

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HL1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Hexaaquanickel(II) D-Camphor-10-sulfonate

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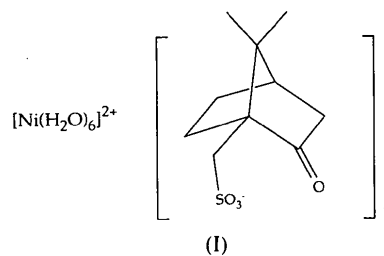
### Abstract

The structure of the title complex,  $[\text{Ni}(\text{H}_2\text{O})_6] \cdot 2\text{C}_{10}\text{H}_{15}\text{O}_4\text{S}$ , consists of D-camphor-10-sulfonate

anions, together with essentially regular octahedral  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cations. An extensive hydrogen-bonded network results in an overall lattice structure in which alternating layers of oppositely charged ions are stacked perpendicular to the *c* axis. The structure contains two independent D-camphor-10-sulfonate anions, with conformations related by rotation about the C(1)—C(10) bond.

### Comment

Metal salts of both phosphonic and sulfonic acids with layered structures have potential applications for ion exchange and for the separation of organic compounds by selective intercalation (Suib, 1993; Cao, Hong & Mallouk, 1992; Zhang, Scott & Clearfield, 1993). Organic derivatives are used to pillar and open-out the inorganic-based layers, and the physical properties of the layered solid can readily be varied by modification of these organic groups (Burwell & Thompson, 1991). Chiral layered materials of this type (Cao, Garcia, Alcalá, Burgess & Mallouk, 1992) offer potential for enantiomeric separations by intercalation and we are investigating layered materials derived from chiral sulfonic and phosphonic acids. Only one simple metal salt (copper) of camphor-10-sulfonic acid has been structurally characterized previously (Couldwell, Prout, Robey, Taylor & Rossotti, 1978). Here we present the crystal structure of  $[\text{Ni}(\text{H}_2\text{O})_6][\text{D-camphor-10-SO}_3]_2$ , (1).



The crystal lattice consists of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cations and two crystallographically independent D-camphor-10-sulfonate anions. The  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion is essentially octahedral with Ni—O distances ranging from 2.029 (3) to 2.073 (5) Å (average 2.051 Å) and O—Ni—O angles between 82.7 (2) and 96.9 (2)°. These Ni—O distances are very similar to those of nickel(II) phenylsulfonate [2.036 (5)–2.073 (5) Å], in which the hexaaquanickel ion is a more regular octahedron with O—Ni—O angles in the range 87.3 (2)–92.7 (2)° (Kosnic, McClymont, Hodder & Squattrito, 1992). There is no coordination of either the sulfonate or the ketone O atoms of the anion, in contrast to observations for related phosphonate salts. This is not unexpected as these ligands show relatively poor coordinating ability when compared

