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

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Hexaaquanickel(II) bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate, [Ni(H2O)6][C6H3(CO2H)(OH)SO3]2·2H2O, (I), crystallizes in the triclinic space group $P\overline{1}$ 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 O—H···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. Hexaaquatocobalt(II) bis(3-carboxybenzenesulfonate) dihydrate, [Co(H2O)6][C6H4(CO2H)SO3]2·2H2O, (II), also crystallizes in triclinic $P\overline{1}$ 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 O—H···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 $[\text{Ni(H}_2\text{O)}_6][\text{C}_6\text{H}_3(\text{CO}_2\text{H})(\text{OH})\text{SO}_3]_2\cdot\text{2H}_2\text{O}$, (I). The compound crystallizes in the triclinic space group $P\overline{1}$ with the asymmetric unit consisting of half a $[\text{Ni(H}_2\text{O)}_6]^{2+}$ 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 H4I 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 crystals that have been identified as [Co(H2O)6][C7H4(CO2H)SO3]2H2O, (II). Like (I), this compound also crystallizes in the triclinic P1 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 H4I 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 hexaaquaniickel(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—
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(H₂O)₆][C₆H₅(CO₂H)(OH)SO₃]·2H₂O structure has also been reported for cobalt (Ma et al., 2003b) and zinc (Ma et al., 2003c). Dihydrates of the formula [M(H₂O)₆][C₆H₅(CO₂H)(OH)SO₃]·2H₂O 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 hexaquacopper(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 hexaquacobalt(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

### Table 1

| D–H⋯A | D–H | H⋯A | D⋯A | D–H⋯A |
|-------|-----|-----|-----|-------|
| O1W–H11⋯O1' | 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' | 0.84 (1) | 1.94 (1) | 2.7802 (14) | 176 (2) |
| O2W–H21⋯O3' | 0.83 (1) | 2.02 (1) | 2.8476 (14) | 174 (2) |
| O3W–H32⋯O4W' | 0.83 (1) | 1.99 (1) | 2.8208 (14) | 172 (2) |
| O3W–H31⋯O3' | 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⋯O3 | 0.84 (1) | 1.83 (1) | 2.6656 (14) | 171 (2) |
| O4W–H42⋯O2' | 0.83 (1) | 1.91 (1) | 2.7420 (14) | 178 (2) |
| O4W–H41⋯O1' | 0.83 (1) | 1.99 (1) | 2.8029 (14) | 165 (2) |

Symmetry codes: (i) x, y, z; (ii) x, y, z; (iii) x, y, z; (iv) x, y; (v) x, y, z; (vi) x, y, z.

### Table 2

| D–H⋯A | D–H | H⋯A | D⋯A | D–H⋯A |
|-------|-----|-----|-----|-------|
| O1W–H12⋯O2' | 0.84 (1) | 1.94 (1) | 2.7757 (15) | 170 (2) |
| O1W–H11⋯O1' | 0.84 (1) | 1.91 (1) | 2.7382 (15) | 175 (2) |
| O3W–H22⋯O4W' | 0.84 (1) | 2.04 (2) | 2.7887 (16) | 150 (2) |
| O3W–H31⋯O3' | 0.84 (1) | 1.95 (1) | 2.7852 (16) | 178 (2) |
| O2W–H22⋯O4W | 0.83 (1) | 1.92 (1) | 2.7516 (15) | 174 (2) |
| O2W–H21⋯O3 | 0.83 (1) | 1.96 (1) | 2.7925 (15) | 176 (2) |
| O4–H4⋯O2' | 0.84 (1) | 1.86 (1) | 2.6703 (15) | 162 (2) |
| O4W–H42⋯O1' | 0.83 (1) | 2.12 (2) | 2.8860 (16) | 158 (2) |
| O4W–H41⋯O5' | 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; (v) –x, –y, z; (vi) –x, –y, 1+z; (vii) x–1, y, z; (viii) –x, –y, 1–z; (ix) x+1, y, z; (x) x, y, z.
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 silver 3-carboxybenzenesulfonate at 293 K (refcode ROJJOQ; 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(NO₃)₂·6H₂O (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 100 ml of water. To this colorless solution was added a red solution of 2.91 g (10.0 mmol) of Co(NO₃)₂·6H₂O (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 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 100 ml of water. To this colorless solution was added a red solution of 2.91 g (10.0 mmol) of Co(NO₃)₂·6H₂O (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

