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Crystal structure of heptaaqua-7-methoxy-4′-hydroxyisoflavone-3′-sulfonato-strontium(II) 7-methoxy-4′-hydroxyisoflavone-3′-sulfonate hexahydrate, $[Sr(H_2O)_7(C_{16}H_{11}O_4SO_3)][C_{16}H_{11}O_4SO_3] \cdot 6H_2O$

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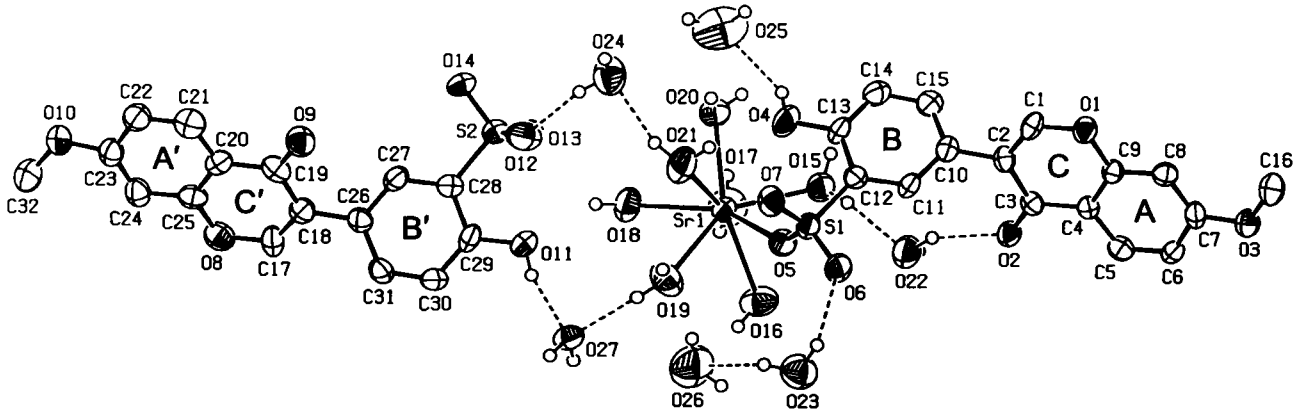

Abstract

$C_{32}H_{48}O_{27}S_2Sr$, triclinic, $P\bar{1}$ (no. 2), $a = 10.220(8)$ Å, $b = 13.83(1)$ Å, $c = 16.36(1)$ Å, $\alpha = 92.44(1)°$, $\beta = 95.63(1)°$, $\gamma = 111.05(1)°$, $V = 2139.8$ Å^3, $Z = 2$, $R_{gt}(F) = 0.054$, $wR_{ref}(F^2) = 0.121$, $T = 298$ K.

Source of material

7-Methoxy-4′-hydrogenisoflavone (1.0 g) was slowly added to sulfuric acid (98 %, 10 mL) with stirring. The mixture was heated at 333 K for 0.5 h. After being cooled at room temperature, the mixture was added into an aqueous solution of saturated sodium chloride (200 mL), colorless precipitate began to occur. 4 h later, the precipitate was filtered and washed with saturated sodium chloride solution until the pH of filtrate was 7. An aqueous solution of $SrCl_2 \cdot 6H_2O$ (10 %, 5 mL) was mixed with the precipitate (0.5 g) in water (10 mL) and the title compound was obtained after 24 h. Colorless prism-like crystals suitable for X-ray analysis were obtained by slow evaporation from water at room temperature in 76 % yield.

Experimental details

While the hydrogen atoms bound to carbon atoms were fixed using rigid body model, all aqua or water H atoms were found from Fourier difference maps and refined freely. The N_{param}/N_{gt} ratio was relatively small due to the poor quality of the crystals.

Discussion

The crystal structure of the title compound consists of three fundamental units: a metal cation coordinated by seven water molecules and a $C_{16}H_{11}O_4SO_3$ ligand, a $C_{16}H_{11}O_4SO_3^-$ anion and six lattice water molecules. Strontium(II) is eight coordinated and the coordinated atoms are all oxygen atoms, of which only one oxygen atom is O5 from the $C_{16}H_{11}O_4SO_3$ ligand, the other seven are O15, O16, O17, O18, O19, O20 and O21 from the coordinated water. The 7-methoxy-4′-hydroxyisoflavone-3′-sulfonate moiety is not only isolated anion as it is in its salts of magnesium [1] or cobalt [2], but also ligand of the cation. The ligand consists of a benzopyranone moiety, including a phenyl ring A (C4 – C9) and a heterocyclic ring C (O1/C1 – C4/C9), a phenyl ring B (C10 – C15), a hydroxy group, a methoxy group and a sulfo group. The anion is also constructed by a benzopyranone moiety, including a phenyl ring A′(C20 – C25) and a heterocyclic ring C′(O8/C17 – C20/C25), a phenyl moiety B′(C26 – C31), a hydroxy group, a methoxy group and sulfo group. The atoms of benzopyranone moiety of the ligand or the anion are coplanar, indicating by the mean deviations from their least-square planes being 0.013 Å and 0.026 Å, respectively. Two rigid ring systems are rotated by 61.9° between B and C, and by 137.3° between B′ and C′ with respect to each other to avoiding steric conflict.

