

# Crystal structures of two new divalent transition-metal salts of carboxybenzenesulfonate anions

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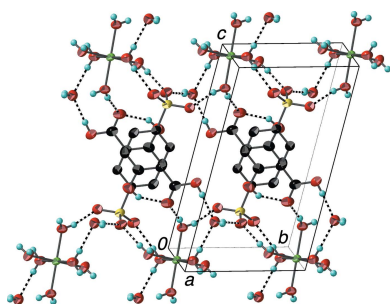
Hexaaquanickel(II) bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate,  $[\text{Ni}(\text{H}_2\text{O})_6][\text{C}_6\text{H}_3(\text{CO}_2\text{H})(\text{OH})\text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$ , (I), crystallizes in the triclinic space group  $P\bar{1}$  with the nickel(II) aqua complexes on centers of inversion. The carboxylate group is protonated and neither it nor the sulfonate group is involved in direct coordination to the metal ions. The structure consists of alternating layers of inorganic cations and organic anions linked by  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds that also include non-coordinated water molecules of crystallization. The first-row divalent transition-metal salts of this anion are reported as both dihydrates and tetrahydrates, with two distinct structures for the dihydrates that are both layered but differ in the hydrogen-bonding pattern. Compound (I) represents the second known example of one of these structures. Hexaaquacobalt(II) bis(3-carboxybenzenesulfonate) dihydrate,  $[\text{Co}(\text{H}_2\text{O})_6][\text{C}_6\text{H}_4(\text{CO}_2\text{H})\text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$ , (II), also crystallizes in triclinic  $P\bar{1}$  with the cobalt(II) aqua complexes on centers of inversion. The structure is also built of alternating layers of complex cations and organic anions without direct coordination to the metal by the protonated carboxylate or unprotonated sulfonate groups. A robust  $\text{O}-\text{H} \cdots \text{O}$  hydrogen-bonding network involving primarily the coordinated and non-coordinated water molecules and sulfonate groups directs the packing. This is the first reported example of a divalent transition-metal salt of the 3-carboxybenzenesulfonate anion.

## 1. Chemical context

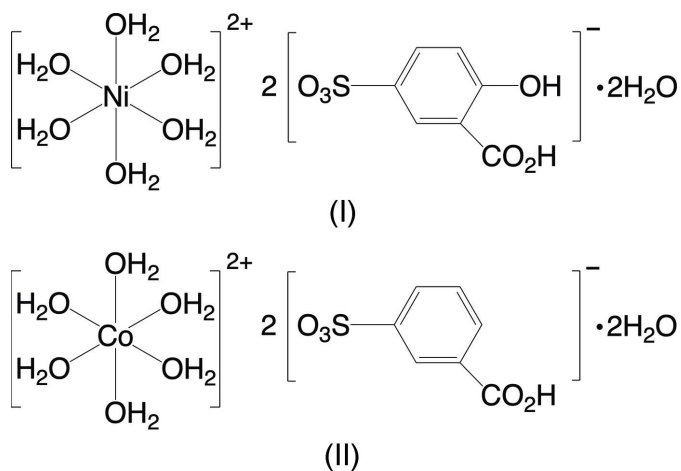
Over the past two decades, organosulfonate and organocarboxylate anions have received significant attention as building blocks for metal-organic framework (MOF) structures (Dey *et al.*, 2014; Shimizu *et al.*, 2009; Cai, 2004). As part of a longstanding interest in metal organosulfonate and mixed organosulfonate/carboxylate salts (Squattrito *et al.*, 2019), we have continued this effort with studies of other arenesulfonates with differing substitution patterns and two structures that resulted from this work are reported here.

## 2. Structural commentary

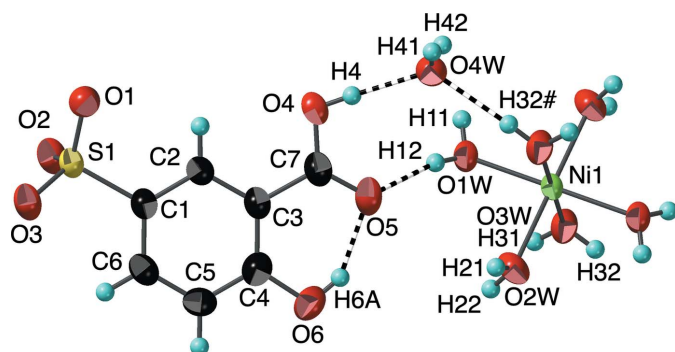
The product of the reaction of nickel nitrate hexahydrate and 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) is  $[\text{Ni}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_3(\text{CO}_2\text{H})(\text{OH})\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ , (I). The compound crystallizes in the triclinic space group  $P\bar{1}$  with the asymmetric unit consisting of half a  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cation on the center of inversion, together with one 3-carboxy-4-hydroxybenzenesulfonate anion and one non-coordinated water molecule in general positions. As a result of the symmetry, the



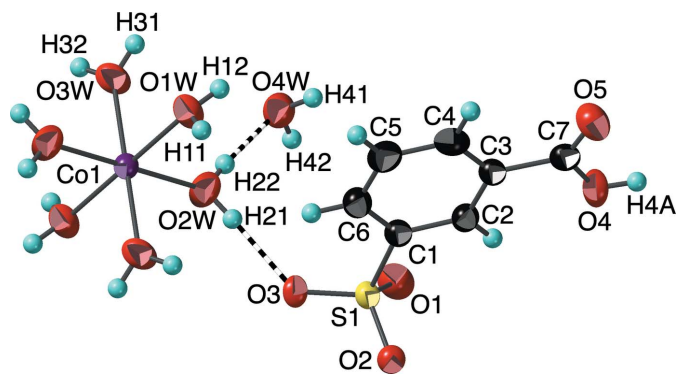
nickel ion has a very regular octahedral coordination of six water molecules (Fig. 1), with Ni–O distances [2.038 (1), 2.050 (1), 2.053 (1) Å] that are consistent with reported values (Cotton *et al.*, 1993), including the pattern of one shorter and two slightly longer distances. The O–Ni–O bond angles [87.97 (4)–91.94 (4)°] are within 2° of the ideal. The carboxylate group is protonated and only slightly rotated out of the plane of the phenyl ring [torsion angle C2–C3–C7–O4 = 5.0 (2)°]. The location of the acidic H atom on O4 is unambiguously confirmed on the difference electron-density map and is supported by the C7–O4 [1.318 (2) Å] and C7–O5 [1.236 (2) Å] distances and the hydrogen-bonding pattern (Fig. 1, Table 1). The single unique water molecule of crystallization forms four approximately linear strong O–H···O hydrogen bonds (Table 1), the two shown in Fig. 1 in which the water oxygen atom O4W is the acceptor from the carboxyl H4 and a coordinated water molecule [H32#, symmetry code: (#)  $-x + 1, -y + 2, -z$ ], and two in which the water hydrogen atoms H41 and H42 are donors to sulfonate oxygen atoms O1 and O2, respectively.