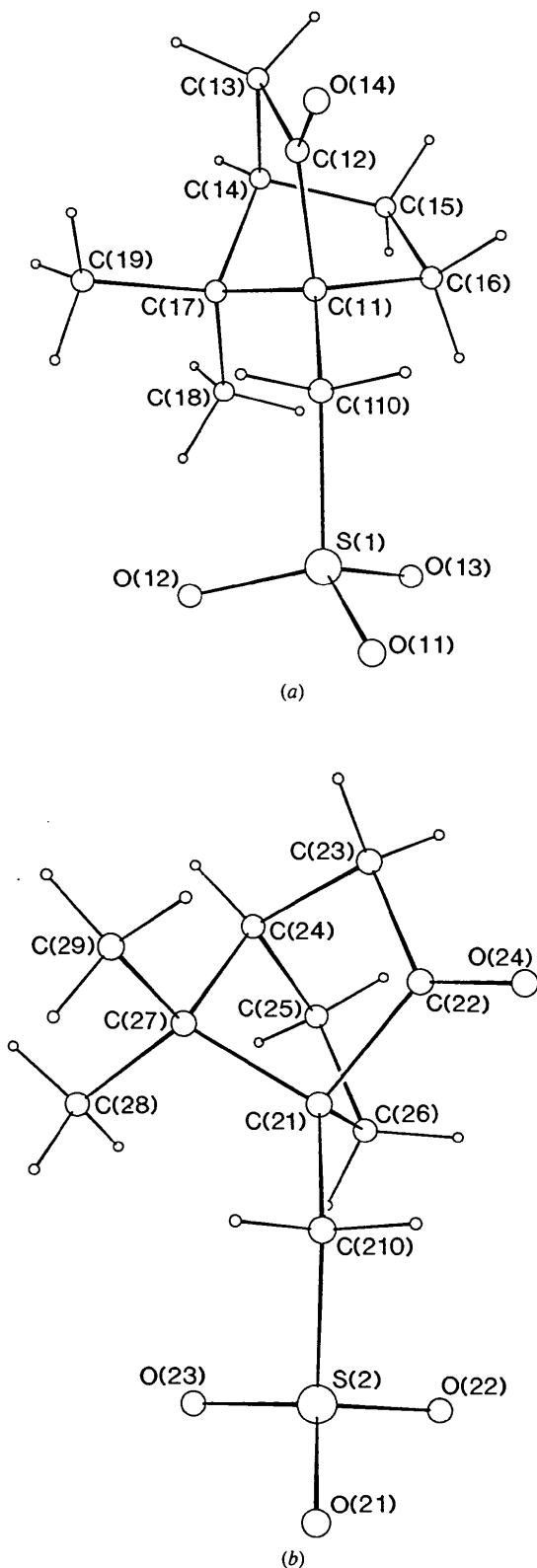


Fig. 1. The two independent anions, (a) and (b), showing the atom-numbering scheme and the different conformations adopted.

to water. The two independent camphor-10-sulfonate anions adopt different conformations, the major difference being a rotation of  $49^\circ$  about the C(1)—C(10) bond, but otherwise they show only small differences in bond parameters. The molecular conformations of the two camphorsulfonate anions are given in Fig. 1. The mean S—C(10)—C(1) angle of  $119.6^\circ$  is relatively large, whereas the S—O (mean  $1.464 \text{ \AA}$ ) and S—C ( $1.776 \text{ \AA}$ ) bonds are of normal length.

There is extensive hydrogen-bonding between the coordinated water molecules and the O atoms of the  $\text{SO}_3^-$  groups, but none involving the ketone O atom. All 12 H atoms are involved with H...O distances ranging from  $1.80$  to  $1.96 \text{ \AA}$ . This network generates a layered packing of ions in the unit cell, stacked perpendicular to the  $c$  axis, with alternating hydrophilic regions containing the hydrated Ni ions and the  $\text{SO}_3^-$  groups, and hydrophobic regions involving van der Waals contacts between the camphor groups in adjacent layers (Fig. 2). The layered structure of (1) is isomorphous with that of the analogous copper salt of camphor-10-sulfonic acid (Couldwell *et al.*, 1978), although detailed parameters differ because of the Jahn-Teller effects involving the cation in the copper case and because of differing anion conformations. The structures of a number of related phenylsulfonate salts which have been characterized are also of this general layered type. Studies into analogous chiral layered phosphonates derived from terpene-phosphonic acids are in progress.

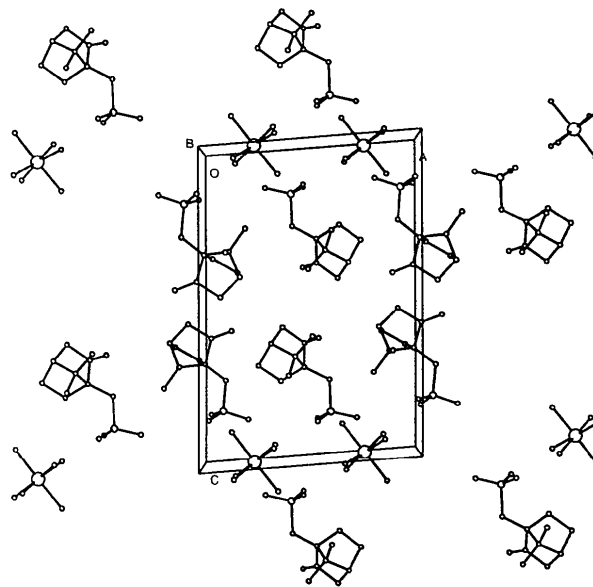


Fig. 2. Unit-cell packing diagram along the  $b$  axis, showing the layered structure of cations and anions.