Furthermore, there are six lattice water molecules and the oxygen atoms of them are O22, O23, O24, O25, O26 and O27. The six lattice water molecules are linked via nine kinds of directed O–H···O hydrogen bonds. Water molecule O22 link the carbonyl of the ligand and the coordinated water O15 via O22–H48···O2 and O15–H33···O22 hydrogen bonds. Water molecule O23 acts as hydrogen donor, via H49 and H50, to oxygen atoms O6 and O26, respectively, thus a bifurcated hydrogen bond is formed and bridges the lattice water and sulfo group of the ligand. Water molecule O24 links the other sulfo group of the anion and coordinated water O21 via hydrogen bonds O24–H51···O12 and O21–H45···O24. O25 interacts with hydroxy group of the ligand via hydrogen bond O4–H4···O25. Water molecule O27, which acts as a bridge, joins the hydroxy group of the anion and coordinated water via a tri-centered hydrogen bond formed by O11–H11···O27 and O19–H41···O27. These nine kinds of hydrogen bonds are all strong indicated by H···O distances ranging from 1.87 Å to 2.25 Å, O···O distances ranging from 2.66 Å to 2.92 Å and bond angles ranging

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from 139° to 173°. Furthermore, aromatic π-π stacking interactions exist between A and A', A and C, A' and C' with inter-centroid distances being 3.420 Å, 3.546 Å and 3.436 Å, respectively. The hydrogen bonds which connect the molecules to layers parallel to the *a,b* plane and aromatic π-π stacking interactions assemble the title compound into a three-dimensional network.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.16 x 0.24 x 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.52 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11411, 7459
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3565
$N(param)_{refined}$:	637
Program:	SHELXTL [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	2*i*	0.8582	0.8267	0.7913	0.122
H(1)	2*i*	0.4434	0.5922	0.4781	0.049
H(5)	2*i*	–0.0513	0.3483	0.6049	0.049
H(6)	2*i*	–0.2233	0.2630	0.4998	0.044
H(8)	2*i*	0.0411	0.3939	0.3348	0.045
H(11)	2*i*	0.4982	0.4775	0.6850	0.046
H(14)	2*i*	0.6944	0.8355	0.6917	0.062
H(15)	2*i*	0.4926	0.7449	0.6049	0.057
H(16A)	2*i*	–0.2839	0.2285	0.2325	0.098
H(16B)	2*i*	–0.1247	0.2448	0.2567	0.098
H(16C)	2*i*	–0.1708	0.3412	0.2523	0.098
H(33)	2*i*	0.518(5)	0.680(2)	0.873(3)	0.080
H(34)	2*i*	0.579(6)	0.792(2)	0.874(3)	0.080
H(35)	2*i*	0.616(6)	0.555(4)	1.089(3)	0.080
H(36)	2*i*	0.516(5)	0.609(4)	1.086(3)	0.080
H(37)	2*i*	0.685(6)	0.901(2)	1.073(3)	0.080
H(38)	2*i*	0.634(7)	0.824(3)	1.132(2)	0.080
H(39)	2*i*	0.948(5)	0.881(4)	1.159(3)	0.080
H(40)	2*i*	1.053(3)	0.839(4)	1.142(3)	0.080
H(41)	2*i*	0.931(6)	0.608(5)	1.120(1)	0.080
H(42)	2*i*	0.954(5)	0.594(5)	1.033(2)	0.080
H(43)	2*i*	0.823(5)	0.952(5)	0.930(3)	0.080
H(44)	2*i*	0.939(5)	0.918(5)	0.922(3)	0.080
H(45)	2*i*	1.104(4)	0.804(3)	0.944(3)	0.080
H(46)	2*i*	1.001(6)	0.745(4)	0.875(1)	0.080
H(47)	2*i*	0.287(5)	0.578(5)	0.856(3)	0.080
H(48)	2*i*	0.333(6)	0.539(5)	0.7833(8)	0.080
H(49)	2*i*	0.631(5)	0.299(4)	0.858(1)	0.080
H(50)	2*i*	0.711(3)	0.313(5)	0.940(3)	0.080
H(11A)	2*i*	1.1571	0.7299	1.2323	0.093
H(17)	2*i*	1.6072	0.9575	1.5396	0.057
H(21)	2*i*	2.0951	1.1650	1.3938	0.066
H(22)	2*i*	2.2784	1.2543	1.4930	0.062
H(24)	2*i*	2.0329	1.1440	1.6718	0.059
H(27)	2*i*	1.5921	1.0503	1.3026	0.050
H(30)	2*i*	1.2971	0.7217	1.3513	0.056
H(32)	2*i*	1.4951	0.8070	1.4394	0.051
H(32B)	2*i*	2.3805	1.2955	1.7554	0.115
H(32A)	2*i*	2.2748	1.1802	1.7365	0.115
H(32C)	2*i*	2.2172	1.2705	1.7459	0.115
H(51)	2*i*	1.321(5)	0.931(5)	0.982(1)	0.080
H(52)	2*i*	1.345(4)	0.930(5)	0.895(2)	0.080
H(53)	2*i*	1.041(6)	0.963(5)	0.7531(8)	0.080
H(54)	2*i*	1.149(2)	0.993(6)	0.824(3)	0.080
H(55)	2*i*	0.745(4)	0.336(3)	1.029(3)	0.080
H(56)	2*i*	0.876(5)	0.414(5)	1.009(2)	0.080
H(57)	2*i*	0.959(5)	0.582(4)	1.268(3)	0.080
H(58)	2*i*	1.073(5)	0.554(4)	1.243(3)	0.080