The reaction of cobalt nitrate hexahydrate and sodium 3-sulfobenzoate (3-carboxybenzenesulfonate) produced crys-



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 90% probability level and hydrogen atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as striped cylinders. Symmetry-equivalent oxygen atoms are included to show the complete coordination environment of the cation. [Symmetry code: (#)  $1 - x, 2 - y, -z$ ]



**Figure 2**  
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 90% probability level and hydrogen atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as striped cylinders. Symmetry-equivalent oxygen atoms are included to show the complete coordination environment of the cation.

tals that have been identified as  $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_4(\text{CO}_2\text{H})\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ , (II). Like (I), this compound also crystallizes in the triclinic  $P\bar{1}$  space group with the cobalt cation on the inversion center and the water molecules and 3-carboxybenzenesulfonate anion in general positions. The hexaaquacobalt(II) ion has a similarly regular octahedral coordination with Co–O distances [2.047 (1), 2.092 (1), 2.111 (1) Å] and O–Co–O angles [87.56 (4)–91.15 (4)°] consistent with prior studies (Cotton *et al.*, 1993). The carboxylate group is unambiguously protonated on O4 [C7–O4 = 1.330 (2) Å vs C7–O5 = 1.213 (2) Å] and rotated slightly out of the plane of the ring [torsion angle C2–C3–C7–O4 = 4.6 (2)°]. The sulfonate group is rotated about 19° from its position in (I) [torsion angle O1–S1–C1–C2 =  $-44.42$  (13)° in (II) vs  $-25.29$  (12)° in (I)]. Presumably this difference is driven by the hydrogen-bonding patterns. The non-coordinated water molecule has a different hydrogen-bonding environment (Table 2), functioning as an H-atom acceptor from two coordinated water molecules (H22···O4W is shown in Fig. 2) and as a donor through H41 and H42 to the carboxylate O5 and the third coordinated water molecule (O1W), respectively. These interactions are somewhat longer and less linear than those seen in (I).

### 3. Supramolecular features

The packing in (I) features layers of hexaaquanickel(II) ions in the *ab* plane alternating with layers of 3-carboxy-4-hydroxybenzenesulfonate anions stacking along the *c*-axis direction (Fig. 3). As has typically been found in related divalent transition-metal arenesulfonate systems (Leonard *et al.*, 1999), the anions are interleaved in the layer with half having the sulfonate groups directed towards the cation layer above and half towards the cation layer below. The structure also contains a non-coordinated water molecule at the interface between the cation and anion layers. The packing is dominated by an extensive network of strong (H···O *ca.* 1.8–

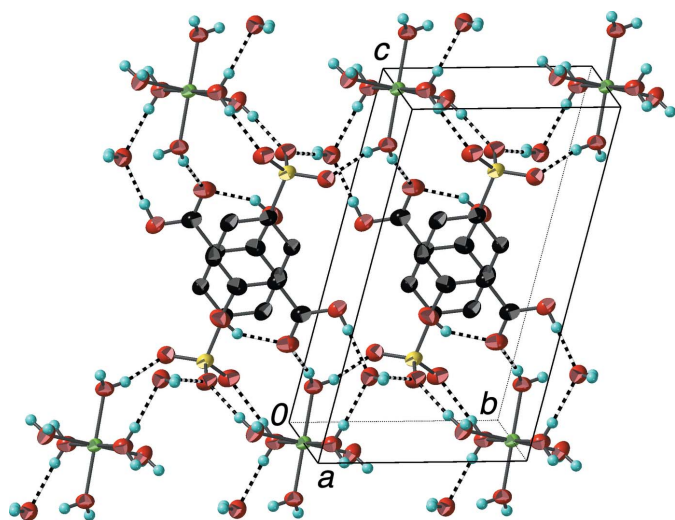
**Table 1**  
Hydrogen-bond geometry (Å, °) for (I).

<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>
O1W—H11···O1 <sup>i</sup>	0.83 (1)	1.98 (1)	2.7895 (14)	165 (2)
O1W—H12···O5	0.83 (1)	1.92 (1)	2.7432 (14)	168 (2)
O2W—H22···O2 <sup>ii</sup>	0.84 (1)	1.94 (1)	2.7802 (14)	176 (2)
O2W—H21···O3 <sup>iii</sup>	0.83 (1)	2.02 (1)	2.8476 (14)	174 (2)
O3W—H32···O4W <sup>iv</sup>	0.83 (1)	1.99 (1)	2.8208 (14)	172 (2)
O3W—H31···O3 <sup>ii</sup>	0.83 (1)	2.05 (1)	2.8790 (14)	175 (2)
O6—H6A···O5	0.84 (1)	1.84 (2)	2.5904 (16)	148 (2)
O4—H4···O4W	0.84 (1)	1.83 (1)	2.6656 (14)	171 (2)
O4W—H42···O2 <sup>i</sup>	0.83 (1)	1.91 (1)	2.7420 (14)	178 (2)
O4W—H41···O1 <sup>v</sup>	0.83 (1)	1.99 (1)	2.8029 (14)	165 (2)

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

2.0 Å) approximately linear O—H···O hydrogen bonds (Table 1, Fig. 3) involving the coordinated water molecules, non-coordinated water molecules, and sulfonate and carboxylate groups. All of the water and carboxylate H atoms participate in such an intermolecular hydrogen bond, while each of the sulfonate and unprotonated carboxylate O atoms function as hydrogen-bond acceptors. The hydroxyl group participates only in an intramolecular hydrogen bond with the adjacent carboxylate O atom (shown in Fig. 1).

A hexaaquanickel(II) salt of 3-carboxy-4-hydroxybenzenesulfonate has been reported previously (Ma *et al.*, 2003a), but unlike (I) it is a tetrahydrate with two independent non-coordinated water molecules. The extended structure is layered like (I), but differs in the incorporation of the additional water, which results in a modest expansion of the unit cell along the stacking axis *c* and changes to the triclinic cell angles. The  $[M(H_2O)_6](C_6H_3(CO_2H)(OH)SO_3)_2 \cdot 4H_2O$  structure has also been reported for cobalt (Ma *et al.*, 2003b) and zinc (Ma *et al.*, 2003c). Dihydrates of the formula



**Figure 3**  
Packing diagram of (I) with the outline of the unit cell. The alternating layers of hexaaquanickel(II) cations and 3-carboxy-4-hydroxybenzenesulfonate anions are evident. O—H···O hydrogen bonds are shown as striped cylinders. H atoms bonded to C atoms have been omitted. Displacement ellipsoids are drawn at the 90% probability level.

