

Tetraaquabis(D-camphor-10-sulfonato)-  
calcium(II)Dejan Jeremić,<sup>a\*</sup> Goran N. Kaluderović,<sup>b</sup> Santiago  
Gómez-Ruiz,<sup>c</sup> Ilija Brčeski<sup>a</sup> and Katarina K. Andelković<sup>a</sup>

<sup>a</sup>Faculty of Chemistry, University of Belgrade, Studentski trg 12–16, PO Box 158, 11000 Belgrade, Republic of Serbia, <sup>b</sup>Department of Chemistry, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Studentski trg 14, 11000 Belgrade, Republic of Serbia, and <sup>c</sup>Departamento de Química Inorgánica y Analítica, ESCET, Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain  
Correspondence e-mail: djeremic@chem.bg.ac.yu

Received 22 December 2008

Accepted 4 February 2009

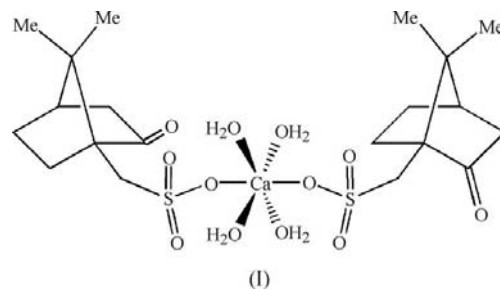
Online 7 March 2009

The structure of the title compound,  $[\text{Ca}(\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_2(\text{H}_2\text{O})_4]$ , is the first example in which two D-camphor-10-sulfonate anions are coordinated to a metal ion, in this case with direct Ca–O bonding. The molecule has crystallographically imposed twofold symmetry with the Ca atom on the twofold axis. Hydrogen bonds are formed between the coordinated water molecules and the O atoms of the  $\text{SO}_3^-$  groups of adjacent molecules, leading to the formation of a two-dimensional layered network. The compound displays sharp wavelength-selective transparency in the UV–visible spectrum, offering the potential for application as an optical filter.

## Comment

As part of our research on new optical materials, we recently prepared and characterized the magnesium salt of D-camphor-10-sulfonate (Jeremić *et al.*, 2008). This compound was found to be similar to other divalent metal ( $\text{Zn}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$ ) salts of this anion that have been reported (Couldwell *et al.*, 1978; Henderson & Nicholson, 1995; Schepke *et al.*, 2007; Zhou *et al.*, 2003). In none of these does the camphorsulfonate anion bond directly to the metal cation. Other examples in which the camphorsulfonate acts as a noncoordinating counter-ion include the salts of bis[(diphenylphosphino)ethane]rhodium(I) (Dorta *et al.*, 2004), bis(imidazolidine-2-thione)gold(I) (Friedrichs & Jones, 2004) and tris(biguanide)chromium(III) (Brubaker & Webb, 1969). Only a few metal complexes with camphorsulfonate coordinated directly to the metal atom have been described to date (Xiao & Loh, 2007; Faller *et al.*, 1995). These organometallic structures contain only one  $M\text{—O}_{\text{sulfonate}}$  bond ( $M = \text{Mo}$  and  $\text{In}$ ). We now report the structure of the title compound, tetraaquabis(D-camphor-10-sulfonato)calcium(II), (I), the first example of a complex with direct coordination between a divalent metal ion and D-camphor-10-sulfonate. Given the very low toxicity of

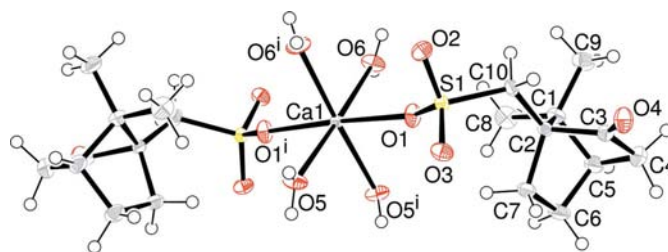
camphorsulfonate (Baldacci, 1938; Sinha, 1940), this type of compound may be useful in medicine as a calcium source (Fantoni, 1940).