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr(1)	2*i*	0.79075(6)	0.73334(4)	0.99648(4)	0.0393(4)	0.0353(4)	0.0544(4)	0.0070(3)	–0.0038(3)	0.0042(3)
O(1)	2*i*	0.2516(4)	0.5002(3)	0.4320(2)	0.033(3)	0.053(3)	0.039(2)	0.011(2)	0.005(2)	0.002(2)
O(2)	2*i*	0.2011(4)	0.4714(3)	0.6751(2)	0.038(3)	0.050(3)	0.034(2)	0.007(2)	0.003(2)	0.002(2)
O(3)	2*i*	–0.2197(4)	0.2659(3)	0.3498(2)	0.050(3)	0.047(3)	0.041(3)	0.011(2)	–0.003(2)	–0.003(2)
O(4)	2*i*	0.8348(5)	0.7643(3)	0.7967(3)	0.069(3)	0.035(3)	0.112(4)	–0.004(2)	–0.034(3)	0.001(3)
O(5)	2*i*	0.7153(4)	0.5703(3)	0.8931(2)	0.047(3)	0.052(3)	0.040(2)	0.015(2)	0.008(2)	0.003(2)
O(6)	2*i*	0.6486(4)	0.4251(3)	0.7906(2)	0.066(3)	0.029(2)	0.071(3)	0.011(2)	–0.019(3)	–0.004(2)
O(7)	2*i*	0.8775(4)	0.5631(3)	0.7983(2)	0.035(3)	0.068(3)	0.058(3)	0.025(2)	0.005(2)	0.007(2)
O(15)	2*i*	0.5719(5)	0.7382(3)	0.9045(3)	0.066(3)	0.039(3)	0.082(3)	0.012(3)	–0.018(3)	0.006(2)
O(16)	2*i*	0.5816(5)	0.5955(4)	1.0598(3)	0.060(4)	0.072(4)	0.096(4)	0.027(3)	0.035(3)	0.023(3)
O(17)	2*i*	0.6691(6)	0.8346(4)	1.0828(3)	0.096(4)	0.082(4)	0.089(4)	0.041(4)	0.020(4)	–0.007(3)
O(18)	2*i*	0.9647(5)	0.8351(3)	1.1246(3)	0.054(3)	0.054(3)	0.080(3)	0.016(3)	–0.016(3)	–0.011(2)
O(19)	2*i*	0.8974(6)	0.6092(4)	1.0664(3)	0.102(4)	0.070(3)	0.071(3)	0.043(3)	–0.015(3)	0.006(3)
O(20)	2*i*	0.8802(6)	0.9237(4)	0.9577(3)	0.084(4)	0.050(3)	0.104(4)	0.003(3)	–0.025(3)	0.025(3)
O(21)	2*i*	1.0262(5)	0.7472(4)	0.9292(3)	0.047(3)	0.094(4)	0.092(4)	0.010(3)	–0.001(3)	0.006(3)
O(22)	2*i*	0.3501(5)	0.5520(4)	0.8391(3)	0.057(3)	0.077(4)	0.057(3)	0.009(3)	–0.001(3)	0.002(3)
O(23)	2*i*	0.6252(5)	0.2815(4)	0.9106(3)	0.089(4)	0.088(4)	0.073(4)	0.032(3)	0.014(3)	0.010(3)
S(1)	2*i*	0.7304(2)	0.5350(1)	0.8115(1)	0.034(1)	0.040(1)	0.045(1)	0.0115(8)	–0.0007(8)	0.0003(8)
C(1)	2*i*	0.3578(6)	0.5493(4)	0.4936(4)	0.023(3)	0.043(4)	0.051(4)	0.008(3)	0.003(3)	–0.005(3)
C(2)	2*i*	0.3506(6)	0.5414(4)	0.5741(3)	0.031(4)	0.045(4)	0.031(4)	0.017(3)	0.002(3)	–0.002(3)
C(3)	2*i*	0.2156(6)	0.4779(4)	0.6016(3)	0.031(4)	0.039(4)	0.034(4)	0.020(3)	0.005(3)	0.004(3)