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.
Table 3
Experimental details.

| (I) | (II) |
| --- | --- |
| **Crystal data** |  
| Chemical formula | [Ni(H₂O)₆](C₇H₅O₆S)₂·2H₂O | [Co(H₂O)₆](C₇H₅O₆S)₂·2H₂O |
| Mᵣ | 637.18 | 605.40 |
| Crystal system, space group | Triclinic, PT | Triclinic, PT |
| Temperature (K) | 150 | 150 |
| a, b, c (Å) | 6.5986 (7), 7.4183 (8), 12.5387 (14) | 6.7774 (11), 6.9866 (11), 13.6532 (19) |
| α, β, γ (°) | 74.1712 (14), 88.6035 (14), 77.9200 (13) | 91.107 (2), 90.401 (2), 117.5832 (19) |
| V (Å³) | 614.11 (11) | 575.66 (16) |
| Z | 1 | 1 |
| Radiation type | Mo Kα | Mo Kα |
| μ (mm⁻¹) | 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 |
| **Absorption correction** | Multi-scan (SADABS; Krause et al., 2015) |
| **T[obs]** | 0.670, 0.746 |
| **T[txt]** | 0.688, 0.746 |
| **No. of measured, independent and observed [I > 2σ(I)] reflections** | 8656, 3047, 2779 |
| **R[diff]** | 0.023, 0.059, 1.08 |
| **R[ref]** | 0.024, 0.062, 1.05 |
| **S** | 2881 |
| **H-atom treatment** | H atoms treated by a mixture of independent and constrained refinement |
| **No. of parameters** | 290 |
| **No. of restraints** | 9 |
| **No. of reflections** | 3047 |
| **H atoms treated by a mixture of independent and constrained refinement** | 98 |
| **Δρmax, Δρmin (e Å⁻³)** | 0.33, −0.41 |
| **Δρmax, Δρmin (e Å⁻³)** | 0.41, −0.43 |

**Computer programs:** APEX3 and SAINT (Bruker, 2015), SHELXT2016/5 (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(eq) constrained to be 1.2 times the U(eq) 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.

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Crystal structures of two new divalent transition-metal salts of carboxybenzene-sulfonate anions

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Computing details
For both structures, data collection: APEX3 (Bruker, 2015); cell refinement: SAINT (Bruker, 2015); data reduction: SAINT (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).

Crystal data
[Ni(H2O)6](C7H5O6S)2·2H2O
Mr = 637.18
Triclinic, P1
a = 6.5986 (7) Å
b = 7.4183 (8) Å
c = 13.2847 (14) Å
α = 74.1712 (14)°
β = 88.6035 (14)°
γ = 77.9200 (13)°
V = 611.41 (11) Å3
Z = 1
F(000) = 330
Dd = 1.731 Mg m−3
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 4943 reflections
θ = 2.9–28.3°
μ = 1.06 mm−1
T = 150 K
Block, green
0.22 × 0.16 × 0.10 mm

Data collection
Bruker Duo with APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)
Tmin = 0.670, Tmax = 0.746
8656 measured reflections
3047 independent reflections
2779 reflections with I > 2σ(I)
Rint = 0.019
θmax = 28.4°, θmin = 2.9°
h = −8→8
k = −9→9
l = −17→17

Refinement
Refinement on F2
Least-squares matrix: full
R[F2 > 2σ(F2)] = 0.023
wR(F2) = 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/[σ2(F2) + (0.0284P)2 + 0.2223P]
where P = (F2 + 2Fc2)/3
(Δ/σ)max < 0.001
Δρmax = 0.33 e Å−3
Δρmin = −0.41 e Å−3
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 (Å²)