## Experimental

Crystals of (1) were obtained by slow evaporation of an aqueous solution of nickel(II) bromide and two mol equivalents of sodium D-camphor-10-sulfonate. Elemental analysis: found C 38.08, H 6.70%;  $C_{20}H_{42}NiO_{14}S_2$  requires C 38.17, H 6.73%.

### Crystal data

$[Ni(H_2O)_6]2C_{10}H_{15}O_4S$

$M_r = 629.37$

Monoclinic

$P2_1$

$a = 11.677 (2) \text{ \AA}$

$b = 7.064 (2) \text{ \AA}$

$c = 17.078 (2) \text{ \AA}$

$\beta = 94.22 (2)^\circ$

$V = 1404.9 (5) \text{ \AA}^3$

$Z = 2$

$D_x = 1.488 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 37 reflections

$\theta = 10\text{--}28^\circ$

$\mu = 0.90 \text{ mm}^{-1}$

$T = 143 \text{ K}$

Tablet

$0.43 \times 0.31 \times 0.12 \text{ mm}$

Pale blue-green

### Data collection

Nicolet R3 diffractometer

$\omega$  scans

Absorption correction:

empirical

$T_{\min} = 0.613$ ,  $T_{\max} =$

0.674

2834 measured reflections

2694 independent reflections

2222 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0192$

$\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -19 \rightarrow 19$

3 standard reflections

monitored every 100

reflections

intensity variation:

0.993–1.006%

### Refinement

Refinement on  $F^2$

$R(F) = 0.0491$

$wR(F^2) = 0.0721$

$S = 1.038$

2694 reflections

375 parameters

H-atom parameters not

refined

$w = [\sigma^2(F_o^2) + (0.0440P)^2 + 0.15P]$

where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.55 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *SHELXL93*

(Sheldrick, 1993)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Ni(1)	0.7587 (1)	0.0000	0.0059 (1)	0.012 (1)
O(1)	0.6674 (4)	0.2152 (7)	0.0523 (3)	0.016 (1)
O(2)	0.6504 (2)	−0.0004 (9)	−0.0926 (2)	0.018 (1)
O(3)	0.8517 (4)	−0.2151 (7)	−0.0422 (3)	0.016 (1)
O(4)	0.8647 (2)	−0.0025 (8)	0.1064 (2)	0.018 (1)
O(5)	0.6669 (4)	−0.2197 (7)	0.0494 (3)	0.016 (1)
O(6)	0.8496 (4)	0.2213 (7)	−0.0374 (3)	0.016 (1)
S(1)	0.0822 (1)	0.0022 (3)	0.8355 (1)	0.012 (1)
O(11)	0.2013 (2)	0.0001 (8)	0.8695 (2)	0.016 (1)
O(12)	0.0188 (4)	0.1686 (6)	0.8600 (3)	0.016 (1)
O(13)	0.0212 (4)	−0.1745 (6)	0.8488 (3)	0.015 (1)

