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Hexaquacobalt(II) bis(5-hydroxy-7-methoxy-4-oxo-2-phenyl-4*H*-chromene-6-sulfonate) tetrahydrate

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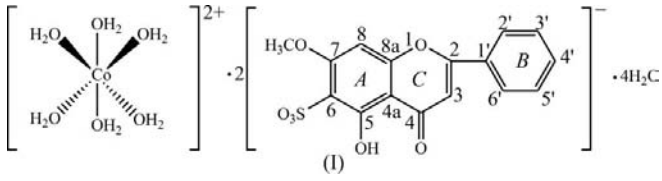
The title compound, $[Co(H_2O)_6](C_{16}H_{11}O_7S)_2\cdot 4H_2O$, with cobalt(II) at the centre of symmetry, exhibits alternating hydrophilic and hydrophobic regions. Hydrophilic regions are generated by O—H···O hydrogen bonds among sulfonate groups, involving solvent water molecules and coordinated water molecules; π–π stacking interactions assemble the flavone skeletons into columns which form the hydrophobic regions. A three-dimensional network is built up from an extensive array of hydrogen bonds, π–π stacking interactions and electrostatic interactions between the cation and anion. As a salt of the sulfonated derivative of naturally occurring tectochrysin (5-hydroxy-7-methoxyflavone), this compound offers enhanced solubility and potential biological activity over the natural product.

Comment

Tectochrysin (5-hydroxy-7-methoxyflavone), a naturally occurring flavonoid and one of the effective components of propolis (Fujimoto *et al.*, 2001), has many different biological activities, including anticancer (Ahmed-Belkacem *et al.*, 2005), antioxidant (Lee *et al.*, 2003) and trypanocidal activity (Takeara *et al.*, 2003). The aqueous solubility of flavonoids in general is poor and their biological utilization rate is low. It is therefore necessary to synthesize water-soluble flavonoid derivatives in order to improve their possible biological activities, and this may be achieved by the introduction of a sulfonate group (Hiroyuki *et al.*, 1996; Jiang *et al.*, 2001). We have synthesized some flavonoid sulfonates (Zhang & Wang, 2005; Wang & Zhang, 2005) and studied the biological activities of sodium 4′,7-dihydroxyisoflavone-3′-sulfonate (Liu *et al.*, 2003) and sodium 4′-hydroxy-7-methoxyisoflavone-3′-sulfonate (Zhang *et al.*, 2002). The results show that the biological activities of flavonoid sulfonates are better in comparison with the corresponding parent flavonoids. Given the biological activity of tectochrysin, it is important to prepare and study sulfonated derivatives that may offer improved properties. In this paper, we report the crystal structure of the cobalt(II) salt of 5-hydroxy-7-methoxyflavone-6-sulfonate, (I).



(I)

As shown in Fig. 1, (I) consists of a $[Co(H_2O)_6]^{2+}$ cation, two 5-hydroxy-7-methoxyflavone-6-sulfonate anions and four water molecules. The Co^{II} ion, lying on an inversion centre, has a nearly ideal octahedral environment consisting of six O atoms from coordinated water molecules. The equatorial plane of the octahedron is defined by atoms O1, O2, $O1^{vi}$ and $O2^{vi}$ [symmetry code: (vi) $-x, -y+2, -z+2$], with an average

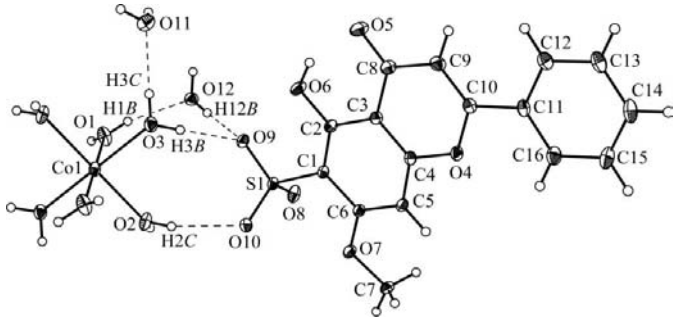


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.