| Atom | x   | y   | z   | U₁₁ | U₂₂ | U₃₃ |
|------|-----|-----|-----|-----|-----|-----|
| Ni1  | 0.5000000 | 1.0000000 | 0.0000000 | 0.01105 (7) | 0.01105 (7) | 0.01105 (7) |
| O1W  | 0.40237 (15) | 0.99422 (14) | 0.14733 (7) | 0.0161 (2) | 0.0161 (2) | 0.0161 (2) |
| H11  | 0.342 (3) | 1.095 (2) | 0.1600 (16) | 0.039 (6)* | 0.039 (6)* | 0.039 (6)* |
| H12  | 0.488 (3) | 0.939 (3) | 0.1966 (12) | 0.041 (6)* | 0.041 (6)* | 0.041 (6)* |
| O2W  | 0.66270 (15) | 0.72230 (14) | 0.0504 (8) | 0.0171 (2) | 0.0171 (2) | 0.0171 (2) |
| H22  | 0.596 (3) | 0.642 (3) | 0.0846 (16) | 0.048 (6)* | 0.048 (6)* | 0.048 (6)* |
| H21  | 0.7789 (19) | 0.701 (3) | 0.0795 (15) | 0.037 (6)* | 0.037 (6)* | 0.037 (6)* |
| O3W  | 0.23500 (15) | 0.91381 (15) | −0.02663 (8) | 0.0168 (2) | 0.0168 (2) | 0.0168 (2) |
| H32  | 0.220 (3) | 0.884 (3) | −0.0816 (11) | 0.037 (6)* | 0.037 (6)* | 0.037 (6)* |
| H31  | 0.182 (3) | 0.840 (2) | 0.0200 (12) | 0.033 (5)* | 0.033 (5)* | 0.033 (5)* |
| S1   | 0.78200 (5) | 0.52327 (5) | 0.79824 (2) | 0.01278 (8) | 0.01278 (8) | 0.01278 (8) |
| O1   | 0.84194 (15) | 0.70694 (14) | 0.78658 (8) | 0.0177 (2) | 0.0177 (2) | 0.0177 (2) |
| O2   | 0.56747 (14) | 0.52970 (14) | 0.83170 (8) | 0.0176 (2) | 0.0176 (2) | 0.0176 (2) |
| O3   | 0.92577 (15) | 0.35961 (14) | 0.86440 (8) | 0.0181 (2) | 0.0181 (2) | 0.0181 (2) |
| O6   | 0.73062 (17) | 0.39614 (16) | 0.38141 (8) | 0.0211 (2) | 0.0211 (2) | 0.0211 (2) |
| H6A  | 0.704 (4) | 0.503 (2) | 0.3355 (14) | 0.051 (7)* | 0.051 (7)* | 0.051 (7)* |
| O5   | 0.68377 (16) | 0.76283 (15) | 0.30157 (8) | 0.0204 (2) | 0.0204 (2) | 0.0204 (2) |
| O4   | 0.72336 (17) | 0.94807 (15) | 0.40456 (8) | 0.0213 (2) | 0.0213 (2) | 0.0213 (2) |
| H4   | 0.727 (3) | 1.025 (3) | 0.3454 (10) | 0.042 (6)* | 0.042 (6)* | 0.042 (6)* |
| C1   | 0.78448 (19) | 0.48905 (19) | 0.67154 (10) | 0.0135 (2) | 0.0135 (2) | 0.0135 (2) |
| C6   | 0.8006 (2) | 0.30381 (19) | 0.66125 (11) | 0.0159 (3) | 0.0159 (3) | 0.0159 (3) |
| H6   | 0.823672 | 0.197124 | 0.721651 | 0.019* | 0.019* | 0.019* |
| C5   | 0.7830 (2) | 0.2757 (2) | 0.56350 (11) | 0.0171 (3) | 0.0171 (3) | 0.0171 (3) |
| H5   | 0.793317 | 0.149826 | 0.556807 | 0.021* | 0.021* | 0.021* |
| C4   | 0.7498 (2) | 0.4327 (2) | 0.47420 (11) | 0.0159 (3) | 0.0159 (3) | 0.0159 (3) |
| C3   | 0.7587 (2) | 0.61877 (19) | 0.48438 (10) | 0.0141 (3) | 0.0141 (3) | 0.0141 (3) |
| H2   | 0.747996 | 0.769976 | 0.591539 | 0.017* | 0.017* | 0.017* |
| O4W  | 0.77781 (16) | 1.17956 (14) | 0.21815 (8) | 0.0167 (2) | 0.0167 (2) | 0.0167 (2) |
| H42  | 0.674 (2) | 1.269 (2) | 0.2040 (16) | 0.035 (6)* | 0.035 (6)* | 0.035 (6)* |
| H41  | 0.879 (2) | 1.230 (3) | 0.2199 (17) | 0.039 (6)* | 0.039 (6)* | 0.039 (6)* |

Atomic displacement parameters (Å²)

|   | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|---|-----|-----|-----|-----|-----|-----|
| 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) |

