

## Hexaaquanickel(II) 3-carboxy-4-hydroxybenzenesulfonate tetrahydrate

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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ 

R factor = 0.038

wR factor = 0.101

Data-to-parameter ratio = 12.5

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the title compound,  $[\text{Ni}(\text{H}_2\text{O})_6]L_2 \cdot 4\text{H}_2\text{O}$ , where  $HL = 3$ -carboxy-4-hydroxybenzenesulfonic acid ( $\text{C}_7\text{H}_6\text{O}_6\text{S}$ ), each  $\text{Ni}^{\text{II}}$  cation lies on an inversion center and is octahedrally coordinated by six water molecules. The  $L^-$  anions do not coordinate to nickel, but act as counter-anions. The crystal structure is composed of alternating layers of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cations and sulfonate anions. The  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cations, water molecules and  $L^-$  anions are connected through a complex pattern of hydrogen-bonding interactions.

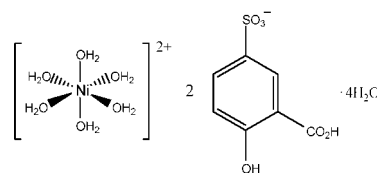
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## Comment

The crystal structures of five transition metal (Mn, Co, Ni, Cu and Zn) 3-carboxy-4-hydroxybenzenesulfonates have been determined. The structures of the manganese (Ma *et al.*, 2003a) and cobalt compound (Ma *et al.*, 2003b) have been reported in the preceding papers. The crystal structure of the nickel compound, (I), is presented here. The crystal structures of the other two related compounds are reported in the following papers.



The  $\text{Ni}^{\text{II}}$  atom is located on an inversion center, and all other atoms are in general positions. Selected bond lengths and angles are given in Table 1. Fig. 1 shows the asymmetric unit, together with the complete coordination environment of the  $\text{Ni}^{\text{II}}$  cation. Compound (I) is isostructural with the cobalt compound (Ma *et al.*, 2003b). The Ni—O distances range from 2.030 (2) to 2.057 (2) Å. The average Ni—O distance of 2.047 Å is similar to the values in other nickel compounds (Gunderman *et al.*, 1997; Kosnic *et al.*, 1992).

The alternating layers of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cations and sulfonate anions in (I) are shown in Fig. 2. Selected hydrogen-bond parameters are listed in Table 2.

## Experimental

A mixture of 3-carboxy-4-hydroxybenzenesulfonic acid (0.44 g, 2 mmol) and  $\text{NiCO}_3$  (0.12 g, 1 mmol) in water (10 ml) was stirred at room temperature for 30 min. Green crystals of compound (I) were obtained after leaving the solution to stand at room temperature for several days. Analysis calculated for  $\text{C}_{14}\text{H}_{30}\text{NiO}_{22}\text{S}_2$ : C 24.98, H 4.49%; found: C 24.82, H 4.47%.

Crystal data

[Ni(H<sub>2</sub>O)<sub>6</sub>](C<sub>7</sub>H<sub>5</sub>O<sub>6</sub>S)<sub>2</sub>·4H<sub>2</sub>O  
*M<sub>r</sub>* = 673.21  
 Triclinic, *P* $\bar{1}$   
*a* = 6.5380 (9) Å  
*b* = 7.2199 (10) Å  
*c* = 14.534 (4) Å  
 $\alpha$  = 92.931 (16)°  
 $\beta$  = 96.494 (16)°  
 $\gamma$  = 102.727 (12)°  
*V* = 662.9 (2) Å<sup>3</sup>

*Z* = 1  
*D<sub>x</sub>* = 1.686 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 20 reflections  
 $\theta$  = 5.9–9.7°  
 $\mu$  = 0.99 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, green  
 0.36 × 0.24 × 0.15 mm

Data collection

Siemens *P4* diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.687, *T<sub>max</sub>* = 0.863  
 3424 measured reflections  
 2599 independent reflections  
 2145 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.026  
 $\theta_{max}$  = 26.0°  
*h* = -1 → 8  
*k* = -8 → 8  
*l* = -17 → 17  
 3 standard reflections every 97 reflections  
 intensity decay: none