O(14)	0.1232 (3)	0.0704 (6)	0.5729 (2)	0.029 (1)
C(11)	−0.0063 (3)	−0.0138 (11)	0.6744 (2)	0.013 (1)
C(12)	0.0268 (4)	0.0431 (7)	0.5926 (3)	0.020 (1)
C(13)	−0.0845 (4)	0.0554 (8)	0.5396 (3)	0.023 (1)
C(14)	−0.1734 (3)	0.0000 (12)	0.5968 (2)	0.017 (1)
C(15)	−0.1578 (4)	−0.2155 (8)	0.6122 (3)	0.020 (1)
C(16)	−0.0415 (4)	−0.2242 (8)	0.6627 (3)	0.016 (1)
C(17)	−0.1259 (4)	0.0878 (8)	0.6764 (3)	0.015 (1)
C(18)	−0.1996 (4)	0.0326 (9)	0.7434 (2)	0.019 (1)
C(19)	−0.1154 (5)	0.3045 (8)	0.6734 (3)	0.024 (1)
C(110)	0.0955 (4)	0.0270 (10)	0.7331 (2)	0.014 (1)
S(2)	0.4080 (1)	−0.0002 (3)	0.1477 (1)	0.012 (1)
O(21)	0.2853 (2)	0.0007 (9)	0.1221 (2)	0.016 (1)
O(22)	0.4665 (4)	−0.1723 (6)	0.1247 (3)	0.017 (1)
O(23)	0.4678 (4)	0.1702 (6)	0.1241 (3)	0.015 (1)
O(24)	0.4618 (4)	−0.2454 (7)	0.3836 (2)	0.024 (1)
C(21)	0.5300 (3)	0.0043 (12)	0.2984 (2)	0.015 (1)
C(22)	0.5293 (5)	−0.1224 (8)	0.3721 (3)	0.019 (1)
C(23)	0.6301 (5)	−0.0570 (8)	0.4274 (3)	0.023 (1)
C(24)	0.6815 (4)	0.1042 (8)	0.3803 (3)	0.017 (1)
C(25)	0.7412 (3)	0.0085 (13)	0.3130 (2)	0.021 (1)
C(26)	0.6388 (4)	−0.0655 (7)	0.2583 (3)	0.015 (1)
C(27)	0.5714 (4)	0.1936 (8)	0.3370 (3)	0.016 (1)
C(28)	0.5994 (4)	0.3517 (8)	0.2798 (3)	0.019 (1)
C(29)	0.4910 (5)	0.2765 (10)	0.3941 (4)	0.024 (2)
C(210)	0.4126 (3)	−0.0007 (12)	0.2519 (2)	0.015 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

All C—C distances lie in the range 1.525–1.573  $\text{\AA}$ .

Ni(1)—O(1)	2.050 (5)	O(14)—C(12)	1.214 (6)
Ni(1)—O(3)	2.073 (5)	S(2)—O(22)	1.462 (5)
Ni(1)—O(5)	2.056 (5)	S(2)—C(210)	1.776 (4)
Ni(1)—O(2)	2.029 (3)	S(1)—O(12)	1.466 (5)
Ni(1)—O(4)	2.041 (3)	S(1)—C(110)	1.776 (4)
Ni(1)—O(6)	2.058 (5)	S(2)—O(21)	1.467 (3)
S(1)—O(11)	1.467 (3)	S(2)—O(23)	1.464 (5)
S(1)—O(13)	1.463 (5)	O(24)—C(22)	1.199 (7)
O(2)—Ni(1)—O(4)	178.7 (2)	C(11)—C(110)—S(1)	120.6 (3)
O(4)—Ni(1)—O(1)	88.9 (2)	O(22)—S(2)—O(21)	112.9 (3)
O(4)—Ni(1)—O(5)	89.4 (2)	O(22)—S(2)—C(210)	106.7 (3)
O(2)—Ni(1)—O(6)	90.5 (2)	O(21)—S(2)—C(210)	104.9 (2)
O(1)—Ni(1)—O(6)	82.7 (2)	C(210)—C(21)—C(22)	110.5 (4)
O(2)—Ni(1)—O(3)	89.0 (2)	O(24)—C(22)—C(23)	127.2 (5)
O(1)—Ni(1)—O(3)	179.2 (2)	C(21)—C(27)—C(24)	94.1 (4)
O(6)—Ni(1)—O(3)	96.6 (2)	O(13)—S(1)—O(11)	112.9 (3)
O(2)—Ni(1)—O(1)	90.7 (2)	O(13)—S(1)—C(110)	108.4 (3)
O(2)—Ni(1)—O(5)	89.4 (2)	O(11)—S(1)—C(110)	103.9 (2)
O(1)—Ni(1)—O(5)	96.9 (2)	C(110)—C(11)—C(16)	116.9 (5)
O(4)—Ni(1)—O(6)	90.7 (2)	O(14)—C(12)—C(11)	126.6 (4)
O(5)—Ni(1)—O(6)	179.6 (2)	C(14)—C(17)—C(11)	93.4 (4)
O(4)—Ni(1)—O(3)	91.4 (2)	O(22)—S(2)—O(23)	111.6 (2)
O(5)—Ni(1)—O(3)	83.8 (2)	O(23)—S(2)—O(21)	112.9 (3)
O(13)—S(1)—O(12)	112.2 (2)	O(23)—S(2)—C(210)	107.3 (3)
O(12)—S(1)—O(11)	112.3 (3)	C(210)—C(21)—C(27)	118.6 (6)
O(12)—S(1)—C(110)	106.5 (3)	C(210)—C(21)—C(26)	119.3 (4)
C(110)—C(11)—C(12)	108.3 (4)	O(24)—C(22)—C(21)	126.6 (5)
C(110)—C(11)—C(17)	123.3 (5)	C(21)—C(210)—S(2)	118.6 (3)
O(14)—C(12)—C(13)	126.2 (4)		