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### Geometric parameters (Å, °)

| Bond/Angle | Distance/Angle |
|------------|----------------|
| Ni1—O1W    | 2.0376 (10)    |
| Ni1—O1W    | 2.0498 (10)    |
| Ni1—O2W    | 2.0498 (10)    |
| Ni1—O3W    | 2.0526 (10)    |
| O1W—H11    | 0.829 (9)      |
| O1W—H12    | 0.832 (10)     |
| O2W—H22    | 0.832 (9)      |
| O3W—H32    | 0.833 (9)      |
| O3W—H31    | 0.831 (9)      |
| S1—O3      | 1.4570 (10)    |
| S1—C1      | 1.7685 (14)    |
| O6—C4      | 1.3466 (17)    |
| O1W—Ni1—O1W| 91.26 (4)     |
| O1W—Ni1—O2W| 88.74 (4)     |
| O1W—Ni2—O2W| 88.74 (4)     |
| O1W—Ni1—O3W| 91.26 (4)     |
| O2W—Ni1—O2W| 180.0        |
| O1W—Ni1—O3W| 92.03 (4)     |
| O1W—Ni2—O3W| 87.97 (4)     |
| O2W—Ni1—O3W| 88.06 (4)     |
| O2W—Ni2—O3W| 91.94 (4)     |
| O1W—Ni1—O3W| 87.97 (4)     |

### Supporting Information

| Atom     | U1    | U2    | U3    | U12   | U13   | U23   |
|----------|-------|-------|-------|-------|-------|-------|
| 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) |
O1W—Ni1—O3W\textsuperscript{iv} 92.03 (4) C6—C5—C4 120.03 (13)
O2W—Ni1—O3W\textsuperscript{iv} 91.94 (4) C6—C5—H5 120.0
O2W—Ni1—O3W\textsuperscript{iv} 88.06 (4) C4—C5—H5 120.0
O3W—Ni1—O3W\textsuperscript{iv} 180.0 O6—C4—C5 117.16 (13)
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 121.91 (12)
H22—O2W—H21 109 (2) C5—C4—C3 123.10 (12)
Ni1—O3W—H32 119.8 (15) C5—C4—C3 119.74 (12)
Ni1—O3W—H31 122.3 (14) C4—C3—C7 117.16 (13)
H32—O3W—H31 106 (2) C5—C4—C3 123.10 (12)
O3—S1—O1 113.84 (6) O6—C4—C3—C7 −2.41 (19)
O3—S1—O2 111.87 (6) O6—C4—C3—C7 −1.56 (19)
O1—S1—O2 111.57 (6) O4—C7—C3—C2 178.67 (12)
C2—C1—C6—C5 −1.6 (2) C4—C3—C7—O5 5.97 (19)
S1—C1—C6—C5 173.82 (10) C5—C4—C3—C2 178.67 (12)
C1—C6—C5—C4 37.34 (12) C6—C1—C2—C3 1.29 (19)
C2—C1—C6—C5 93.39 (11) C6—C1—C2—C3 −174.06 (10)
C1—C6—C5—C4 0.3 (2) C2—C1—C6—C5 1.6 (2)
C2—C1—C6—C5 159.30 (10) C5—C4—C3—C2 −175.12 (12)
C6—C5—C4—O6 −178.94 (12) C4—C3—C2—C1 −174.06 (10)
C6—C5—C4—C3 178.67 (12) O4—C7—C3—C2 5.01 (18)
O6—C4—C3—C2 178.67 (12) O4—C7—C3—C2 −173.89 (12)
O6—C4—C3—C2 −147.25 (11) O4—C7—C3—C2 −178.67 (12)
O1—S1—C1—C2 −25.29 (12) O6—C4—C3—C2 −2.41 (19)
O2—S1—C1—C2 93.39 (11) O6—C4—C3—C2 178.67 (12)
O3—S1—C1—C2 37.34 (12) O6—C4—C3—C2 178.67 (12)