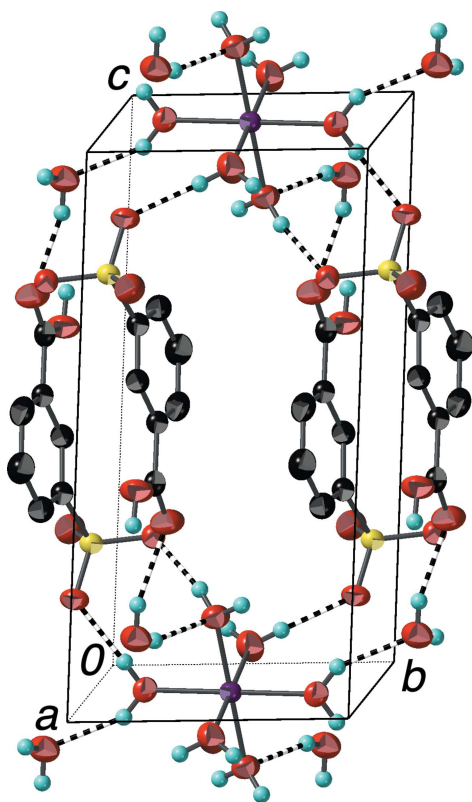
**Table 2**  
Hydrogen-bond geometry (Å, °) for (II).

<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>
O1W—H12···O2 <sup>i</sup>	0.84 (1)	1.94 (1)	2.7757 (15)	170 (2)
O1W—H11···O1 <sup>ii</sup>	0.84 (1)	1.91 (1)	2.7382 (15)	175 (2)
O3W—H32···O4W <sup>iii</sup>	0.84 (1)	2.04 (2)	2.7887 (16)	150 (2)
O3W—H31···O3 <sup>i</sup>	0.84 (1)	1.95 (1)	2.7852 (16)	178 (2)
O2W—H22···O4W	0.83 (1)	1.92 (1)	2.7516 (16)	174 (2)
O2W—H21···O3	0.83 (1)	1.96 (1)	2.7925 (15)	176 (2)
O4—H4A···O2 <sup>iv</sup>	0.84 (1)	1.86 (1)	2.6703 (15)	162 (2)
O4W—H42···O1W <sup>v</sup>	0.83 (1)	2.12 (1)	2.8960 (16)	158 (2)
O4W—H41···O5 <sup>vi</sup>	0.83 (1)	2.08 (1)	2.8503 (16)	153 (2)

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

$[M(H_2O)_6](C_6H_3(CO_2H)(OH)SO_3)_2 \cdot 2H_2O$  have been reported for manganese (Ma *et al.*, 2003d), cobalt (Abdelhak *et al.*, 2005), copper (Ma *et al.*, 2003e), and zinc (Lamshöft *et al.*, 2011). The Mn and Co compounds are isostructural, but the structure is not the same as (I). Specifically, the non-coordinated water molecule is situated differently. In (I) it acts as a hydrogen-bond acceptor from the carboxyl H atom and a coordinated water molecule, while acting as an H-atom donor to two sulfonate O atoms. In the reported Mn and Co dihydrates, the non-coordinated water molecule is a hydrogen-bond acceptor from two coordinated water molecules and an H-atom donor to the unprotonated carboxylate O atom and a coordinated water molecule. The copper dihydrate is superficially similar to the Mn and Co analogs, although the hexaaquacopper(II) cation has the expected Jahn–Teller distortion. Perhaps as a result of this, the non-coordinated water molecule has yet a different hydrogen-bonding pattern, accepting from two coordinated water molecules but donating to a sulfonate O atom and a coordinated water molecule. Of the reported dihydrates, only the Zn analog appears to have the same structure as (I) based on the space group and unit-cell dimensions. According to the deposited CIF, only a few of the water H atoms were included in the model and only a cursory description of the extended structure is provided in the paper (Lamshöft *et al.*, 2011). Thus, (I) represents the first complete structure determination of this dihydrate variant. A recent study of the zinc 3-carboxy-4-hydroxybenzenesulfonate system (Song *et al.*, 2019) demonstrates that it is possible to interconvert the dihydrate and tetrahydrate structures by exposure to different relative humidities at moderate temperatures (303 or 313 K). This suggests that the structures are close in energy, as are presumably the dihydrate structures.

The extended structure of (II) is similar to that of (I) with layers of hexaaquacobalt(II) cations in the *ab* plane alternating with layers of interleaved 3-carboxybenzenesulfonate anions (Fig. 4). Two water molecules per formula unit are found in the interface between the layers. The hydrogen-bonding network is somewhat different from that in (I) (Table 2). The non-coordinated water molecule acts as an H-atom donor to a coordinated water molecule and the unprotonated carboxylate O atom (interactions shown in Fig. 4), and as an H-atom acceptor from the other coordinated water molecules (one of which is shown in Fig. 2). Other O—H···O



**Figure 4**  
Packing diagram of (II) with the outline of the unit cell showing the alternating layers of hexaaquacobalt(II) cations and 3-carboxybenzenesulfonate anions. O—H...O hydrogen bonds are shown as striped cylinders. H atoms bonded to C atoms have been omitted. Displacement ellipsoids are drawn at the 90% probability level.

interactions between the coordinated water molecules, the carboxylate H atom, and the sulfonate O atoms complete the hydrogen-bonding scheme. This is the first reported structure of a divalent *d*-block transition-metal salt of 3-carboxybenzenesulfonate, so it represents a new member of the metal arenesulfonate family of layered compounds.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of November 2020; Groom *et al.*, 2016) for the COOH-protonated 3-carboxy-4-hydroxybenzenesulfonate ion yielded 21 hits. The ten reported structures containing only metal ions and 3-carboxybenzenesulfonate ions, with or without water molecules, are triaqua(3-carboxy-4-hydroxybenzenesulfonato)silver monohydrate (refcode FETHES; Gao *et al.*, 2005a), pentaqua-oxo-vanadium(IV) 3-carboxy-4-hydroxybenzenesulfonate dihydrate (refcode OBUZUH; Li *et al.*, 2004), hexaaquamanganese(II) 3-carboxy-4-hydroxybenzenesulfonate dihydrate (refcode KAGMOV; Ma *et al.*, 2003d), hexaaquacobalt(II) 3-carboxy-4-hydroxybenzenesulfonate dihydrate (refcode SAYVEU; Abdelhak *et al.*, 2005), hexaaquacobalt(II) 3-carboxy-4-hydroxybenzenesulfonate tetrahydrate (refcode KAGMUB; Ma *et al.*, 2003b), hexaaquanickel(II) 3-carboxy-4-hydroxybenz-

enesulfonate tetrahydrate (refcode KAGNAI; Ma *et al.*, 2003a), hexaaquacobalt(II) 3-carboxy-4-hydroxybenzenesulfonate dihydrate (refcode KAGNEM; Ma *et al.*, 2003e), hexaaquazinc(II) 3-carboxy-4-hydroxybenzenesulfonate tetrahydrate (refcode KAGNIQ; Ma *et al.*, 2003c), hexaaquazinc(II) 3-carboxy-4-hydroxybenzenesulfonate dihydrate (refcode FARFOV; Lamshöft *et al.*, 2011), and bis(3-carboxy-4-hydroxybenzenesulfonato)diaquazinc(II) hydrate (refcode VOJYEB; Song *et al.*, 2019). Of these structures, only FETHES and VOJYEB feature direct bonding between the sulfonate O atoms and the metal ions, while all of the others are similar to the structures reported herein.

