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## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
 $R$  factor = 0.041  
 $wR$  factor = 0.118  
Data-to-parameter ratio = 12.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Hexaaquacobalt(II) 3-carboxy-4-hydroxy-  
benzenesulfonate tetrahydrate

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

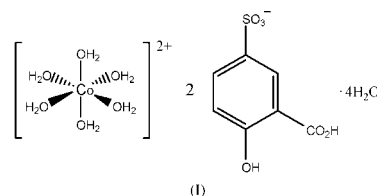
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## Comment

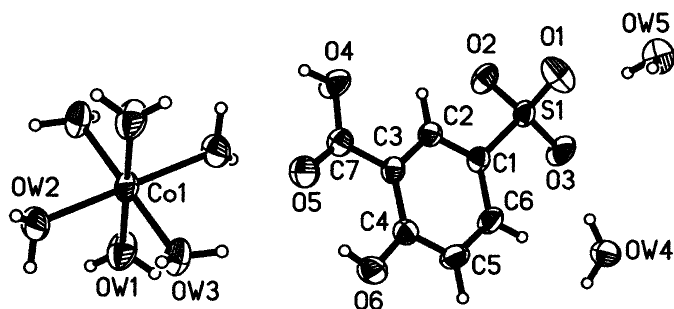
The crystal structures of five transition metal (Mn, Co, Ni, Cu and Zn) 3-carboxy-4-hydroxybenzenesulfonates have been determined. The structure of the manganese compound has been reported in the preceding paper (Ma *et al.*, 2003). The crystal structure of the cobalt compound, (I), is presented here.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



The  $\text{Co}^{\text{II}}$  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  $\text{Co}^{\text{II}}$  cation. The coordination of  $\text{Co}^{\text{II}}$  is similar to that of  $\text{Mn}^{\text{II}}$  (Ma *et al.*, 2003). The distances from cobalt to oxygen range from 2.051 (2) to 2.113 (2) Å. The average  $\text{Co}-\text{O}$  distance of 2.083 Å is similar to the values in other cobalt compounds (Kosnic *et al.*, 1992; Shubnell *et al.*, 1994).

The crystal structure of (I) is composed of alternating layers of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cations and sulfonate anions, as shown in Fig. 2. Within the sulfonate layer, there are rows of anions with alternating orientations of the organic group. The dihedral angle between the aromatic ring and the layer of cations is 80.4 (3)°, similar to the value of the manganese compound, 78.2 (2)° (Ma *et al.*, 2003).

There are two additional, uncoordinated water molecules in the asymmetric unit. The  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cations, water molecules and  $L^-$  anions are connected through a complex pattern of hydrogen-bonding interactions. Selected hydrogen-bond parameters are listed in Table 2.



**Figure 1**  
View of the asymmetric unit, expanded to show the complete coordination of  $\text{Co}^{\text{II}}$ , with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

## Experimental

A mixture of 3-carboxy-4-hydroxybenzenesulfonic acid (0.44 g, 2 mmol) and  $\text{CoCO}_3$  (0.12 g, 1 mmol) in water (10 ml) was stirred at room temperature for 30 min. Pink crystals of compound (I) were obtained after leaving the solution to stand at room temperature for several days. Analysis calculated for  $\text{C}_{14}\text{H}_{30}\text{CoO}_{22}\text{S}_2$ : C 24.97, H 4.49%; found: C 24.79, H 4.43%.

### Crystal data

$[\text{Co}(\text{H}_2\text{O})_6](\text{C}_7\text{H}_5\text{O}_6\text{S})_2 \cdot 4\text{H}_2\text{O}$	$Z = 1$
$M_r = 673.43$	$D_x = 1.674 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.5281(11) \text{ \AA}$	Cell parameters from 21 reflections
$b = 7.2358(18) \text{ \AA}$	$\theta = 4.9\text{--}9.8^\circ$
$c = 14.627(4) \text{ \AA}$	$\mu = 0.89 \text{ mm}^{-1}$
$\alpha = 92.73(2)^\circ$	$T = 293(2) \text{ K}$
$\beta = 96.274(18)^\circ$	Block, pink
$\gamma = 102.803(16)^\circ$	$0.50 \times 0.42 \times 0.40 \text{ mm}$
$V = 667.9(3) \text{ \AA}^3$	