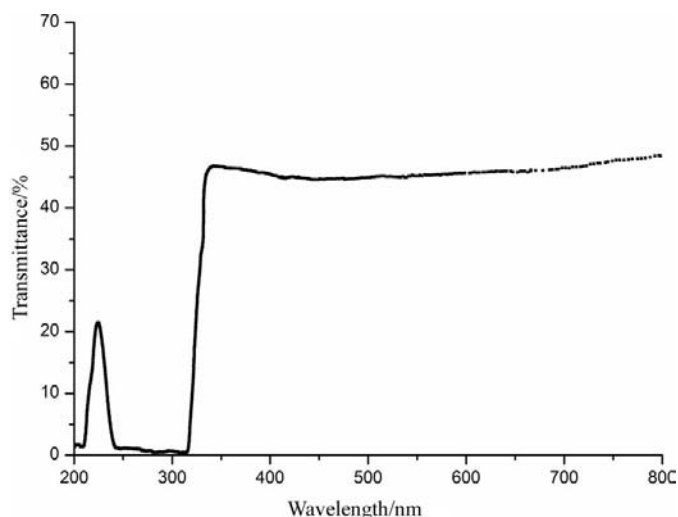
Compound (I) exists as discrete complexes (Fig. 1) containing one  $\text{Ca}^{\text{II}}$  cation coordinated in a fairly regular octahedral arrangement by four water molecules and two *trans*-positioned sulfonate anions. The cation rests on a twofold rotation axis, so the asymmetric unit consists of one half-complex. In the  $[\text{M}(\text{H}_2\text{O})_6](\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_2$  analogues ( $M$  is  $\text{Zn}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$ ), the metal ion is hexacoordinated by water and these metal complexes interact with the sulfonate by hydrogen bonding only. The Ca– $\text{O}_{\text{sulfonate}}$  bond lengths in (I) (Table 1) are a little shorter than those of Ca– $\text{O}_{\text{water}}$ , indicating the strong covalent interaction between Ca and the O atoms of the sulfonate ligands, contrasting with the ionic structure observed in the above  $M^{\text{II}}$  salts. There are several known  $\text{Ca}^{\text{II}}$  complexes with Ca– $\text{O}_{\text{sulfonate}}$  bonding, most of which exhibit one-dimensional chain structures (Denis *et al.*, 2001; Francis *et al.*, 2003; Kennedy *et al.*, 2004), while a few are monomeric complexes with coordination number 6 or 7 (Shubnell *et al.*, 1994; Fewings *et al.*, 2001; Kennedy *et al.*, 2001; Barboiu & van der Lee, 2003; Kennedy *et al.*, 2004).

Solid state UV–vis spectroscopy was carried out on crystals of (I) (Fig. 2). The transparency range is well defined for specific wavelengths and sharply separated from the non-transparent ranges. Considering these spectroscopic characteristics, it may be possible for this compound to be used as an optical filter material, since the crystals are obtainable with dimensions of up to 2 cm (Fig. 3).

The IR spectrum of (I) exhibits the following significant bands: weak–medium (CH–, CH<sub>2</sub>–, CH<sub>3</sub>– aliphatic) 2965  $\text{cm}^{-1}$ ; very strong (coordinated water) 3401  $\text{cm}^{-1}$ ; medium (C=O) 1735  $\text{cm}^{-1}$ ; strong, two bands ( $R\text{—SO}_3^-$ )



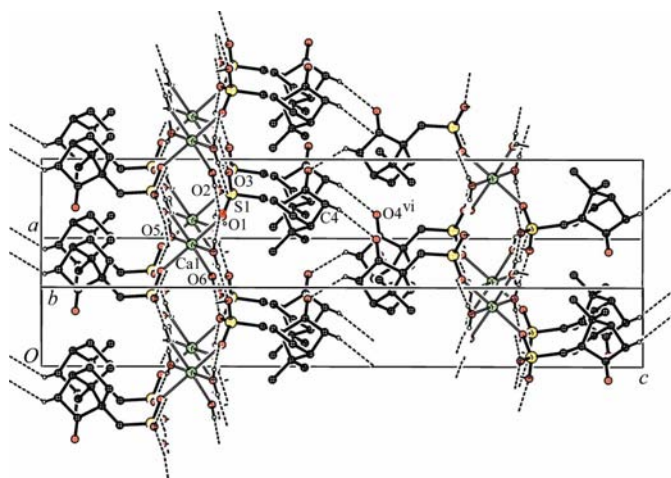
**Figure 1**  
The molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i)  $-x + 1, y, -x + \frac{1}{2}$ ]



**Figure 2**  
Solid-state UV-vis spectrum of (I). The thickness of the crystal used was 3.853 mm.



**Figure 3**  
Crystals of (I).



**Figure 4**  
A packing diagram for (I), with hydrogen-bonding interactions shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. The symmetry code is as in Table 2.