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

**Hydrogen-bond geometry (Å, °)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O1W—H11—O1\textsuperscript{ii} | 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\textsuperscript{iii} | 0.84 (1) | 2.02 (1) | 2.8476 (14) | 174 (2) |
| O2W—H21—O3\textsuperscript{iv} | 0.83 (1) | 1.99 (1) | 2.8208 (14) | 172 (2) |
| O3W—H32—O4\textsuperscript{iv} | 0.83 (1) | 2.05 (1) | 2.8790 (14) | 175 (2) |
| O3W—H31—O3\textsuperscript{iii} | 0.83 (1) | 1.84 (1) | 2.5904 (16) | 148 (2) |
| O6—H64—O5 | 0.84 (1) | 1.83 (1) | 2.6656 (14) | 171 (2) |
| O4—H4—O4\textsuperscript{ii} | 0.83 (1) | 1.91 (1) | 2.7420 (14) | 178 (2) |
| O4—H41—O1\textsuperscript{iv} | 0.83 (1) | 1.99 (1) | 2.8029 (14) | 165 (2) |

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

[Co(H₂O)₆](C₇H₅O₅S)₂·2H₂O

Mr = 605.40
Triclinic, P₁

a = 6.7774 (11) Å
b = 6.9866 (11) Å
c = 13.721 (2) Å
α = 91.107 (2)°
β = 90.401 (2)°
γ = 117.5832 (19)°
V = 575.66 (16) Å³

Z = 1
F(000) = 313
Dₐ = 1.746 Mg m⁻³

Crystal data

Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 4422 reflections
θ = 3.0–28.3°
µ = 1.01 mm⁻¹
T = 150 K
Plate, red-pink

0.30 × 0.14 × 0.08 mm

Data collection

Bruker Duo with APEXII CCD
diffractometer
Radiation source: fine focus sealed tube
ω scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)

θmin = 0.688, θmax = 0.746
8197 measured reflections
2881 independent reflections
2578 reflections with I > 2σ(I)
Rint = 0.020
θmax = 28.4°, θmin = 3.0°
h = −9→9
k = −9→9
l = −18→18

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.024
wR(F²) = 0.062
S = 1.05
2881 reflections
196 parameters
9 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
W = 1/[σ²(Fo²) + (0.030P)² + 0.2552P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max < 0.001
Δρmax = 0.41 e Å⁻³
Δρmin = −0.43 e Å⁻³

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 (Å²)

|     | x    | y    | z    | U(eq) |
|-----|------|------|------|-------|
| Co1 | 0.50 | 0.50 | 0.00 | 0.011 | (8)  |
| O1W | 0.59 | 0.45 | 0.14 | 0.016 | (2)  |
| H12 | 0.38 | 0.37 | 0.18 | 0.049 | (7)  |
| H11 | 0.56 | 0.55 | 0.17 | 0.033 | (6)  |
| O3W | 0.30 | 0.16 | −0.01| 0.022 | (2)  |
| H32 | 0.28 | 0.09 | −0.06| 0.051 | (7)  |
| H31 | 0.29 | 0.08 | 0.03 | 0.035 | (6)  |
| O2W | 0.23 | 0.52 | 0.05 | 0.020 | (2)  |
### Atomic displacement parameters (Å²)

|      | U¹¹   | U²²   | U³³   | U¹²   | U¹³   | U²³   |
|------|-------|-------|-------|-------|-------|-------|
| 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  | 0.0037 (6) | 0.0026 (5) | 0.0038 (5) | 0.0046 (5) | 0.0004 (5) | 0.0003 (4) |
| O2W  | 0.00180 (5) | 0.00178 (5) | 0.00261 (6) | 0.0086 (5) | 0.0071 (4) | 0.0011 (5) |
| S1   | 0.01491 (17) | 0.00270 (16) | 0.001041 (16) | 0.00627 (13) | 0.00180 (12) | 0.00044 (12) |
| O1   | 0.0014 (5) | 0.00194 (5) | 0.00195 (5) | 0.0046 (4) | -0.0025 (4) | 0.0004 (4) |
| O3   | 0.00318 (6) | 0.00214 (5) | 0.00121 (5) | 0.00167 (5) | 0.0064 (4) | 0.0020 (4) |
| O4   | 0.0024 (6) | 0.00276 (6) | 0.00142 (5) | 0.00153 (5) | 0.0057 (4) | 0.0015 (4) |
| O5   | 0.00289 (6) | 0.00276 (6) | 0.00135 (5) | 0.0004 (4) | 0.0003 (4) | 0.0011 (4) |
| O2   | 0.00182 (5) | 0.00132 (5) | 0.00157 (5) | 0.0072 (4) | 0.0040 (4) | 0.0011 (4) |
| C2   | 0.00129 (6) | 0.00123 (6) | 0.00144 (7) | 0.0052 (5) | 0.0017 (5) | -0.0002 (5) |
| C5   | 0.00150 (7) | 0.00176 (7) | 0.00244 (8) | 0.0093 (6) | 0.0029 (6) | 0.0021 (6) |
| C6   | 0.00160 (7) | 0.00151 (7) | 0.00177 (7) | 0.0067 (6) | 0.0044 (5) | 0.0015 (5) |
| C7   | 0.00162 (7) | 0.00107 (6) | 0.00128 (6) | 0.0048 (5) | 0.0018 (5) | 0.0004 (5) |
| C8   | 0.00184 (7) | 0.00102 (6) | 0.00156 (7) | 0.0046 (5) | 0.0010 (5) | 0.0000 (5) |
| C1   | 0.00140 (6) | 0.00113 (6) | 0.00129 (6) | 0.0047 (5) | 0.0010 (5) | 0.0002 (5) |
| C4   | 0.00178 (7) | 0.00140 (7) | 0.00194 (7) | 0.0073 (6) | -0.0014 (5) | 0.0022 (5) |
| O4W  | 0.00233 (6) | 0.00231 (5) | 0.00152 (5) | 0.0134 (5) | -0.0012 (4) | -0.0005 (4) |
### Geometric parameters (Å, °)

