-2-carboxy-4-hydroxypyrrolidin-1-yl)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate (3.02 g) was obtained. **^{1}H-NMR** (400 MHz, D_2O) *δ:* 7.98 (s, 1H, H9), 7.77 (d, *J* = 8.9 Hz, 1H, H3), 7.67 (s, 1H, H11), 7.17 (d, *J* = 8.4 Hz, 1H, H15), 6.86 (d, *J* = 8.9 Hz, 1H, H2), 6.83 (d, *J* = 8.4 Hz, 1H, H14), 4.58 (m, 1H, H19), 4.50 (s, 2H, H16A, H16B), 4.24 (m, 1H, H17), 3.77 (m, 1H, H20A), 3.28 (m, 1H, H20B), 2.43 (m, 1H,

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

Atom	x	y	z	U_{iso}*/U_{eq}
S1	0.57877 (8)	1.08139 (6)	0.58175 (3)	0.02550 (15)
O1	0.7463 (3)	0.47611 (19)	0.23022 (7)	0.0286 (4)
H1	0.787942	0.512351	0.204348	0.043*
O2	0.8515 (3)	0.87833 (18)	0.40909 (7)	0.0276 (4)
O3	0.5893 (2)	0.54869 (17)	0.40125 (7)	0.0239 (4)
O4	0.7040 (3)	0.8824 (2)	0.65896 (7)	0.0294 (4)
H4	0.673745	0.956861	0.661412	0.044*
O5	0.6809 (3)	1.1576 (2)	0.54750 (11)	0.0471 (6)
O6	0.3944 (2)	1.0892 (2)	0.57065 (9)	0.0338 (5)
O7	0.6172 (3)	1.1030 (2)	0.63621 (9)	0.0438 (6)
O8	0.6169 (3)	0.1521 (2)	0.24948 (7)	0.0340 (5)
H8	0.676190	0.171327	0.223466	0.051*
O9	0.5580 (3)	0.2432 (2)	0.44122 (7)	0.0351 (5)
O10	0.3575 (3)	0.09911 (18)	0.42274 (7)	0.0282 (4)
O11	0.4541 (3)	0.4166 (3)	0.52979 (10)	0.0468 (6)
H11A	0.510741	0.399618	0.558412	0.070*
H11B	0.413711	0.481578	0.546422	0.070*
N1	0.6433 (3)	0.2934 (2)	0.34493 (8)	0.0215 (4)
H1A	0.684130	0.323801	0.379306	0.035 (9)*
C1	0.7489 (3)	0.5534 (3)	0.27112 (10)	0.0240 (5)
C2	0.8322 (4)	0.6699 (3)	0.26934 (10)	0.0262 (5)
H2	0.883529	0.697815	0.238094	0.031*
C3	0.8392 (3)	0.7429 (3)	0.31259 (10)	0.0251 (5)
H3	0.897340	0.820425	0.310994	0.030*
C4	0.7618 (3)	0.7052 (2)	0.35946 (10)	0.0226 (5)
C5	0.6740 (3)	0.5923 (3)	0.35862 (10)	0.0225 (5)
C6	0.6641 (3)	0.5147 (3)	0.31557 (10)	0.0221 (5)
C7	0.7752 (3)	0.7769 (3)	0.40717 (10)	0.0235 (5)
C8	0.6946 (3)	0.7183 (3)	0.45212 (10)	0.0246 (5)
C9	0.6072 (3)	0.6109 (3)	0.44585 (10)	0.0261 (6)
H9	0.553693	0.576261	0.475559	0.031*
C10	0.7030 (3)	0.7688 (3)	0.50536 (10)	0.0237 (5)
C11	0.6487 (3)	0.8873 (3)	0.51764 (10)	0.0250 (5)
H11	0.611995	0.941684	0.490995	0.030*
C12	0.6473 (3)	0.9278 (3)	0.56894 (9)	0.0231 (5)
C13	0.7020 (3)	0.8478 (3)	0.60870 (10)	0.0235 (5)
C14	0.7577 (4)	0.7302 (3)	0.59613 (10)	0.0253 (5)
H14	0.796583	0.676006	0.622571	0.030*
C15	0.7575 (3)	0.6905 (3)	0.54538 (10)	0.0245 (5)
H15	0.794889	0.608796	0.537510	0.029*
C16	0.5549 (3)	0.3997 (3)	0.31741 (10)	0.0241 (5)
H16A	0.526839	0.373901	0.281719	0.029*
H16B	0.443935	0.418681	0.335143	0.029*
C17	0.5184 (3)	0.1853 (3)	0.35387 (9)	0.0234 (5)
H17	0.409794	0.197456	0.333227	0.028*
C18	0.6173 (4)	0.0720 (3)	0.33422 (10)	0.0260 (5)
H18A	0.689775	0.035148	0.361808	0.035 (9)*
H18B	0.536391	0.008292	0.320844	0.041*
C19	0.7296 (4)	0.1249 (3)	0.29125 (10)	0.0265 (5)
H19	0.825174	0.067078	0.281034	0.032*
C20	0.7992 (3)	0.2428 (3)	0.31594 (10)	0.0242 (5)
H20A	0.896474	0.224312	0.339776	0.016 (7)*
H20B	0.839792	0.302040	0.289414	0.020*
C21	0.4740 (3)	0.1766 (3)	0.41114 (10)	0.0245 (5)
Na1[a]	0.7198 (2)	0.33397 (18)	0.50240 (6)	0.0272 (3)
Na1A[b]	0.8296 (4)	0.2694 (3)	0.49229 (9)	0.0272 (3)
O12	0.8998 (3)	0.53901 (19)	0.14507 (7)	0.0305 (4)
H12A	0.822199	0.562859	0.123928	0.046*
H12B	0.955649	0.484429	0.128218	0.046*