A search of the Cambridge Structural Database (CSD, Version 5.42, update of November 2020; Groom *et al.*, 2016) for the COOH-protonated 3-carboxybenzenesulfonate ion yielded 15 hits. The five reported structures containing only metal ions and 3-carboxybenzenesulfonate ions, with or without water molecules, are silver 3-carboxybenzenesulfonate at 293 K (refcode ROJJUW; Prochniak *et al.*, 2008) and 100 K (refcode ROJJUW01; Bettinger *et al.*, 2020), sodium 3-carboxybenzenesulfonate dihydrate (refcode ROJJOQ; Prochniak *et al.*, 2008), bismuth(III) 3-carboxybenzenesulfonate tetrahydrate (refcode LEXKAD; Senevirathna *et al.*, 2018), and barium 3-carboxybenzenesulfonate trihydrate (refcode FOBXUQ; Gao *et al.*, 2005b). All of these structures feature direct bonding between the sulfonate O atoms and the metal ions with resulting frameworks of varying dimensionalities.

#### 5. Synthesis and crystallization

A 2.54 g (10.0 mmol) sample of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) (EMD Chemicals, >99%) was dissolved in 100 ml of water. To this colorless solution was added a green solution of 2.91 g (10.0 mmol) of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich) in 50 ml of water. The resulting clear green solution was stirred for about 30 minutes and transferred to a porcelain evaporating dish that was set out to evaporate in a fume hood. After several days, the water had completely evaporated leaving behind large elongated (>1 cm) green slab-shaped crystals, 2.57 g of which were collected by hand from the dish. These were identified as (I) through the single-crystal X-ray study. A 2.24 g (10.0 mmol) sample of sodium 3-sulfobenzoate (Aldrich, 97%) was dissolved in 45 ml of water. To this colorless solution was added a red solution of 2.91 g (10.0 mmol) of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich) in 50 ml of water. The resulting red solution was stirred for 30 minutes, transferred to a porcelain dish, and set out to evaporate. The final red product was primarily polycrystalline but some small red-pink plates were found to be suitable for single-crystal X-ray analysis, leading to their identification as (II).

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms bonded to carbon

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	[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> ·2H <sub>2</sub> O	[Co(H <sub>2</sub> O) <sub>6</sub> ](C <sub>7</sub> H <sub>5</sub> O <sub>5</sub> S) <sub>2</sub> ·2H <sub>2</sub> O
<i>M<sub>r</sub></i>	637.18	605.40
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.5986 (7), 7.4183 (8), 13.2847 (14)	6.7774 (11), 6.9866 (11), 13.721 (2)
$\alpha$ , $\beta$ , $\gamma$ (°)	74.1712 (14), 88.6035 (14), 77.9200 (13)	91.107 (2), 90.401 (2), 117.5832 (19)
<i>V</i> (Å <sup>3</sup> )	611.41 (11)	575.66 (16)
<i>Z</i>	1	1
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.06	1.01
Crystal size (mm)	0.22 × 0.16 × 0.10	0.30 × 0.14 × 0.08
Data collection		
Diffractometer	Bruker Duo with APEXII CCD	Bruker Duo with APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.670, 0.746	0.688, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	8656, 3047, 2779	8197, 2881, 2578
<i>R</i> <sub>int</sub>	0.019	0.020
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.669	0.669
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.023, 0.059, 1.08	0.024, 0.062, 1.05
No. of reflections	3047	2881
No. of parameters	209	196
No. of restraints	10	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.33, -0.41	0.41, -0.43

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), and *CrystalMaker* (Palmer, 2014).

atoms were located in difference electron-density maps, constrained on idealized positions, and included in the refinement as riding atoms with C–H = 0.95 Å and their *U*<sub>iso</sub> constrained to be 1.2 times the *U*<sub>eq</sub> of the bonding atom. Oxygen-bound hydrogen atoms were located in difference electron-density maps and refined with isotropic displacement parameters while the O–H distances were restrained to 0.84 (1) Å.

## References

- Abdelhak, J., Namouchi Cherni, S. & Jouini, T. (2005). *Z. Kristallogr.* **220**, 183–184.
- Bettinger, R. T., Squattrito, P. J. & Aulakh, D. (2020). *Acta Cryst.* **E76**, 1275–1278.
- Bruker (2015). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cai, J. (2004). *Coord. Chem. Rev.* **248**, 1061–1083.
- Cotton, F. A., Daniels, L. M., Murillo, C. A. & Quesada, J. F. (1993). *Inorg. Chem.* **32**, 4861–4867.
- Dey, C., Kundu, T., Biswal, B. P., Mallick, A. & Banerjee, R. (2014). *Acta Cryst.* **B70**, 3–10.
- Gao, S., Zhu, Z.-B., Huo, L.-H. & Ng, S. W. (2005a). *Acta Cryst.* **E61**, m279–m281.
- Gao, S., Zhu, Z.-B., Huo, L.-H. & Ng, S. W. (2005b). *Acta Cryst.* **E61**, m517–m518.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Lamshöft, M., Storp, J., Ivanova, B. & Spittler, M. (2011). *Polyhedron*, **30**, 2564–2573.
- Leonard, M. A., Squattrito, P. J. & Dubey, S. N. (1999). *Acta Cryst.* **C55**, 35–39.
- Li, L.-Z., Xu, T., Wang, D.-Q. & Niu, M.-J. (2004). *Acta Cryst.* **E60**, m1374–m1375.
- Ma, J.-F., Yang, J. & Liu, J.-F. (2003a). *Acta Cryst.* **E59**, m483–m484.
- Ma, J.-F., Yang, J. & Liu, J.-F. (2003b). *Acta Cryst.* **E59**, m481–m482.
- Ma, J.-F., Yang, J. & Liu, J.-F. (2003c). *Acta Cryst.* **E59**, m487–m488.
- Ma, J.-F., Yang, J. & Liu, J.-F. (2003d). *Acta Cryst.* **E59**, m478–m480.
- Ma, J.-F., Yang, J. & Liu, J.-F. (2003e). *Acta Cryst.* **E59**, m485–m486.
- Palmer, D. (2014). *CrystalMaker*. CrystalMaker Software Ltd, Yarnton, England.
- Prochniak, G., Videnova-Adrabinska, V., Daszkiewicz, M. & Pietraszko, A. (2008). *J. Mol. Struct.* **891**, 178–183.
- Senevirathna, D. C., Werrett, M. V., Blair, V. L., Mehring, M. & Andrews, P. C. (2018). *Chem. Eur. J.* **24**, 6722–6726.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shimizu, G. K. H., Vaidyanathan, R. & Taylor, J. M. (2009). *Chem. Soc. Rev.* **38**, 1430–1449.
- Song, J. H., Kim, D. W., Kang, D. W., Lee, W. R. & Hong, C. S. (2019). *Chem. Commun.* **55**, 9713–9716.
- Squattrito, P. J., Lambright-Mutthamsetty, K. J., Giolando, P. A. & Kirschbaum, K. (2019). *Acta Cryst.* **E75**, 1801–1807.