1174 and 1052  $\text{cm}^{-1}$ . The strong band belonging to the coordinated water molecules does not exist in the IR spectrum of the pure acid. The presence of the  $\text{SO}_3^-$  group (two bands in the IR spectrum) may be confirmed by the fact that the  $-\text{SO}_3\text{H}$  group gives only one band. Band positions for the aliphatic alkyl groups ( $\text{CH}-$ ,  $\text{CH}_2-$  and  $\text{CH}_3-$ ) and for  $\text{C}=\text{O}$  are not significantly changed compared with the free acid.

The crystal structures of the related  $[\text{M}(\text{H}_2\text{O})_6](\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_2$  complexes ( $M = \text{Zn}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$ ; Couldwell *et al.*, 1978; Henderson & Nicholson, 1995; Schepke *et al.*, 2007; Zhou *et al.*, 2003; Jeremić *et al.* 2008) consist of  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  cations and two crystallographically independent *D*-camphor-10-sulfonate anions arranged in alternating layers held together by hydrogen bonds. All the complexes crystallize in the chiral monoclinic  $P2_1$  space group and are isostructural.

In contrast, the title  $\text{Ca}^{\text{II}}$  complex,  $[\text{Ca}(\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_2(\text{H}_2\text{O})_4]$ , (I), crystallizes in the orthorhombic chiral space group  $C222_1$ . Each water molecule coordinated to a given  $\text{Ca}^{\text{II}}$  ion interacts, *via* nearly linear robust hydrogen bonds ( $\text{H}\cdots\text{O}$  *ca* 2.0 Å), with two neighbouring *D*-camphor-10-sulfonate anions (Table 2 and Fig. 4). In this way, each complex molecule interacts with six neighbouring complex molecules to generate a layered packing of molecules in the unit cell. The complexes are positioned such that the layers, which are parallel to the *ab* plane, are effectively sulfonate– $\text{Ca}(\text{H}_2\text{O})_4$ –sulfonate sandwiches that then stack along the *c* direction. Weak  $\text{C}-\text{H}\cdots\text{O}$  interactions may play a role in interconnecting these layers (Table 2 and Fig. 4).

## Experimental

Elemental analyses were carried out with an Elemental Vario EL III microanalyser. IR spectra were recorded on a Perkin-Elmer FT-IR 31725X spectrometer (4000–400  $\text{cm}^{-1}$ ). The UV-vis spectrum was recorded using the double-beam technique in the 200–800 nm range on a Specord M40 instrument (Carl Zeiss, Jena). Crystals of appropriate size, form and shape (typically  $5 \times 5 \times 3$  mm) were used for the UV-vis experiment.

*D*-Camphorsulfonic acid monohydrate (25 g) was dissolved in deionized water (80 ml). Calcium chips were added and the suspension was left at room temperature until vigorous reaction had finished. The solution was filtered, and a further quantity of the acid (1 g) was added to lower the pH to about 2. A titanium wire (0.5 mm diameter, 80 mm long) was added to give a controlled cooling zone, as well as to provide nucleation centres. The solution was left at room temperature for two weeks. By this method it was possible to produce crystals with large dimensions (Fig. 3) that are transparent to visible light and suitable for X-ray analysis. Analysis calculated for  $\text{C}_{20}\text{H}_{38}\text{CaO}_{12}\text{S}_2$ : C 41.80, H 6.66, S 11.16%; found: C 41.24, H 6.41, S 10.84%.

### Crystal data

$[\text{Ca}(\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_2(\text{H}_2\text{O})_4]$	$V = 2631.17 (12) \text{ \AA}^3$
$M_r = 574.7$	$Z = 4$
Orthorhombic, $C222_1$	Mo $K\alpha$ radiation
$a = 7.5020 (2) \text{ \AA}$	$\mu = 0.46 \text{ mm}^{-1}$
$b = 10.8274 (3) \text{ \AA}$	$T = 130 \text{ K}$
$c = 32.3927 (9) \text{ \AA}$	$0.4 \times 0.3 \times 0.1 \text{ mm}$

**Table 1**

Selected geometric parameters (Å, °).