[a]Occupancy: 0.605 (2). [b]Occupancy: 0.395 (2).

H18A), 2.12 (m, 1H, H18B). **^{13}C-NMR** (100 MHz, D_2O) *δ*:176.53 (C7), 172.64 (C21), 161.64 (C1), 155.80 (C13), 153.81 (C5), 153.15 (C9), 132.93 (C15), 128.74 (C11), 127.64 (C12), 127.58 (C3), 122.25 (C10), 121.97 (C8), 117.03 (C4), 115.91 (C14), 114.69 (C2), 103.90 (C6), 69.60 (C17), 68.28 (C19), 60.89 (C20), 48.71 (C16), 37.87 (C18). A mixture of sodium salt described before (0.050 g), water (1 mL) and saturated sodium chloride solution (14 mL) was sealed in a 20 mL vial and sonicated for 5 min. Then the mixture was heated at 358 K for 6 h. Colourless block crystals of the title compound were obtained after 7 days. **IR spectra** (potassium bromide pellet) were recorded on a Nicolet 6700. IR (ν/cm^{-1}): 3,460, 2,068, 1,627, 1,491, 1,441, 1,402, 1,352, 1,329, 1,288, 1,249, 1,163, 1,096, 1,022, 1,001, 958, 906, 844, 831, 794, 781, 725, 713, 636, 541, 478, 466.

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. The sodium atoms were disordered. The absolute structure was established by refinement of the Flack parameter (0.020(9) from 1795 selected quotients) using the Parsons–Flack method [5].

Comment

Trans-4-hydroxy-L-proline is an important amino acid that is a valuable chiral building block for the synthesis of pharmaceutical intermediates [6–8]. In the past decade, *trans*-4-hydroxy-L-proline derivatives have been gradually recognized as chiral catalysts for many asymmetric reactions, such as Aldol reaction and Michael reaction [9–14]. Our previous investigations showed that sodium 2-hydroxy-5-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)benzenesulfonate (DSS) can react with amino acids by Mannich reaction [15–18]. In this paper, we report a *trans*-4-hydroxy-L-proline derivative of DSS.