## supporting information

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## Crystal structures of two new divalent transition-metal salts of carboxybenzenesulfonate anions

Reuben T. Bettinger, Philip J. Squattrito, Darpandeeep Aulakh and Christopher G. Gianopoulos

### Computing details

For both structures, data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *CrystalMaker* (Palmer, 2014).

(I)

#### Crystal data



$M_r = 637.18$

Triclinic,  $P\bar{1}$

$a = 6.5986$  (7) Å

$b = 7.4183$  (8) Å

$c = 13.2847$  (14) Å

$\alpha = 74.1712$  (14)°

$\beta = 88.6035$  (14)°

$\gamma = 77.9200$  (13)°

$V = 611.41$  (11) Å<sup>3</sup>

$Z = 1$

$F(000) = 330$

$D_x = 1.731$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4943 reflections

$\theta = 2.9$ – $28.3$ °

$\mu = 1.06$  mm<sup>-1</sup>

$T = 150$  K

Block, green

$0.22 \times 0.16 \times 0.10$  mm

#### Data collection

Bruker Duo with APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Krause et al., 2015)

$T_{\min} = 0.670$ ,  $T_{\max} = 0.746$

8656 measured reflections

3047 independent reflections

2779 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 28.4$ °,  $\theta_{\min} = 2.9$ °

$h = -8$ → $8$

$k = -9$ → $9$

$l = -17$ → $17$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.059$

$S = 1.08$

3047 reflections

209 parameters

10 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 0.2223P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.33$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.41$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.500000	1.000000	0.000000	0.01105 (7)
O1W	0.40237 (15)	0.99422 (14)	0.14733 (7)	0.0161 (2)
H11	0.342 (3)	1.095 (2)	0.1600 (16)	0.039 (6)*
H12	0.488 (3)	0.939 (3)	0.1966 (12)	0.041 (6)*
O2W	0.66270 (15)	0.72230 (14)	0.05040 (8)	0.0171 (2)
H22	0.596 (3)	0.642 (3)	0.0846 (16)	0.048 (6)*
H21	0.7789 (19)	0.701 (3)	0.0795 (15)	0.037 (6)*
O3W	0.23500 (15)	0.91381 (15)	-0.02663 (8)	0.0168 (2)
H32	0.220 (3)	0.884 (3)	-0.0816 (11)	0.037 (6)*
H31	0.182 (3)	0.840 (2)	0.0200 (12)	0.033 (5)*
S1	0.78200 (5)	0.52327 (5)	0.79824 (2)	0.01278 (8)
O1	0.84194 (15)	0.70694 (14)	0.78658 (8)	0.0177 (2)
O2	0.56747 (14)	0.52970 (14)	0.83170 (8)	0.0176 (2)
O3	0.92577 (15)	0.35961 (14)	0.86440 (8)	0.0181 (2)
O6	0.73062 (17)	0.39614 (16)	0.38141 (8)	0.0211 (2)
H6A	0.704 (4)	0.503 (2)	0.3355 (14)	0.051 (7)*
O5	0.68377 (16)	0.76283 (15)	0.30157 (8)	0.0204 (2)
O4	0.72336 (17)	0.94807 (15)	0.40456 (8)	0.0213 (2)
H4	0.727 (3)	1.025 (3)	0.3454 (10)	0.042 (6)*
C1	0.78448 (19)	0.48905 (19)	0.67154 (10)	0.0135 (2)
C6	0.8006 (2)	0.30381 (19)	0.66125 (11)	0.0159 (3)
H6	0.823672	0.197124	0.721651	0.019*
C5	0.7830 (2)	0.2757 (2)	0.56350 (11)	0.0171 (3)
H5	0.793317	0.149826	0.556807	0.021*
C4	0.7498 (2)	0.4327 (2)	0.47420 (11)	0.0159 (3)
C3	0.7387 (2)	0.61877 (19)	0.48438 (10)	0.0141 (3)
C7	0.7129 (2)	0.7820 (2)	0.38932 (11)	0.0160 (3)
C2	0.7559 (2)	0.64496 (19)	0.58405 (10)	0.0140 (2)
H2	0.747996	0.769976	0.591539	0.017*
O4W	0.77781 (16)	1.17956 (14)	0.21815 (8)	0.0167 (2)
H42	0.674 (2)	1.269 (2)	0.2040 (16)	0.035 (6)*
H41	0.879 (2)	1.230 (3)	0.2199 (17)	0.039 (6)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.01121 (12)	0.01190 (12)	0.00927 (12)	-0.00301 (8)	-0.00053 (8)	-0.00113 (8)
O1W	0.0184 (5)	0.0172 (5)	0.0110 (4)	-0.0021 (4)	-0.0004 (4)	-0.0025 (4)
O2W	0.0140 (5)	0.0145 (5)	0.0199 (5)	-0.0035 (4)	-0.0020 (4)	0.0005 (4)

O3W	0.0168 (5)	0.0226 (5)	0.0129 (5)	-0.0095 (4)	0.0003 (4)	-0.0043 (4)
S1	0.01103 (15)	0.01454 (16)	0.01148 (15)	-0.00312 (11)	0.00037 (11)	-0.00112 (12)
O1	0.0193 (5)	0.0183 (5)	0.0175 (5)	-0.0079 (4)	0.0035 (4)	-0.0054 (4)
O2	0.0122 (4)	0.0205 (5)	0.0172 (5)	-0.0030 (4)	0.0032 (4)	-0.0009 (4)
O3	0.0150 (5)	0.0208 (5)	0.0147 (5)	-0.0010 (4)	-0.0024 (4)	0.0001 (4)
O6	0.0239 (5)	0.0249 (6)	0.0174 (5)	-0.0068 (4)	-0.0005 (4)	-0.0093 (4)
O5	0.0211 (5)	0.0251 (5)	0.0132 (5)	-0.0040 (4)	-0.0028 (4)	-0.0024 (4)
O4	0.0306 (6)	0.0159 (5)	0.0142 (5)	-0.0040 (4)	-0.0003 (4)	0.0007 (4)
C1	0.0103 (6)	0.0161 (6)	0.0132 (6)	-0.0030 (5)	-0.0002 (4)	-0.0021 (5)
C6	0.0130 (6)	0.0153 (6)	0.0174 (6)	-0.0038 (5)	0.0008 (5)	-0.0005 (5)
C5	0.0157 (6)	0.0154 (6)	0.0215 (7)	-0.0050 (5)	0.0015 (5)	-0.0058 (5)
C4	0.0101 (6)	0.0219 (7)	0.0166 (6)	-0.0042 (5)	0.0004 (5)	-0.0062 (5)
C3	0.0104 (6)	0.0169 (6)	0.0134 (6)	-0.0027 (5)	0.0002 (5)	-0.0015 (5)
C7	0.0112 (6)	0.0192 (7)	0.0149 (6)	-0.0012 (5)	0.0001 (5)	-0.0014 (5)
C2	0.0124 (6)	0.0141 (6)	0.0145 (6)	-0.0029 (5)	0.0004 (5)	-0.0024 (5)
O4W	0.0160 (5)	0.0164 (5)	0.0178 (5)	-0.0044 (4)	-0.0009 (4)	-0.0039 (4)