| Bond/Angle | Distance/Angle (Å/°) | Distance/Angle (Å/°) |
|------------|----------------------|----------------------|
| Co1—O2W   | 2.0470 (11)          | O4—C7                | 1.3298 (18)           |
| Co1—O2Wi  | 2.0470 (11)          | O4—H4A               | 0.841 (10)            |
| Co1—O3W   | 2.0921 (11)          | O5—C7                | 1.2126 (18)           |
| Co1—O3Wi  | 2.0921 (11)          | C2—C1                | 1.3898 (19)           |
| Co1—O1W   | 2.1107 (11)          | C2—C3                | 1.3921 (19)           |
| Co1—O1Wi  | 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 | 180.0                  | O1—S1—C1             | 106.70 (7)            |
| O2W—Co1—O3W | 88.95 (5)              | O3—S1—C1             | 106.69 (7)            |
| O2W—Co1—O3W | 91.05 (5)              | O2—S1—C1             | 106.62 (6)            |
| O2W—Co1—O3W | 91.05 (5)              | C7—O4—H4A           | 112.1 (17)            |
| O2W—Co1—O3W | 88.95 (5)              | C1—C2—C3            | 119.60 (13)           |
| O3W—Co1—O3W | 180.0                  | C1—C2—H2            | 120.2                 |
| O2W—Co1—O1W | 91.15 (4)              | C3—C2—H2             | 120.2                 |
| O2W—Co1—O1W | 88.85 (4)              | C4—C5—C6            | 120.60 (13)           |
| O3W—Co1—O1W | 87.56 (4)              | C4—C5—H5            | 119.7                 |
| O3W—Co1—O1W | 92.44 (4)              | C6—C5—H5            | 119.7                 |
| O2W—Co1—O1W | 88.85 (4)              | C5—C6—C1            | 119.12 (13)           |
| O2W—Co1—O1W | 91.15 (4)              | C5—C6—H6            | 120.4                 |
| O3W—Co1—O1W | 92.44 (4)              | C1—C6—H6            | 120.4                 |
| O3W—Co1—O1W | 87.56 (4)              | C2—C3—C4            | 120.01 (13)           |
| O1W—Co1—O1W | 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)           |

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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 (Å, °)

| D—H···A     | D—H  | H···A | D····A | D—H···A |
|-------------|------|-------|--------|---------|
| O1W—H12···O2^ii | 0.84 (1) | 1.94 (1) | 2.7757 (15) | 170 (2) |
| O1W—H11···O1^iii | 0.84 (1) | 1.91 (1) | 2.7382 (15) | 175 (2) |
| O3W—H32···O4W^iv | 0.84 (1) | 2.04 (2) | 2.7887 (16) | 150 (2) |
| O3W—H31···O3^vi | 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—H4.4···O2^v | 0.84 (1) | 1.86 (1) | 2.6703 (15) | 162 (2) |
| O4W—H42···O1W^vi | 0.83 (1) | 2.12 (1) | 2.8960 (16) | 158 (2) |
| O4W—H41···O5^iii | 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.