Ca1—O1	2.3005 (12)	Ca1—O5	2.3394 (15)
Ca1—O6	2.3256 (15)		
O1—Ca1—O1 <sup>i</sup>	176.91 (8)	O6—Ca1—O6 <sup>i</sup>	86.85 (9)
O1—Ca1—O6	91.65 (6)	O6—Ca1—O5	177.88 (6)

Symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$ .**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5A...O2 <sup>ii</sup>	0.83 (3)	2.02 (3)	2.834 (2)	175 (3)
O5—H5B...O3 <sup>iii</sup>	0.84 (3)	1.97 (3)	2.808 (2)	178 (4)
O6—H6A...O3 <sup>iv</sup>	0.76 (3)	2.14 (3)	2.881 (2)	166 (3)
O6—H6B...O2 <sup>v</sup>	0.79 (3)	1.97 (3)	2.751 (2)	172 (2)
C4—H4B...O4 <sup>vi</sup>	0.99	2.59	3.386 (2)	138
C10—H10B...O4	0.99	2.32	2.858 (2)	113

Symmetry codes: (ii)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + 2, y, -z + \frac{1}{2}$ ; (iv)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (v)  $x - 1, y, z$ ; (vi)  $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$ .**Data collection**

Oxford Xcalibur S CCD diffractometer  
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction Ltd, 2008)

$T_{\min} = 0.964, T_{\max} = 1.000$   
(expected range = 0.921–0.955)  
30549 measured reflections  
3263 independent reflections  
3008 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.065$   
 $S = 1.05$   
3263 reflections  
177 parameters  
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{Å}^{-3}$   
Absolute structure: Flack (1983),  
with 1408 Friedel pairs  
Flack parameter: 0.00 (4)

The water H atoms were refined isotropically and yielded reasonable bond lengths and angles [O—H = 0.76 (3)–0.83 (3) Å]. All other H atoms were positioned geometrically and treated as riding, with C—H = 0.98–1.00 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97*

(Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors are grateful to the Ministry of Science and Technological Development of the Republic of Serbia for financial support (grant No. 142062).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3182). Services for accessing these data are described at the back of the journal.

**References**

- Baldacci, U. (1938). *Arch. Farmacol. Sper.* **65**, 102–104.  
Barboiu, M. & van der Lee, A. (2003). *Acta Cryst.* **C59**, m366–m368.  
Brubaker, G. R. & Webb, L. E. (1969). *J. Am. Chem. Soc.* **91**, 7199–7200.  
Couldwell, C., Prout, K., Robey, D., Taylor, R. & Rossotti, F. J. C. (1978). *Acta Cryst.* **B34**, 1491–1499.  
Denis, A., Palvadeau, P., Molinie, P., Chauvet, O. & Boubekeur, K. (2001). *Solid State Sci.* **3**, 715–725.  
Dorta, R., Shimon, L. & Milstein, D. (2004). *J. Organomet. Chem.* **689**, 751–758.  
Faller, J. W., Chase, K. J. & Mazzieri, M. R. (1995). *Inorg. Chim. Acta*, **229**, 39–45.  
Fantoni, C. R. (1940). *Ateneo Parmense*, **12**, 40–42.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
Fewings, K. R., Junk, P. C., Georganopoulou, D., Prince, P. D. & Steed, J. W. (2001). *Polyhedron*, **20**, 643–649.  
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
Francis, S., Muthiah, P. T., Rychlewska, U. & Warzajtis, B. (2003). *Acta Cryst.* **E59**, m1160–m1163.  
Friedrichs, S. & Jones, P. G. (2004). *Z. Naturforsch. Teil B*, **59**, 793–801.  
Henderson, W. & Nicholson, B. K. (1995). *Acta Cryst.* **C51**, 37–40.  
Jeremić, D., Kaluderović, G. N., Brčeski, I., Gómez-Ruiz, S. & Anđelković, K. K. (2008). *Acta Cryst.* **E64**, m952.  
Kennedy, A. R., Hughes, M. P., Monaghan, M. L., Staunton, E., Teat, S. J. & Smith, W. E. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2199–2205.  
Kennedy, A. R., Kirkhouse, J. B. A., McCarney, K. M., Puissegur, O., Smith, W. E., Staunton, E., Teat, S. J., Cherryman, J. C. & James, R. (2004). *Chem. Eur. J.* **10**, 4606–4615.  
Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.15. Oxford Diffraction Ltd, Abingdon, England.  
Schepke, M., Edelmann, F. T. & Blaurock, S. (2007). *Acta Cryst.* **E63**, m2071.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Shubnell, A. J., Kosnic, E. J. & Squattrito, P. J. (1994). *Inorg. Chim. Acta*, **216**, 101–112.  
Sinha, H. K. (1940). *Indian J. Pharm.* **2**, 114–116.  
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.  
Xiao, J. & Loh, T.-P. (2007). *Synlett*, **5**, 815–817.  
Zhou, J.-S., Cai, J.-W. & Ng, S. W. (2003). *Acta Cryst.* **E59**, o1185–o1186.