C(4)	2*i*	0.1031(6)	0.4244(4)	0.5353(3)	0.032(4)	0.029(3)	0.030(3)	0.014(3)	0.001(3)	–0.002(3)
C(5)	2*i*	–0.0324(6)	0.3576(4)	0.5507(3)	0.045(4)	0.041(4)	0.040(4)	0.020(3)	0.006(3)	0.006(3)
C(6)	2*i*	–0.1353(6)	0.3070(4)	0.4882(3)	0.031(4)	0.033(3)	0.040(4)	0.005(3)	0.003(3)	0.002(3)
C(7)	2*i*	–0.1093(6)	0.3210(4)	0.4069(4)	0.036(4)	0.036(4)	0.042(4)	0.016(3)	–0.009(3)	–0.005(3)
C(8)	2*i*	0.0220(6)	0.3854(4)	0.3890(3)	0.041(4)	0.035(3)	0.039(4)	0.015(3)	0.006(3)	0.003(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(9)	2*i*	0.1235(6)	0.4364(4)	0.4540(3)	0.028(4)	0.035(4)	0.036(4)	0.014(3)	0.003(3)	0.002(3)
C(10)	2*i*	0.4757(6)	0.6009(4)	0.6330(3)	0.031(4)	0.042(4)	0.037(4)	0.010(3)	0.002(3)	–0.002(3)
C(11)	2*i*	0.5382(6)	0.5496(4)	0.6862(3)	0.026(3)	0.035(3)	0.046(4)	0.003(3)	0.000(3)	–0.001(3)
C(12)	2*i*	0.6578(6)	0.6022(4)	0.7407(3)	0.032(4)	0.040(4)	0.039(4)	0.012(3)	0.005(3)	0.009(3)
C(13)	2*i*	0.7166(6)	0.7103(5)	0.7424(4)	0.034(4)	0.041(4)	0.051(4)	–0.004(3)	–0.005(3)	–0.002(3)
C(14)	2*i*	0.6548(7)	0.7634(5)	0.6906(4)	0.048(4)	0.035(4)	0.066(5)	0.009(3)	0.002(4)	0.009(3)
C(15)	2*i*	0.5351(6)	0.7088(5)	0.6380(4)	0.043(4)	0.044(4)	0.054(4)	0.014(3)	0.002(4)	0.008(3)
C(16)	2*i*	–0.1981(7)	0.2705(5)	0.2662(4)	0.064(5)	0.060(5)	0.053(5)	0.008(4)	–0.014(4)	–0.008(4)
O(8)	2*i*	1.8063(5)	1.0415(3)	1.5791(2)	0.061(3)	0.061(3)	0.046(3)	0.027(3)	0.012(3)	0.008(2)
O(9)	2*i*	1.8405(4)	1.0487(3)	1.3338(3)	0.054(3)	0.071(3)	0.046(3)	0.022(2)	0.009(2)	0.006(2)
O(10)	2*i*	2.2915(4)	1.2625(3)	1.6419(3)	0.054(3)	0.057(3)	0.051(3)	0.013(2)	–0.007(3)	0.001(2)
O(11)	2*i*	1.2029(4)	0.7873(3)	1.2182(2)	0.050(3)	0.045(3)	0.073(3)	–0.002(2)	–0.008(3)	0.012(2)
O(12)	2*i*	1.3640(5)	0.9186(3)	1.0973(2)	0.122(5)	0.048(3)	0.048(3)	0.009(3)	–0.005(3)	0.001(2)
O(13)	2*i*	1.2473(5)	1.0093(3)	1.1750(3)	0.041(3)	0.070(3)	0.107(4)	0.020(3)	–0.004(3)	0.029(3)
O(14)	2*i*	1.4991(4)	1.0872(3)	1.1654(2)	0.054(3)	0.036(2)	0.079(3)	0.000(2)	–0.004(3)	0.018(2)
