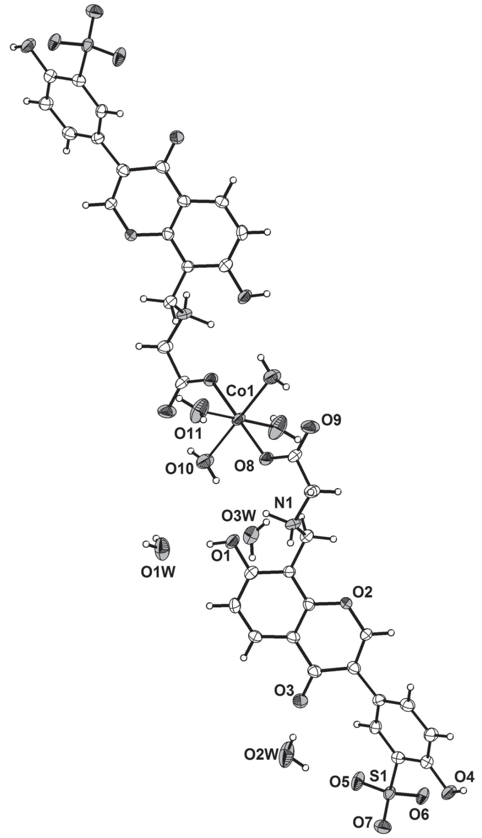
Hai-Lin Chen[†], Hong-Fang Lai[†]*, Lian-Qiang Wei*, Li-Rong Jiang and Yan-Xiang Su

Synthesis and crystal structure of *trans*-tetraqua-bis(2-(((7-hydroxy-3-(4-hydroxy-3-sulfonatophenyl)-4-oxo-4*H*-chromen-8-yl)methyl) ammonio)acetato-κ*O*)cobalt(II) hexahydrate, $C_{36}H_{48}CoN_2O_{28}S_2$



https://doi.org/10.1515/ncrs-2017-0153
Received June 2, 2017; accepted September 29, 2017; available online October 16, 2017

Abstract

$C_{36}H_{48}CoN_2O_{28}S_2$, monoclinic, $P2_1/c$ (no. 14), $a = 18.2239(13)$ Å, $b = 7.1282(6)$ Å, $c = 17.8550(13)$ Å, $\beta = 97.883(2)°$, $V = 2297.5(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0906$, $wR_{ref}(F^2) = 0.1998$, $T = 293(2)$ K.

CCDC no.: 1577246

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.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.30 × 0.28 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.56 mm^{-1}
Diffractometer, scan mode:	Bruker AXS, φ and ω-scans
$2\theta_{max}$, completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	35845, 5274, 0.163
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2811
$N(param)_{refined}$:	313
Programs:	Bruker programs [1], SHELX [2, 3], DIAMOND [4]

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

Atom	x	y	z	$U_{iso}*/U_{eq}$
Co1	−0.5000	−0.5000	0.0000	0.0275(3)
S1	0.25874(7)	−0.39005(18)	−0.20198(7)	0.0255(3)
O1	−0.27920(17)	−0.2399(5)	0.00580(18)	0.0373(9)
H1B	−0.2718	−0.2036	0.0516	0.056*
O2	−0.15556(16)	−0.3760(5)	−0.20032(17)	0.0263(8)
O3	0.04170(18)	−0.1889(6)	−0.0903(2)	0.0456(11)
O4	0.21838(17)	−0.3221(5)	−0.36571(18)	0.0355(9)
H4A	0.2018	−0.2920	−0.4109	0.053*
O5	0.25134(19)	−0.4202(5)	−0.12272(18)	0.0388(10)
O6	0.28921(18)	−0.5570(5)	−0.23371(18)	0.0319(9)
O7	0.29976(18)	−0.2211(5)	−0.2152(2)	0.0382(9)
O8	−0.45071(18)	−0.3699(5)	−0.08387(18)	0.0334(9)
O9	−0.52745(19)	−0.4283(6)	−0.19075(19)	0.0449(10)
O10	−0.40980(19)	−0.4143(5)	0.08001(19)	0.0423(10)
H10A	−0.4168	−0.4608	0.1223	0.064*
H10B	−0.3667	−0.4332	0.0683	0.064*
O11	−0.4435(2)	−0.7398(6)	−0.0231(2)	0.0602(12)
H11W	−0.4185	−0.7629	−0.0589	0.090*
H11C	−0.4417	−0.8310	0.0078	0.090*
N1	−0.34356(19)	−0.2345(6)	−0.1521(2)	0.0270(10)
H1A	−0.3676	−0.1859	−0.1066	0.040*
H1C	−0.3223	−0.1360	−0.1646	0.040*
C1	−0.2140(3)	−0.2488(7)	−0.0217(3)	0.0277(12)
C2	−0.2169(2)	−0.3164(6)	−0.0953(3)	0.0223(11)
C3	−0.1516(3)	−0.3153(7)	−0.1266(3)	0.0231(11)
C4	−0.0844(2)	−0.2549(7)	−0.0876(3)	0.0262(12)

[†] These authors contributed equally to this work.