*Geometric parameters (Å, °)*

Ni1—O1W <sup>i</sup>	2.0376 (10)	O6—H6A	0.843 (10)
Ni1—O1W	2.0376 (10)	O5—C7	1.2364 (17)
Ni1—O2W <sup>i</sup>	2.0498 (10)	O4—C7	1.3179 (18)
Ni1—O2W	2.0498 (10)	O4—H4	0.839 (9)
Ni1—O3W	2.0526 (10)	C1—C2	1.3821 (18)
Ni1—O3W <sup>i</sup>	2.0526 (10)	C1—C6	1.3996 (19)
O1W—H11	0.829 (9)	C6—C5	1.3816 (19)
O1W—H12	0.832 (10)	C6—H6	0.9500
O2W—H22	0.838 (10)	C5—C4	1.4016 (19)
O2W—H21	0.832 (9)	C5—H5	0.9500
O3W—H32	0.833 (9)	C4—C3	1.4098 (19)
O3W—H31	0.831 (9)	C3—C2	1.4003 (18)
S1—O3	1.4570 (10)	C3—C7	1.4762 (19)
S1—O1	1.4644 (10)	C2—H2	0.9500
S1—O2	1.4685 (10)	O4W—H42	0.832 (9)
S1—C1	1.7685 (14)	O4W—H41	0.834 (10)
O6—C4	1.3466 (17)		
O1W <sup>i</sup> —Ni1—O1W	180.0	O3—S1—C1	106.97 (6)
O1W <sup>i</sup> —Ni1—O2W <sup>i</sup>	91.26 (4)	O1—S1—C1	106.29 (6)
O1W—Ni1—O2W <sup>i</sup>	88.74 (4)	O2—S1—C1	105.69 (6)
O1W <sup>i</sup> —Ni1—O2W	88.74 (4)	C4—O6—H6A	107.2 (16)
O1W—Ni1—O2W	91.26 (4)	C7—O4—H4	107.2 (15)
O2W <sup>i</sup> —Ni1—O2W	180.0	C2—C1—C6	120.45 (12)
O1W <sup>i</sup> —Ni1—O3W	92.03 (4)	C2—C1—S1	120.22 (10)
O1W—Ni1—O3W	87.97 (4)	C6—C1—S1	119.17 (10)
O2W <sup>i</sup> —Ni1—O3W	88.06 (4)	C5—C6—C1	120.19 (12)
O2W—Ni1—O3W	91.94 (4)	C5—C6—H6	119.9
O1W <sup>i</sup> —Ni1—O3W <sup>i</sup>	87.97 (4)	C1—C6—H6	119.9



O1W—Ni1—O3W <sup>i</sup>	92.03 (4)	C6—C5—C4	120.03 (13)
O2W <sup>i</sup> —Ni1—O3W <sup>i</sup>	91.94 (4)	C6—C5—H5	120.0
O2W—Ni1—O3W <sup>i</sup>	88.06 (4)	C4—C5—H5	120.0
O3W—Ni1—O3W <sup>i</sup>	180.0	O6—C4—C5	117.16 (13)
Ni1—O1W—H11	119.4 (15)	O6—C4—C3	123.10 (12)
Ni1—O1W—H12	117.2 (15)	C5—C4—C3	119.74 (12)
H11—O1W—H12	106 (2)	C2—C3—C4	119.51 (12)
Ni1—O2W—H22	116.1 (16)	C2—C3—C7	121.27 (12)
Ni1—O2W—H21	118.9 (15)	C4—C3—C7	119.21 (12)
H22—O2W—H21	109 (2)	O5—C7—O4	122.61 (13)
Ni1—O3W—H32	119.8 (15)	O5—C7—C3	121.89 (13)
Ni1—O3W—H31	122.3 (14)	O4—C7—C3	115.49 (12)
H32—O3W—H31	106 (2)	C1—C2—C3	120.05 (12)
O3—S1—O1	113.84 (6)	C1—C2—H2	120.0
O3—S1—O2	111.87 (6)	C3—C2—H2	120.0
O1—S1—O2	111.57 (6)	H42—O4W—H41	106 (2)
O3—S1—C1—C2	-147.25 (11)	C5—C4—C3—C2	-1.56 (19)
O1—S1—C1—C2	-25.29 (12)	O6—C4—C3—C7	-2.41 (19)
O2—S1—C1—C2	93.39 (11)	C5—C4—C3—C7	177.36 (12)
O3—S1—C1—C6	37.34 (12)	C2—C3—C7—O5	-175.12 (12)
O1—S1—C1—C6	159.30 (10)	C4—C3—C7—O5	5.97 (19)
O2—S1—C1—C6	-82.02 (11)	C2—C3—C7—O4	5.01 (18)
C2—C1—C6—C5	-1.6 (2)	C4—C3—C7—O4	-173.89 (12)
S1—C1—C6—C5	173.82 (10)	C6—C1—C2—C3	1.29 (19)
C1—C6—C5—C4	0.3 (2)	S1—C1—C2—C3	-174.06 (10)
C6—C5—C4—O6	-178.94 (12)	C4—C3—C2—C1	0.28 (19)
C6—C5—C4—C3	1.3 (2)	C7—C3—C2—C1	-178.62 (12)
O6—C4—C3—C2	178.67 (12)		

Symmetry code: (i)  $-x+1, -y+2, -z$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H11 $\cdots$ O1 <sup>ii</sup>	0.83 (1)	1.98 (1)	2.7895 (14)	165 (2)
O1W—H12 $\cdots$ O5	0.83 (1)	1.92 (1)	2.7432 (14)	168 (2)
O2W—H22 $\cdots$ O2 <sup>iii</sup>	0.84 (1)	1.94 (1)	2.7802 (14)	176 (2)
O2W—H21 $\cdots$ O3 <sup>iv</sup>	0.83 (1)	2.02 (1)	2.8476 (14)	174 (2)
O3W—H32 $\cdots$ O4W <sup>i</sup>	0.83 (1)	1.99 (1)	2.8208 (14)	172 (2)
O3W—H31 $\cdots$ O3 <sup>iii</sup>	0.83 (1)	2.05 (1)	2.8790 (14)	175 (2)
O6—H6A $\cdots$ O5	0.84 (1)	1.84 (2)	2.5904 (16)	148 (2)
O4—H4 $\cdots$ O4W	0.84 (1)	1.83 (1)	2.6656 (14)	171 (2)
O4W—H42 $\cdots$ O2 <sup>ii</sup>	0.83 (1)	1.91 (1)	2.7420 (14)	178 (2)
O4W—H41 $\cdots$ O1 <sup>v</sup>	0.83 (1)	1.99 (1)	2.8029 (14)	165 (2)