S(2)	2*i*	1.3766(2)	0.9910(1)	1.1664(1)	0.054(1)	0.037(1)	0.057(1)	0.0050(9)	–0.008(1)	0.0085(9)
C(17)	2*i*	1.6931(7)	0.9939(5)	1.5210(4)	0.045(4)	0.048(4)	0.048(4)	0.021(3)	–0.012(4)	–0.008(3)
C(18)	2*i*	1.6956(6)	0.9954(4)	1.4396(4)	0.038(4)	0.038(4)	0.053(4)	0.020(3)	0.003(4)	0.005(3)
C(19)	2*i*	1.8297(7)	1.0484(5)	1.4072(4)	0.058(5)	0.046(4)	0.041(4)	0.032(4)	0.009(4)	0.005(3)
C(20)	2*i*	1.9505(6)	1.1029(4)	1.4703(4)	0.035(4)	0.032(4)	0.057(4)	0.017(3)	0.010(4)	0.004(3)
C(21)	2*i*	2.0815(7)	1.1612(5)	1.4491(4)	0.054(5)	0.060(5)	0.062(5)	0.033(4)	0.015(4)	0.007(4)
C(22)	2*i*	2.1915(7)	1.2133(5)	1.5081(4)	0.049(5)	0.049(4)	0.056(5)	0.017(4)	0.004(4)	0.004(4)
C(23)	2*i*	2.1730(7)	1.2049(5)	1.5910(4)	0.043(5)	0.040(4)	0.057(5)	0.020(4)	–0.005(4)	–0.001(3)
C(24)	2*i*	2.0455(7)	1.1481(4)	1.6163(4)	0.055(5)	0.042(4)	0.051(4)	0.024(4)	–0.008(4)	–0.002(3)
C(25)	2*i*	1.9341(7)	1.0961(4)	1.5526(4)	0.054(5)	0.035(4)	0.050(4)	0.022(3)	0.009(4)	0.008(3)
C(26)	2*i*	1.5662(6)	0.9396(4)	1.3820(3)	0.042(4)	0.035(4)	0.044(4)	0.019(3)	0.001(3)	0.003(3)
C(27)	2*i*	1.5323(6)	0.9842(4)	1.3125(3)	0.033(4)	0.031(3)	0.058(4)	0.008(3)	0.002(3)	0.003(3)
C(28)	2*i*	1.4128(6)	0.9337(4)	1.2577(3)	0.044(4)	0.037(4)	0.041(4)	0.014(3)	0.008(3)	0.007(3)
C(29)	2*i*	1.3220(6)	0.8334(5)	1.2735(4)	0.028(4)	0.041(4)	0.056(4)	0.005(3)	–0.005(3)	–0.005(3)
C(30)	2*i*	1.3559(6)	0.7880(5)	1.3414(4)	0.044(4)	0.043(4)	0.051(4)	0.011(3)	0.008(4)	0.017(3)
C(31)	2*i*	1.4741(6)	0.8393(4)	1.3939(3)	0.042(4)	0.047(4)	0.043(4)	0.021(3)	0.001(3)	0.010(3)
C(32)	2*i*	2.2910(7)	1.2513(5)	1.7266(4)	0.072(6)	0.060(5)	0.077(6)	0.006(4)	–0.018(5)	–0.001(4)
O(24)	2*i*	1.2823(5)	0.9297(5)	0.9299(3)	0.072(4)	0.112(4)	0.066(3)	0.028(3)	0.005(3)	0.000(4)
O(25)	2*i*	1.0545(8)	0.9712(6)	0.8098(4)	0.168(7)	0.116(5)	0.121(5)	0.045(6)	0.077(5)	–0.004(5)
O(26)	2*i*	0.8225(8)	0.3910(5)	1.0502(4)	0.133(6)	0.081(5)	0.149(6)	0.034(4)	0.002(5)	–0.006(4)
O(27)	2*i*	1.0235(4)	0.5950(3)	1.2315(2)	0.045(3)	0.044(3)	0.064(3)	0.013(2)	0.016(2)	0.012(2)

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