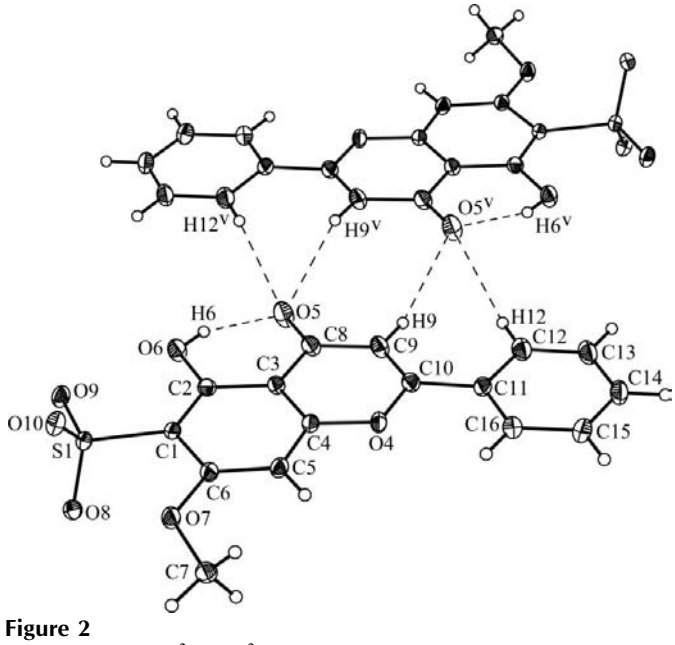


Figure 2
Hydrogen-bond $R_2^2(8)$, $R_2^2(14)$ and $S(6)$ motifs in (I). Displacement ellipsoids are drawn at the 30% probability level and dashed lines indicate hydrogen bonds. [Symmetry code: (v) $-x, -y+2, -z+1$.]

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Co—O bond length 2.072 (2) Å. The axes of the octahedron are defined by O3 and O3^{vi}, with Co—O3/O3^{vi} bond lengths of 2.1107 (19) Å. The dihedral angle between rings *A* (C1–C6) and *C* (C3–C4/O4/C8–C10) is 1.85 (11)°, and that between the benzopyran system (*A*/*C*, atoms C1–C6/O4/C8–C10) and ring *B* (C11–C16) is 1.95 (11)°. The flavone skeleton is essentially planar, with the mean deviation from the least-squares plane being 0.0248 Å; this is similar to what was found in tectochrysin itself (Chantrapromma *et al.*, 1989).

Sulfonate groups, coordinated water molecules and solvent water molecules in (I) are linked by numerous O—H···O hydrogen bonds (Fig. 1 and Table 1). For example, a hydrogen-bond O1—H1*B*···O12—H12*B*···O9 chain exists between the sulfonate group and a coordinated water molecule, bridged by the solvent water molecule O12. Sulfonate atom O9 is involved in a three-centred hydrogen bond, *viz.* O3—H3*B*···O9 and O12—H12*B*···O9. Additionally, cyclic hydrogen-bond motifs $R_2^2(8)$ and $R_2^2(14)$ (Fig. 2) are formed by paired 'soft' hydrogen bonds C9—H9···O5^{v} and C12—H12···O5^{v} [symmetry code: (v) $-x, -y+2, -z+1$], respectively. An independent hydrogen bond (O6—H6···O5) forms an intramolecular *S*(6) motif (Fig. 2). The three sulfonate O atoms are involved in seven O—H···O hydrogen bonds. According to Haynes *et al.* (2004), this indicates that the sulfonate group behaves as a steric tightener, *i.e.* brings several hydrogen-bond acceptors into close contact. The extensive array of hydrogen bonds makes this region hydrophilic (Fig. 3).

Additionally, π–π stacking interactions between the flavone skeletons are observed (Fig. 3). Ring *B* of the flavone skeleton at (x, y, z) has stacking interactions with ring *C* of the flavone at ($-x+1, -y+2, -z+1$), with a centroid–centroid [*CgB*–*CgC**; * indicates the symmetry operation ($-x, -y+2, -z+1$)] distance of 3.5553 (16) Å and a perpendicular distance (*CgB* on ring *C**) of 3.429 (2) Å. Ring *B* of the flavone at (x, y, z) has stacking interactions with ring *A* of the flavone at ($-x+1, -y+1, -z+1$), with a centroid–centroid [*CgB*–*CgA*#; # indicates the symmetry operation ($-x+1, -y+1, -z+1$)] distance of 3.6396 (16) Å and a perpendicular distance (*CgB* on ring *A*#) of 3.458 (2) Å. These values are close to those reported for typical aromatic π–π stacking interactions (Hunter, 1994). The arrangement of the flavone skeletons of (I) in an antiparallel fashion and stacked into columns along the (101) direction is driven by these interactions. The columns are linked by hydrogen-bond motifs $R_2^2(8)$ and $R_2^2(14)$, forming the hydrophobic regions of (I) (Fig. 3). The structure of (I) is quite different from the zinc complex of the related 5,7-dihydroxyflavone-6-sulfonate, [Zn-(5,7-dihydroxyflavone-6-sulfonate)(DMSO)]$_2$·H$_2$O (DMSO = dimethyl sulfoxide) (Zhang *et al.*, 2006). The Zn compound is a coordination polymer in which the cation and anion are linked by Zn—O coordination bonds. By contrast, (I) is a metal salt of 5-hydroxy-7-methoxyflavone-6-sulfonate in which the cation and anion are linked together by hydrogen bonds and electrostatic interactions.