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

(II)

*Crystal data*[Co(H<sub>2</sub>O)<sub>6</sub>](C<sub>7</sub>H<sub>5</sub>O<sub>5</sub>S)<sub>2</sub>·2H<sub>2</sub>O $M_r = 605.40$ Triclinic,  $P\bar{1}$  $a = 6.7774$  (11) Å $b = 6.9866$  (11) Å $c = 13.721$  (2) Å $\alpha = 91.107$  (2)° $\beta = 90.401$  (2)° $\gamma = 117.5832$  (19)° $V = 575.66$  (16) Å<sup>3</sup> $Z = 1$  $F(000) = 313$  $D_x = 1.746$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4422 reflections

 $\theta = 3.0$ – $28.3$ ° $\mu = 1.01$  mm<sup>-1</sup> $T = 150$  K

Plate, red-pink

 $0.30 \times 0.14 \times 0.08$  mm*Data collection*Bruker Duo with APEXII CCD  
diffractometer

Radiation source: fine focus sealed tube

 $\omega$  scansAbsorption correction: multi-scan  
(SADABS; Krause et al., 2015) $T_{\min} = 0.688$ ,  $T_{\max} = 0.746$ 

8197 measured reflections

2881 independent reflections

2578 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.020$  $\theta_{\max} = 28.4$ °,  $\theta_{\min} = 3.0$ ° $h = -9 \rightarrow 9$  $k = -9 \rightarrow 9$  $l = -18 \rightarrow 18$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.024$  $wR(F^2) = 0.062$  $S = 1.05$ 

2881 reflections

196 parameters

9 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 0.2552P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.41$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.43$  e Å<sup>-3</sup>*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.500000	0.500000	0.000000	0.01139 (8)
O1W	0.59207 (18)	0.45162 (17)	0.14109 (8)	0.0168 (2)
H12	0.490 (3)	0.376 (3)	0.1797 (14)	0.049 (7)*
H11	0.691 (3)	0.558 (2)	0.1710 (14)	0.033 (6)*
O3W	0.3051 (2)	0.16486 (17)	-0.01333 (8)	0.0224 (2)
H32	0.273 (4)	0.088 (3)	-0.0641 (12)	0.051 (7)*
H31	0.290 (4)	0.086 (3)	0.0345 (11)	0.035 (6)*
O2W	0.22949 (19)	0.52152 (18)	0.05338 (8)	0.0205 (2)

H22	0.113 (3)	0.421 (3)	0.0736 (17)	0.051 (7)*
H21	0.239 (4)	0.632 (2)	0.0817 (15)	0.040 (6)*
S1	0.15442 (6)	0.93233 (5)	0.23000 (2)	0.01271 (8)
O1	-0.08728 (17)	0.81710 (17)	0.23196 (8)	0.0193 (2)
O3	0.25157 (19)	0.89453 (17)	0.14174 (7)	0.0200 (2)
O4	-0.04855 (19)	0.77393 (18)	0.59079 (8)	0.0204 (2)
H4A	-0.102 (4)	0.773 (4)	0.6461 (10)	0.049 (7)*
O5	0.19717 (19)	0.69905 (18)	0.67033 (8)	0.0230 (2)
O2	0.23686 (17)	1.16534 (16)	0.24926 (7)	0.0157 (2)
C2	0.1502 (2)	0.8151 (2)	0.41772 (10)	0.0135 (3)
H2	0.026154	0.842780	0.423772	0.016*
C5	0.5099 (2)	0.7283 (2)	0.39875 (11)	0.0183 (3)
H5	0.631065	0.696301	0.392134	0.022*
C6	0.4323 (2)	0.7927 (2)	0.31792 (11)	0.0165 (3)
H6	0.500627	0.806287	0.256469	0.020*
C3	0.2302 (2)	0.7524 (2)	0.49829 (10)	0.0138 (3)
C7	0.1271 (2)	0.7374 (2)	0.59558 (10)	0.0156 (3)
C1	0.2530 (2)	0.8369 (2)	0.32839 (10)	0.0132 (3)
C4	0.4119 (2)	0.7104 (2)	0.48891 (11)	0.0171 (3)
H4	0.468088	0.669793	0.544051	0.020*
O4W	-0.15844 (19)	0.20955 (18)	0.12941 (8)	0.0191 (2)
H42	-0.242 (3)	0.263 (3)	0.1173 (16)	0.037 (6)*
H41	-0.145 (4)	0.214 (4)	0.1900 (7)	0.045 (7)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.01209 (13)	0.01120 (13)	0.01100 (13)	0.00549 (10)	0.00119 (9)	0.00036 (9)
O1W	0.0156 (5)	0.0169 (5)	0.0132 (5)	0.0035 (4)	0.0007 (4)	0.0009 (4)
O3W	0.0337 (6)	0.0126 (5)	0.0138 (5)	0.0046 (5)	0.0004 (5)	0.0003 (4)
O2W	0.0180 (5)	0.0178 (5)	0.0261 (6)	0.0086 (5)	0.0071 (4)	-0.0011 (5)
S1	0.01491 (17)	0.01270 (16)	0.01041 (16)	0.00627 (13)	0.00180 (12)	0.00044 (12)
O1	0.0148 (5)	0.0194 (5)	0.0195 (5)	0.0046 (4)	-0.0025 (4)	0.0004 (4)
O3	0.0318 (6)	0.0214 (5)	0.0121 (5)	0.0167 (5)	0.0064 (4)	0.0020 (4)
O4	0.0242 (6)	0.0270 (6)	0.0142 (5)	0.0153 (5)	0.0057 (4)	0.0015 (4)
O5	0.0289 (6)	0.0270 (6)	0.0138 (5)	0.0135 (5)	0.0004 (4)	0.0033 (4)
O2	0.0182 (5)	0.0132 (5)	0.0157 (5)	0.0072 (4)	0.0040 (4)	0.0011 (4)
C2	0.0129 (6)	0.0123 (6)	0.0144 (7)	0.0052 (5)	0.0017 (5)	-0.0002 (5)
C5	0.0150 (7)	0.0176 (7)	0.0244 (8)	0.0093 (6)	0.0029 (6)	0.0021 (6)
C6	0.0160 (7)	0.0151 (7)	0.0177 (7)	0.0067 (6)	0.0044 (5)	0.0015 (5)
C3	0.0162 (7)	0.0107 (6)	0.0128 (6)	0.0048 (5)	0.0018 (5)	0.0004 (5)
C7	0.0184 (7)	0.0102 (6)	0.0156 (7)	0.0046 (5)	0.0010 (5)	0.0000 (5)
C1	0.0140 (6)	0.0113 (6)	0.0129 (6)	0.0047 (5)	0.0010 (5)	0.0002 (5)
C4	0.0178 (7)	0.0140 (7)	0.0194 (7)	0.0073 (6)	-0.0014 (5)	0.0022 (5)
O4W	0.0223 (6)	0.0231 (5)	0.0152 (5)	0.0134 (5)	-0.0012 (4)	-0.0005 (4)