***Corresponding authors: Hong-Fang Lai and Lian-Qiang Wei,** College of Chemistry and Bio-engineering, Hechi University, Yizhou, Guangxi 546300, China, e-mail: laihongfang263@163.com (H.-F. Lai); wlq259@163.com (L.-Q. Wei)
Hai-Lin Chen, Li-Rong Jiang, and Yan-Xiang Su: College of Chemistry and Bio-engineering, Hechi University, Yizhou, Guangxi 546300, China

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C5	−0.0848(3)	−0.1916(7)	−0.0140(3)	0.0307(13)
H5B	−0.0406	−0.1512	0.0137	0.037*
C6	−0.1473(3)	−0.1872(8)	0.0184(3)	0.0352(13)
H6B	−0.1460	−0.1429	0.0675	0.042*
C7	−0.0174(3)	−0.2490(7)	−0.1237(3)	0.0283(12)
C8	−0.0261(3)	−0.3161(7)	−0.2019(3)	0.0263(11)
C9	−0.0933(2)	−0.3743(7)	−0.2331(3)	0.0253(11)
H9A	−0.0974	−0.4180	−0.2825	0.030*
C10	0.0374(2)	−0.3201(6)	−0.2455(3)	0.0231(11)
C11	0.1084(3)	−0.3592(6)	−0.2112(3)	0.0238(11)
H11A	0.1160	−0.3870	−0.1598	0.029*
C12	0.1682(2)	−0.3582(6)	−0.2507(3)	0.0229(11)
C13	0.1584(3)	−0.3220(7)	−0.3281(3)	0.0272(12)
C14	0.0869(3)	−0.2850(7)	−0.3634(3)	0.0301(12)
H14A	0.0788	−0.2619	−0.4152	0.036*
C15	0.0285(3)	−0.2821(7)	−0.3224(3)	0.0304(12)
H15A	−0.0186	−0.2538	−0.3470	0.037*
C16	−0.2881(2)	−0.3888(7)	−0.1362(3)	0.0267(11)
H16A	−0.3078	−0.4846	−0.1059	0.032*
H16B	−0.2792	−0.4459	−0.1835	0.032*
C17	−0.4132(3)	−0.2899(8)	−0.2005(3)	0.0333(13)
H17A	−0.4019	−0.3822	−0.2372	0.040*
H17B	−0.4344	−0.1810	−0.2279	0.040*
C18	−0.4687(3)	−0.3708(7)	−0.1545(3)	0.0271(12)
O1W	−0.2605(2)	−0.1193(6)	0.1468(2)	0.0550(12)
H1WA	−0.2859	−0.0245	0.1563	0.082*
H1WB	−0.2626	−0.2042	0.1799	0.082*
O2W	0.1838(2)	−0.2563(7)	−0.0094(2)	0.0707(14)
H2WB	0.2140	−0.2935	−0.0386	0.106*
H2WA	0.1413	−0.2516	−0.0359	0.106*
O3W	−0.3944(2)	0.1807(6)	−0.1622(2)	0.0569(12)
H3WA	−0.4259	0.1622	−0.2012	0.085*
H3WB	−0.3588	0.2486	−0.1724	0.085*

Source of material

The educt sodium 5-(8-(((carboxymethyl)amino)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate was synthesized *via* a Mannich reaction. 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, 95%) and stirred for 0.5 h at 338 K. Then, the saturated solution of glycine (1.12 g, 0.015 mol) was added to the reaction mixture. Then, water was added until a transparent solution was obtained. After 11 h reaction time, the mixture was filtered, and the residue was collected. Then the residue was dried at 383 K. Sodium 5-(8-(((carboxymethyl)amino)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate (2.262 g, 0.005 mol) was obtained. NMR spectra were recorded on a Bruker AV400 NMR instrument. **^{1}H-NMR** (400 MHz, DMSO-d_6) δ: 10.59 (s, 1H, H4A), 8.34 (s, 1H, H9A), 7.98 (d, J = 8.9 Hz, 1H, H5B), 7.71 (d, J = 2.3 Hz, 1H, H11A), 7.39 (dd, J = 8.4, 2.3 Hz, 1H, H15A), 7.08 (d, J = 8.9 Hz, 1H, H6B), 6.85 (d, J = 8.5 Hz, 1H, H14A), 4.30 (s, 2H, H16A, H16B), 3.39 (s, 2H, H17A, H17B); **^{13}C-NMR** (100 MHz, DMSO-d_6) δ: 174.62 (C7), 168.87 (C18), 163.16 (C1), 155.87 (C3), 153.25 (C13), 152.73 (C9), 131.48 (C15), 130.64 (C12), 127.74 (C5), 127.20 (C11), 123.02 (C10), 122.25 (C8), 116.29 (C4), 115.85 (C14), 115.12 (C6), 106.64 (C2), 48.87 (C17), 39.73 (C16). **IR spectra** (potassium bromide pellet) Nicolet 6700. IR (v/cm^{-1}): 3493, 3041, 2876, 1633, 1505, 1448, 1396, 1360, 1323, 1277, 1207, 1178, 1065, 1052, 1205, 899, 844, 820, 797, 729, 678, 623, 543, 491. **ESI-MS**: m/z 420.17 $[M{-}Na]^-$. The saturated solution of $CoCl_2{\cdot}H_2O$ (0.238 g, 0.001 mol) was added to the saturated solution of sodium salt described before (0.443 g, 0.001 mol). The mixture was stirred for 30 min at 343 K and a pink solution was obtained. After cooling to room temperature, red block-shaped crystals of the title compound were obtained. **IR spectra** (potassium bromide pellet) Nicolet 6700. IR (v/cm^{-1}): 3448, 1629, 1529, 1458, 1432, 1414, 1334, 1285, 1210, 1175, 1100, 1028, 910, 826, 741, 629, 517, 487.