The H atoms in the cation were included in calculated positions with a tied common isotropic displacement factor, while those of the anion were included in calculated positions with isotropic displacement factors 1.2 times the equivalent isotropic displacement factor of the C atom to which they are bonded. The assignment of absolute configuration was confirmed by a Flack  $\chi$  parameter of 0.00(3) from the final refinement. Computer programs used were *SHELXS86* (Sheldrick, 1985), *SHELXL93* (Sheldrick, 1993) and *PLUTO* (Motherwell, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: OH1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## *trans*-Dichlorotetrakis(pyridine-*N*)-ruthenium(II)

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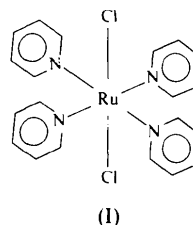
## Abstract

We present here the crystal structure of *trans*-[RuCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>], which exhibits notably shorter *M*—N and *M*—Cl bond lengths, and hence reduced unit-cell dimensions, when compared with the pre-

viously reported isomorphous compounds of the first transition series. [MCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>] (*M* = Fe, Co, Ni).

## Comment

As part of our studies (Elsegood & Tocher, 1988, 1989; Aronson, Elsegood, Steed & Tocher, 1991; Elsegood, 1991) on ruthenium(II)[2<sub>2</sub>(1.4)-cyclophane compounds, we have investigated the reactivity of the dinuclear triply chloro-bridged compound [Ru<sub>2</sub>(η<sup>6</sup>-C<sub>16</sub>H<sub>16</sub>)<sub>2</sub>(μ-Cl)<sub>3</sub>][PF<sub>6</sub>] towards various reagents. Prolonged exposure (12 h) to pyridine in methanol, resulted in cleavage of the dimer and displacement of the aromatic ligands giving the well known compound *trans*-[RuCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>]. (I) (Long & Clarke, 1978; Robertson & Stephenson, 1976; Robertson, Stephenson & Arthur, 1978; Abel, Bennett & Wilkinson, 1959), the crystal structure of which we report here.



The structures of a number of *trans*-dichloride metal tetrakis(pyridine) complexes have been reported (Al-Zamil *et al.*, 1982; Bachman, Whitmire, Mandal & Bharadwaj, 1992; Rozière, Lehmann & Potier, 1979; Dobinson, Mason & Russell, 1967; Pullman, Hensen & Bats, 1982; Sinclair, Small & Worrall, 1981). These fall into two main categories: those with metal ions in the 2+ oxidation state and those with metal ions in the 3+ oxidation state. The most comprehensive study in this field, by Long & Clarke (1978), reports the structures of the three isomorphous anhydrous compounds *trans*-[MCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>] (*M* = Fe, Co, Ni), and the hydrated compound *trans*-[FeCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>].H<sub>2</sub>O. The structure of the Ni compound was redetermined by Bachman *et al.* (1992) at low temperature, with the cell parameters and interatomic distances being slightly smaller than those determined at ambient temperature by Long & Clarke (1978). The data from Long & Clarke's experiment is used for comparison with the present room-temperature data.

The crystals of *trans*-[FeCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>].H<sub>2</sub>O were grown by the slow evaporation of a reaction solution open to the air (Long & Clarke, 1978). The anhydrous analogue was obtained only under a moisture-free atmosphere. In contrast, the anhydrous compound *trans*-[RuCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>] was obtained simply by evaporation of the methanolic reaction solution in an open vessel. The crystals of com-