## Geometric parameters (Å, °)

Co1—O2W	2.0470 (11)	O4—C7	1.3298 (18)
Co1—O2W <sup>i</sup>	2.0470 (11)	O4—H4A	0.841 (10)
Co1—O3W	2.0921 (11)	O5—C7	1.2126 (18)
Co1—O3W <sup>i</sup>	2.0921 (11)	C2—C1	1.3898 (19)
Co1—O1W	2.1107 (11)	C2—C3	1.3921 (19)
Co1—O1W <sup>i</sup>	2.1107 (11)	C2—H2	0.9500
O1W—H12	0.844 (10)	C5—C4	1.389 (2)
O1W—H11	0.835 (9)	C5—C6	1.393 (2)
O3W—H32	0.836 (10)	C5—H5	0.9500
O3W—H31	0.839 (9)	C6—C1	1.393 (2)
O2W—H22	0.832 (10)	C6—H6	0.9500
O2W—H21	0.830 (10)	C3—C4	1.398 (2)
S1—O1	1.4534 (11)	C3—C7	1.494 (2)
S1—O3	1.4594 (11)	C4—H4	0.9500
S1—O2	1.4735 (10)	O4W—H42	0.827 (10)
S1—C1	1.7742 (14)	O4W—H41	0.834 (10)
O2W—Co1—O2W <sup>i</sup>	180.0	O1—S1—C1	106.70 (7)
O2W—Co1—O3W	88.95 (5)	O3—S1—C1	106.69 (7)
O2W <sup>i</sup> —Co1—O3W	91.05 (5)	O2—S1—C1	106.26 (6)
O2W—Co1—O3W <sup>i</sup>	91.05 (5)	C7—O4—H4A	112.1 (17)
O2W <sup>i</sup> —Co1—O3W <sup>i</sup>	88.95 (5)	C1—C2—C3	119.60 (13)
O3W—Co1—O3W <sup>i</sup>	180.0	C1—C2—H2	120.2
O2W—Co1—O1W	91.15 (4)	C3—C2—H2	120.2
O2W <sup>i</sup> —Co1—O1W	88.85 (4)	C4—C5—C6	120.60 (13)
O3W—Co1—O1W	87.56 (4)	C4—C5—H5	119.7
O3W <sup>i</sup> —Co1—O1W	92.44 (4)	C6—C5—H5	119.7
O2W—Co1—O1W <sup>i</sup>	88.85 (4)	C5—C6—C1	119.12 (13)
O2W <sup>i</sup> —Co1—O1W <sup>i</sup>	91.15 (4)	C5—C6—H6	120.4
O3W—Co1—O1W <sup>i</sup>	92.44 (4)	C1—C6—H6	120.4
O3W <sup>i</sup> —Co1—O1W <sup>i</sup>	87.56 (4)	C2—C3—C4	120.01 (13)
O1W—Co1—O1W <sup>i</sup>	180.0	C2—C3—C7	120.06 (13)
Co1—O1W—H12	118.4 (17)	C4—C3—C7	119.90 (13)
Co1—O1W—H11	117.6 (15)	O5—C7—O4	123.99 (14)
H12—O1W—H11	110 (2)	O5—C7—C3	123.95 (14)
Co1—O3W—H32	127.8 (18)	O4—C7—C3	112.06 (12)
Co1—O3W—H31	120.3 (15)	C2—C1—C6	120.86 (13)
H32—O3W—H31	108 (2)	C2—C1—S1	117.65 (11)
Co1—O2W—H22	127.0 (17)	C6—C1—S1	121.45 (11)
Co1—O2W—H21	122.7 (16)	C5—C4—C3	119.79 (13)
H22—O2W—H21	105 (2)	C5—C4—H4	120.1
O1—S1—O3	114.70 (7)	C3—C4—H4	120.1
O1—S1—O2	111.06 (6)	H42—O4W—H41	106 (2)
O3—S1—O2	110.90 (6)		
C4—C5—C6—C1	-0.7 (2)	C5—C6—C1—S1	176.87 (11)

C1—C2—C3—C4	-0.4 (2)	O1—S1—C1—C2	-44.42 (13)
C1—C2—C3—C7	177.42 (12)	O3—S1—C1—C2	-167.47 (11)
C2—C3—C7—O5	-174.55 (14)	O2—S1—C1—C2	74.15 (12)
C4—C3—C7—O5	3.3 (2)	O1—S1—C1—C6	137.89 (12)
C2—C3—C7—O4	4.61 (19)	O3—S1—C1—C6	14.84 (14)
C4—C3—C7—O4	-177.56 (13)	O2—S1—C1—C6	-103.54 (12)
C3—C2—C1—C6	1.3 (2)	C6—C5—C4—C3	1.5 (2)
C3—C2—C1—S1	-176.42 (10)	C2—C3—C4—C5	-1.0 (2)
C5—C6—C1—C2	-0.7 (2)	C7—C3—C4—C5	-178.82 (13)

Symmetry code: (i)  $-x+1, -y+1, -z$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1 <i>W</i> —H12 $\cdots$ O2 <sup>ii</sup>	0.84 (1)	1.94 (1)	2.7757 (15)	170 (2)
O1 <i>W</i> —H11 $\cdots$ O1 <sup>iii</sup>	0.84 (1)	1.91 (1)	2.7382 (15)	175 (2)
O3 <i>W</i> —H32 $\cdots$ O4 <i>W</i> <sup>iv</sup>	0.84 (1)	2.04 (2)	2.7887 (16)	150 (2)
O3 <i>W</i> —H31 $\cdots$ O3 <sup>iii</sup>	0.84 (1)	1.95 (1)	2.7852 (16)	178 (2)
O2 <i>W</i> —H22 $\cdots$ O4 <i>W</i>	0.83 (1)	1.92 (1)	2.7516 (16)	174 (2)
O2 <i>W</i> —H21 $\cdots$ O3	0.83 (1)	1.96 (1)	2.7925 (15)	176 (2)
O4—H4 <i>A</i> $\cdots$ O2 <sup>v</sup>	0.84 (1)	1.86 (1)	2.6703 (15)	162 (2)
O4 <i>W</i> —H42 $\cdots$ O1 <i>W</i> <sup>vi</sup>	0.83 (1)	2.12 (1)	2.8960 (16)	158 (2)
O4 <i>W</i> —H41 $\cdots$ O5 <sup>vii</sup>	0.83 (1)	2.08 (1)	2.8503 (16)	153 (2)

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