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 dihedral angle between planar rings B (C10–C15) and C (C7–C9/O3/C5/C4) is 53.46°. There exist various O–H···O and N–H···O hydrogen bonds. The nitrogen atom N1 is protonated. The sodium atoms were disordered. The Na1 ion is five-coordinated. The Na1A ion is six-coordinated. The bond lengths are Na1–O9 = 2.241 (3) Å, Na1–O11 = 2.339 (3) Å, Na1–O5A = 2.255 (3) Å, Na1–O6A = 2.465 (3) Å, Na1–O10A = 2.326 (3) Å, Na1A–O9 = 2.485 (4) Å, Na1A–O5A = 2.194 (3), Na1A–O6A = 2.290 (3) Å, Na1A–O9A = 2.464 (3) Å, Na1A–O10A = 2.630 (3) Å, Na1A–O11A = 2.298 (4) Å, respectively, which is in the normal range [19]. 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 title structure.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was financially supported by the Foundation of Hechi University (No. XJ2018GKQ012), Guangxi Natural Science Foundation of China (No. 2020GXNSFBA297138) and 2021 High-level Talents Scientifific Research Startup Fund of Hechi University (No. 2021GCC021).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rigaku. CrysAlis^{Pro}; Rigaku Corporation: Yarnton, Oxfordshire, England, 2020.
2. Brandenburg K. Diamond. Visual Crystal Structure Information System. Ver. 3.2; Crystal Impact: Bonn, Germany, 2012.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. M. *SHELXTL*- integrated space-group andcrystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
5. Parsons S., Flack H. D., Wagner T. Use of intensity quotients and differences in absolute structure refinement. *Acta Crystallogr.* 2013, *B69*, 249–259.
6. Comesse S., Daïch A. An unprecedented straightforward synthesis of chiral pyrrolo[3,4-*b*]quinolone and pyrrolo[3,2-*b*] quinolone backbones starting from *trans*-4-hydroxy-L-proline. *J. Chem.* 2016, *2016*, 1504682.
7. Zhang Y., Hubbard J. W., Akhmedov N. G., Petersen J. L., Söderberg B. C. G. Total synthesis of the tetracyclic indole alkaloid ht-13-B. *J. Org. Chem.* 2015, *80*, 4783–4790.
8. Singh R., Panda G. l-Proline derived nitrogenous steroidal systems: an asymmetric approach to 14-azasteroids. *RSC Adv.* 2013, *3*, 19533–19544.
9. Bacha K., Aguibi K., Mbakidi J.-P., Bouquillon S. Beneficial contribution of biosourced ionic liquids and microwaves in the Michael reaction. *Catalysts* 2020, *10*, 814.
10. Patel H. A., Gutal A., Sahoo S. K., Soni H. P. Asymmetric direct Aldol reaction in confined space: molecular conformations of organocatalyst affect chiral induction. *ChemistrySelect* 2019, *4*, 13210–13218.
11. Gurka A. A., Szőri K., Bartók M., London G. Dual stereocontrol in aldol reactions catalysed by hydroxyproline derivatives in the presence of a large amount of water. *Tetrahedron: Asymmetry* 2016, *27*, 936–942.
12. Yadav G. D., Singh S. Direct asymmetric aldol reactions catalysed by trans-4-hydroxy-(*S*)-prolinamide in solvent-free conditions. *Tetrahedron: Asymmetry* 2015, *26*, 1156–1166.
13. Gauchot V., Gravel J., Schmitzer A. R. Asymmetric Michael addition induced by the anion of an imidazolium salt. *Eur. J. Org. Chem.* 2012, *2012*, 6280–6284.
14. Yang H., Li S., Wang X., Zhang F., Zhong X., Dong Z., Ma J. Core–shell silica magnetic microspheres supported proline as a recyclable organocatalyst for the asymmetric aldol reaction. *J. Mol. Catal. Chem.* 2012, *363–364*, 404–410.
15. Chen H.-L., Huang X. X., Yao D. M., Wang Y. P., Lu X. B. Synthesis and crystal structure of 5-(8-((3-carboxyazetidin-1-ium-1-yl) methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate monohydrate, $C_{20}H_{19}NO_{10}S$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1371–1373.
16. Chen H.-L., Pan L.-W., Qin Y.-L., Xie Y.-J., Zhang P. 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-κ*O*)zinc(II) tetrahydrate, $C_{38}H_{48}N_2O_{26}S_2Zn$. *Z. Kristallogr. N. Cryst. Struct.* 2019, *234*, 217–219.
17. Chen H.-L., Yin X.-J. Synthesis and crystal structure of 5-(8-(((2-carboxyethyl)ammonio)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate trihydrate, $C_{19}H_{23}NO_{12}S$. *Z. Kristallogr. N. Cryst. Struct.* 2019, *234*, 265–267.
18. Chen H.-L., Lai H.-F., Wei L.-Q., Jiang L.-R., Su Y.-X. Synthesis and crystal structure of *trans*-tetraqua-bis($m_3$2-(((7-hydroxy-3-(4-hydroxy-3-sulfonatophenyl)-4-oxo-4*H*-chromen-8-yl)methyl) ammonio)acetato-κ*O*)cobalt(II) hexahydrate, $C_{36}H_{48}CoN_2O_{28}S_2$. *Z. Kristallogr. N. Cryst. Struct.* 2017, *232*, 1025–1027.
19. Tai X.-S., Wang L.-H., Xia Y.-P. The crystal structure of poly[μ_2-aqua- aqua-(μ_3-(*E*)-2-(4-((2-carbamothioylhydrazineylidene) methyl)phenoxy)acetato-κ^3*O:S:S*)sodium(I)], $C_{10}H_{14}N_3O_5SNa$. *Z. Kristallogr. N. Cryst. Struct.* 2022, *237*, 277–279.