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-bound H atoms were located on a difference Fourier map and refined freely.

Discussion

In the last decade, much attention has been focused on flavonoids. The Mannich reaction has been considered as an effective method in introducing aminomethyl substituents into the desired flavonoid molecules to improve their biological activities [5–11]. The goal of our work is to synthesize amino-acid derivatives of daidzein to obtain substances which have a good water solubility. Increasing the solubility of daidzein derivatives expands the capability for studying their biological activity and increases their bioavailability. To extend this research, we used sodium 5-(8-(((carboxymethyl)amino)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate to react with Co^{2+} ions and got a new complex. The studies on the bioactivity of the title compound are presently ongoing.

The asymmetric unit of the title structure consists of one half of a monomer complex (cf. the figure, the asymmetric unit is labeled) and three uncoordinated water molecules. The Co(II) atom lies on the inversion center and is six-coordinated by four O atoms from four coordinated water molecules and two O atoms from two monodentate coordinating ligands. The Co(II) atom adopts a slightly distorted octahedral geometry. The Co—O bond distances are in the range of 2.066(4) Å and 2.115(3) Å. The chromen moiety

(C1/C6/C5/C4/C7/C8/C9/O2/C3/C2) is essentially planar, with a mean deviation of 0.0182 Å. The carboxylate groups adopt *trans* conformations, with the C18—C17—N1—C16 torsion angles to be −86.54°. The nitrogen atom N1 is protonated. There exist extensive H-bonding interactions between the ligands *via* the coordinated water molecules and uncoordinated water molecules to form a 3D supramolecular network. 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 Education Department of Guangxi Zhuang Autonomous Region of China (No. KY2015ZD104), the Education Department of Guangxi Zhuang Autonomous Region of China (No. KY2016LX290) and the Natural Science Foundation of Guangxi Province (2014GXNSFBA118062).

References

1. Bruker: APEX2, SAINT and SADABS. Brucker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: SADABS 2.05. University Göttingen: Göttingen, Germany (2002).
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
4. Brandenburg, K.: DIAMOND. Visual crystal structure information system. Version 3.2i. Crystal Impact, Bonn, Germany (2012).
5. Li, Y.; Qiang, X.; Luo, L.; Yang, X.; Xiao, G.; Zheng, Y.; Cao, Z.; Sang, Z.; Su, F.; Deng, Y.: Multitarget drug design strategy against alzheimers disease: Homoisoflavonoid Mannich base derivatives serve as acetylcholinesterase and monoamine oxidase B dual inhibitors with multifunctional properties. Bioorg. Med. Chem. **25** (2017) 714–726.
6. Frasinyuk, M. S.; Mrug, G. P.; Bondarenko, S. P.; Khilya, V. P.; Sviripa, V. M.; Syrotchuk, O. A.; Zhang, W.; Cai, X.; Fiandalo, M. V.; Mohler, J. L.: Antineoplastic isoflavonoids derived from intermediate ortho-quinone methides generated from mannich bases. ChemMedChem. **11** (2016) 600–611.
7. Frasinyuk, M. S.; Mrug, G. P.; Bondarenko, S. P.; Sviripa, V. M.; Zhang, W.; Cai, X.; Fiandalo, M. V.; Mohler, J. L.; Liu, C.; Watt, D. S.: Application of mannich bases to the synthesis of hydroxymethylated isoflavonoids as potential antineoplastic agents. Org. Biomol. Chem. **13** (2015) 11292–11301.
8. 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.
9. Frasinyuk, M. S.; Mrug, G. P.; Fedoryak, O. D.; Bondarenko, S. P.: Nitrogen-containing apigenin analogs: preparation and biological activity. Molecules **17** (2012) 14748–14764.
10. Frasinyuk, M. S.; Bondarenko, S. P.; Khilya, V. P.: Synthesis of analogs of natural 2′-methoxyisoflavones. Chem. Nat. Compd. **42** (2006) 142–147.
11. Aitmambetov, A.; Khilya, V. P.: Mannich bases and their salts in a series of synthetic isoflavone analogs. Chem. Nat. Compd. **30** (1994) 576–579.