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.101  
*S* = 1.09  
 2599 reflections  
 208 parameters  
 H atoms treated by a mixture of independent and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0506*P*)<sup>2</sup> + 0.1374*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.58 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.47 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

C4—O6	1.346 (3)	O3—S1	1.4569 (19)
C7—O5	1.226 (3)	OW1—Ni1	2.030 (2)
C7—O4	1.313 (3)	OW2—Ni1	2.057 (2)
O1—S1	1.462 (2)	OW3—Ni1	2.054 (2)
O2—S1	1.437 (2)		
O5—C7—O4	123.3 (3)	OW1—Ni1—OW3	88.96 (9)
O2—S1—O3	112.45 (13)	OW1—Ni1—OW2	89.92 (10)
O2—S1—O1	113.34 (15)	OW3—Ni1—OW2	90.05 (9)
O3—S1—O1	109.89 (14)		

Table 2

Hydrogen-bonding 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>
OW1—H1A...OW4 <sup>i</sup>	0.898 (18)	1.973 (19)	2.820 (3)	156 (3)
OW1—H1B...OW5 <sup>ii</sup>	0.883 (18)	1.934 (19)	2.786 (3)	162 (3)
OW2—H2A...O2 <sup>ii</sup>	0.902 (18)	2.001 (19)	2.867 (3)	161 (3)
OW2—H2B...OW4 <sup>iii</sup>	0.893 (18)	1.888 (19)	2.773 (3)	170 (3)
OW3—H3B...OW5 <sup>iv</sup>	0.894 (18)	1.861 (19)	2.745 (3)	169 (3)
OW3—H3A...O5 <sup>v</sup>	0.882 (18)	2.099 (19)	2.946 (3)	161 (3)
OW4—H4B...O2	0.902 (18)	1.964 (19)	2.837 (3)	163 (3)
OW4—H4A...O1 <sup>vi</sup>	0.894 (18)	1.989 (19)	2.871 (3)	169 (3)
OW5—H5B...O3 <sup>vii</sup>	0.902 (18)	1.860 (19)	2.731 (3)	162 (3)
OW5—H5A...O1	0.872 (18)	1.955 (19)	2.789 (3)	160 (3)
O4—H4...O3 <sup>viii</sup>	0.82	1.88	2.650 (3)	155
O6—H6A...O5	0.82	1.91	2.631 (3)	146

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

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The H

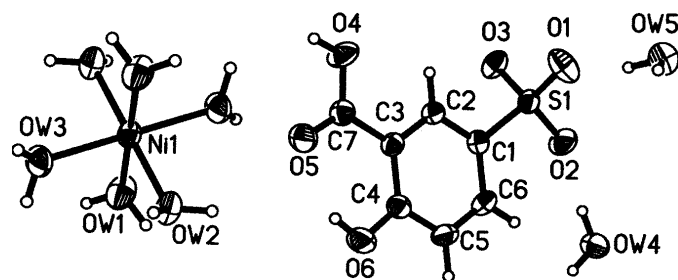


Figure 1

View of the asymmetric unit, expanded to show the complete coordination of Ni<sup>II</sup>, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

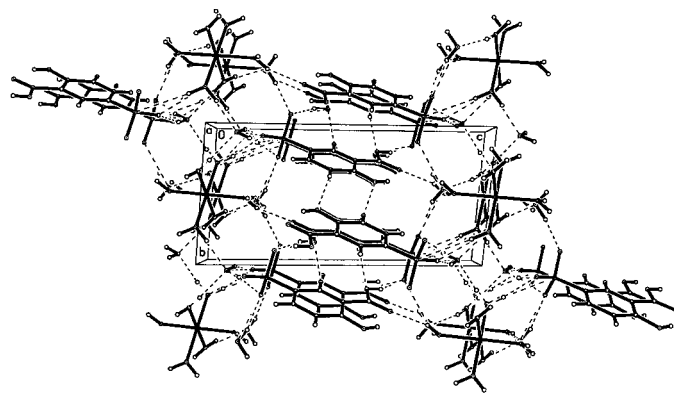


Figure 2

View of the alternating layers of cations and anions, along the *a* axis.

atoms of the carboxyl group and hydroxyl group were also positioned geometrically and refined as riding atoms, with O—H = 0.82 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O). The water H atoms were located in a difference Fourier map and refined with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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