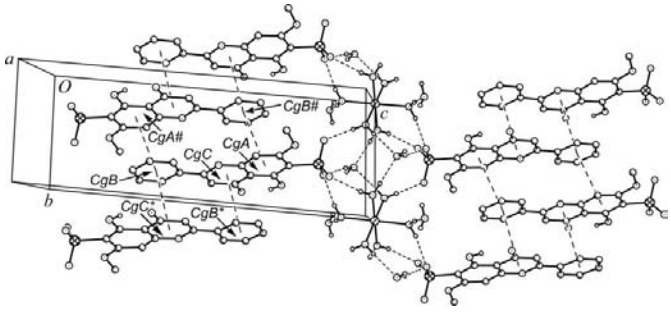

Figure 3
A view of the packing of (I), illustrating the alternating hydrophilic and hydrophobic regions and nonbonded contacts. *CgA*, *CgB* and *CgC* are the centroids of rings *A*, *B* and *C*, respectively. Labels marked with a hash (#) or an asterisk (*) are generated by the symmetry operations ($-x+1, -y+1, -z+1$) and ($-x+1, -y+2, -z+1$), respectively.

Experimental

Tectochrysin (2.0 g) was added slowly to concentrated sulfuric acid (10 ml) while stirring. The reaction was maintained at room temperature for 15 h, then poured into a saturated aqueous NaCl solution (50 ml) and a yellow precipitate appeared. After 5 h, the precipitate was filtered and washed with saturated aqueous NaCl solution until the pH value of the filtrate was 7. The precipitate was recrystallized from an ethanol–water solution (1:1 *v*/*v*) to afford sodium tectochrysin-6-sulfonate. The product was dried at 378 K for 10 h under vacuum (yield 75%). IR (cm^{-1}, KBr): ν 3465, 1646, 1607, 1487, 1447, 1205, 1144, 1099, 1045, 899, 807, 771, 687. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.15 (*s*, 1H, H–C5–OH), 7.58–7.88 (*m*, 5H, H–C2′, C3′, C4′, C5′, C6′), 6.77 (*s*, 1H, H–C8), 6.53 (*s*, 1H, H–C3), 3.88 (*s*, 3H, C7–OCH$_3$). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 177.5 (C4), 162.1 (C7), 160.4 (C2), 158.8 (C8*A*), 156.2 (C5), 131.6 (C1′), 130.5 (C4′), 129.0 (C3′, C5′), 126.0 (C2′, C6′), 115.6 (C6), 107.6 (C4*A*), 106.6 (C3), 91.4 (C8), 56.4 (C7–OCH$_3$). Analysis calculated for C$_{16}$H$_{11}$NaO$_7$S (%): C 51.89, H 2.99; found C 51.15, H 3.21. An aqueous solution of CoCl$_2$·6H$_2$O (10%, 5 ml) was mixed with a hot aqueous solution of sodium tectochrysin-6-sulfonate (5%, 10 ml) and (I) was obtained after 24 h. The compound was recrystallized from an ethanol–water solution (3:1 *v*/*v*). Pink block-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent for about 5 d at room temperature (yield 81%). IR (cm^{-1}, KBr): ν 3460, 1646, 1611, 1488, 1445, 1208, 1179, 1099, 1042, 887, 804, 769, 687.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···O12	0.82 (3)	1.97 (3)	2.765 (3)	164 (3)
O1—H1*C*···O8^{i}	0.81 (2)	2.00 (3)	2.801 (3)	172 (3)
O2—H2*B*···O12^{i}	0.81 (3)	1.94 (3)	2.751 (3)	173 (4)
O2—H2*C*···O10	0.82 (2)	2.10 (3)	2.894 (3)	164 (3)
O3—H3*B*···O9	0.83 (3)	1.98 (3)	2.793 (3)	165 (4)
O3—H3*C*···O11	0.82 (2)	1.93 (2)	2.744 (3)	168 (3)
O6—H6···O5	0.82	1.80	2.549 (3)	151
O11—H11*B*···O10^{ii}	0.82 (4)	2.19 (4)	2.976 (3)	160 (4)
O11—H11*C*···O8^{iii}	0.83 (3)	2.10 (3)	2.912 (3)	166 (4)
O12—H12*B*···O9	0.82 (3)	2.02 (3)	2.837 (3)	169 (4)
O12—H12*C*···O10^{ii}	0.82 (3)	2.02 (2)	2.789 (3)	158 (3)
C7—H7*C*···O6^{iv}	0.96	2.52	3.430 (3)	159
C9—H9···O5^{v}	0.93	2.48	3.340 (3)	154
C12—H12···O5^{v}	0.93	2.54	3.429 (4)	159

Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $x-1, y, z$; (iii) $x-1, y+1, z$; (iv) $x+1, y, z$; (v) $-x, -y+2, -z+1$.

Crystal data

$[Co(H_2O)_6](C_{16}H_{11}O_7S)_2\cdot 4H_2O$
M_r = 933.71
Triclinic, $P\overline{1}$
a = 6.978 (2) Å
b = 7.2034 (2) Å
c = 20.145 (1) Å
α = 83.970 (2)°
β = 89.286 (3)°
γ = 83.597 (2)°
V = 1000.7 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.62 mm^{-1}
T = 296 (2) K
0.34 × 0.25 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.814, T_{max} = 0.915
5062 measured reflections
3500 independent reflections
2949 reflections with $I > 2\sigma(I)$
R_{int} = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.131
S = 1.04
3500 reflections
311 parameters
10 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

H atoms bonded to C atoms were positioned geometrically (C—H = 0.93–0.96 Å) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C). H atoms of the water molecules were found in difference maps and positionally refined with restraints of O—H = 0.82 (4) Å and U_{iso}(H) = 1.5U_{eq}(O). The phenol H atom was positioned geometrically, with O—H = 0.82 Å, and included as a riding atom, with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3126). Services for accessing these data are described at the back of the journal.

References

Ahmed-Belkacem, A., Pozza, A., Munoz-Martinez, F., Bates, S. E., Castanys, S., Gamarro, F., Di Pietro, A. & Perez-Victoria, J. M. (2005). *Cancer Res.* **65**, 4852–4860.
Bruker (1999). *SMART* (Version 5.624), *SAINT-Plus* (Version 6.02A) and *SADABS* (Version 2.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Chantrapromma, K., Pakawatchai, C., Skelton, B. W., White, A. H. & Worapatamasri, S. (1989). *Aust. J. Chem.* **42**, 2289–2293.
Fujimoto, T., Nakamura, J. & Matsuka, M. (2001). *Honeybee Sci.* **22**, 9–16.
Haynes, D. A., Chisholm, J. A., Jones, W. & Motherwell, W. D. S. (2004). *CrystEngComm*, **6**, 584–588.
Hiroyuki, H., Isao, O., Sachiko, S. & Ayumi, F. (1996). *J. Nat. Prod.* **59**, 443–445.
Hunter, C. A. (1994). *Chem. Soc. Rev.* **23**, 101–109.
Jiang, R. W., He, Z. D. & Chen, Y. M. (2001). *Chem. Pharm. Bull.* **49**, 1166–1169.
Lee, S., Kim, K. S., Park, Y., Shin, K. H. & Kim, B. K. (2003). *Arch. Pharm. Res.* **26**, 43–46.
Liu, Q. G., Zhang, Z. T. & Xue, D. (2003). *Chem. J. Chin. Univ.* **24**, 820–825.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Takeara, R., Albuquerque, S., Lopes, N. P. & Lopes, J. L. C. (2003). *Phytomedicine*, **10**, 490–493.
Wang, X. B. & Zhang, Z. T. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 223–225.
Zhang, Z. T., Liu, Q. G. & Liu, X. H. (2002). *Acta Chim. Sin.* **60**, 1846–1853.
Zhang, Z. T., Shi, J. & He, Y. (2006). *Acta Chim. Sin.* **64**, 930–934.
Zhang, Z. T. & Wang, Q. Y. (2005). *Struct. Chem.* **16**, 415–420.