### Data collection

Siemens P4 diffractometer	$\theta_{\text{max}} = 26.0^\circ$
$\omega$ scans	$h = -1 \rightarrow 8$
Absorption correction: none	$k = -8 \rightarrow 8$
3436 measured reflections	$l = -18 \rightarrow 18$
2603 independent reflections	3 standard reflections
2167 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.028$	intensity decay: none

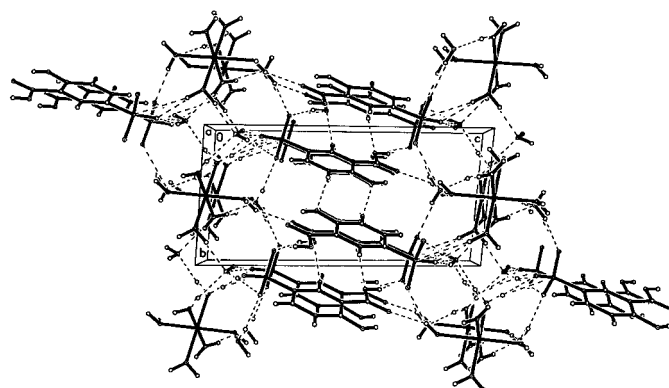
### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.118$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
2603 reflections	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
209 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.191 (11)

**Table 1**

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

C4—O6	1.349 (3)	O3—S1	1.439 (2)
C7—O5	1.226 (3)	OW1—Co1	2.051 (2)
C7—O4	1.301 (3)	OW2—Co1	2.113 (2)
O1—S1	1.459 (2)	OW3—Co1	2.085 (2)
O2—S1	1.459 (2)		
O5—C7—O4	123.7 (3)	OW1—Co1—OW3	89.27 (10)
O3—S1—O1	113.39 (15)	OW1—Co1—OW2	88.46 (9)
O3—S1—O2	112.25 (13)	OW3—Co1—OW2	90.71 (9)
O1—S1—O2	109.67 (14)		



**Figure 2**  
View of the alternating layers of cations and anions, along the  $a$  axis.

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
OW1—H1A $\cdots$ OW4 <sup>i</sup>	0.898 (18)	2.002 (19)	2.823 (3)	151 (3)
OW1—H1B $\cdots$ OW5 <sup>ii</sup>	0.872 (18)	1.917 (19)	2.780 (3)	170 (3)
OW2—H2B $\cdots$ O5 <sup>iii</sup>	0.885 (18)	2.114 (19)	2.941 (3)	155 (3)
OW2—H2A $\cdots$ OW5 <sup>iv</sup>	0.892 (18)	1.871 (19)	2.759 (3)	173 (3)
OW3—H3A $\cdots$ OW4 <sup>v</sup>	0.909 (18)	1.873 (19)	2.776 (3)	172 (3)
OW3—H3B $\cdots$ O3 <sup>ii</sup>	0.916 (18)	1.978 (19)	2.886 (3)	171 (3)
OW4—H4A $\cdots$ O3	0.893 (18)	1.992 (19)	2.847 (3)	160 (3)
OW4—H4B $\cdots$ O1 <sup>vi</sup>	0.903 (18)	1.961 (19)	2.862 (3)	174 (3)
OW5—H5A $\cdots$ O2 <sup>vii</sup>	0.868 (18)	1.911 (19)	2.735 (3)	158 (3)
OW5—H5B $\cdots$ O1	0.879 (18)	1.961 (19)	2.791 (3)	157 (3)
O4—H4 $\cdots$ O2 <sup>viii</sup>	0.82	1.88	2.652 (3)	156
O6—H6A $\cdots$ O5	0.82	1.91	2.633 (3)	146

Symmetry codes: (i)  $x, y, 1 + z$ ; (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $1 - x, 1 - y, 2 - z$ ; (iv)  $1 + x, y, 1 + z$ ; (v)  $x, 1 + y, 1 + z$ ; (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  $\text{C—H} = 0.93 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The H atoms of the carboxyl group and hydroxyl group were also positioned geometrically and refined as riding atoms, with  $\text{O—H} = 0.82 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The water H atoms were located in a difference Fourier map and refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

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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