Reaction of the ligand 2,2′,2″,2‴-[[pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(sulfanediyl)]tetraacetic acid (H₄L₁), with NiCl₂ leads to the formation of a binuclear complex, (μ-2,2′,2″,2‴-[[pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(sulfanediyl)]tetraacetato-N₂S₂O₃N₂)[Ni₂(C₁₀H₁₀N₂O₈S₄)(H₂O)₂]·7H₂O (I). It crystallizes with two half molecules in the asymmetric unit. The complete molecules are generated by inversion symmetry, with the center of the pyrazine rings being located at crystallographic centres of inversion. The ligand coordinates two NiII ions in a bis-pentadentate manner and the sixfold coordination sphere of each nickel(II) atom (NiS₂O₃N) is completed by a water molecule. The complex crystallized as a hepta-hydrate. The binuclear complexes are linked by O—H⋯Ocarbonyl hydrogen bonds, forming layers parallel to the (101) plane. This layered structure is additionally stabilized by weak C—H⋯O hydrogen bonds. Further O—H⋯O hydrogen bonds involving binuclear complexes and solvent water molecules, together with weak C—H⋯S hydrogen bonds, link the layers to form a supramolecular framework.

Structure description

The tetrakis-substituted pyrazine carboxylic acid ligand, 2,2′,2″,2‴-[[pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(sulfanediyl)]tetraacetic acid (H₄L₁), is one of a series of tetrakis-substituted pyrazine ligands containing NₓS₄ and N₂S₄O₈ donor atoms synthesized to study their coordination behaviour with various first-row transition metals and the magnetic exchange properties of the complexes (Pacifico, 2003). Crystal struc-
tudes of two polymorphs of the tetrapropionic acid analogue of the title ligand, $3',3',3',3''-[\text{pyrazine-2,3,5,6-tetrayltetra-kis(methylene)]tetrakis(sulfanediyl)}$tetrapropionic acid ($H_4L_2$), and of two potassium–organic frameworks have been reported (Pacifico & Stoeckli-Evans, 2021).

Reaction of $H_4L_1$ with NiCl$_2$ yielded the binuclear complex I, with the ligand coordinating two Ni$^{II}$ ions in a bis-pentadentate manner. Complex I was shown to exhibit a weak antiferromagnetic coupling between the Ni centres via the pyrazine ring with a $J$ value of $-1.78$ cm$^{-1}$ (Pacifico, 2003).

A similar ligand, $2,2',2',2''-[\text{pyrazine-2,3,5,6-tetrayltetra-kis(methylene)]tetrakis(sulfanediyl)}$tetraakis(ethan-1-amine) ($H_4L_3$; CSD refcode PUXJUQ for the tetraperchlorate salt: Pacifico & Stoeckli-Evans, 2020), has also been shown to form binuclear nickel(II) complexes (TAGTUU and EHUBOB) with similar antiferromagnetic couplings ($J = -1.78$ cm$^{-1}$; Pacifico, 2003).

Reaction of $H_4L_1$ with nickel(II) chloride leads to the formation of the binuclear title compound I, which crystallizes with two half molecules in the asymmetric unit (Fig. 1 and Table 1). The complete molecules are generated by inversion symmetry, with the centres of the pyrazine rings being located at crystallographic centres of inversion.

The best fit for the molecular overlap of the two molecules is shown in Fig. 2. The r.m.s. deviation is 0.3168 Å, with a maximum deviation of 0.7435 Å (Mercury; Macrae et al., 2020). The two molecules differ essentially in the conformations of the four chelate rings as shown by the torsion angles given in Table 1. The calculation of the mean planes of the chelate rings (PLATON; Spek, 2020) indicate that: ring Ni1/N1/C1/C2/S1 is twisted on the S1—C2 bond compared to ring Ni2/N2/C13/C14/S4, which is flat; ring Ni1/N1/C5/C6/S2 has an envelope conformation with atom S2 as the flap, while ring Ni2/N2/C9/C10/S3 is flat; ring Ni1/S1/C3/C4/O2 is flat...
atom (NiS₂O₃N) is completed by a water molecule. The manner and the sixfold coordination sphere of each nickel(II) complex crystallized as a hepta-hydrate. Selected bond lengths involving the nickel atoms of the two molecules are given in Table 1. There is a slight difference in the Ni—N bond lengths [Ni1—N1 = 2.081 (2) Å, Ni2—N2 = 2.057 (2) Å; Table 1], otherwise the bond lengths involving the nickel atoms are similar and close to those reported for the complex aqua(2,2'-
(pyridine-2,6-diyl)bis[methylene(sulfanediyl)]dipropanoato)nickel(II) (CSD refcode DUYFOU; Rheingold, 2015).

In the crystal structure of I, binuclear nickel(II) complexes are linked by O_{water}—H···O_{carbonyl} hydrogen bonds, forming layers parallel to the (101) plane (Fig. 3, Table 2). Within the layers, weak C—H···O hydrogen bonds are present (Table 2). Solvent water molecules are linked by O—H_{water}···O_{water} hydrogen bonds to form ribbons propagating along the b-axis direction that consist of eight and twenty-four membered rings of the R₂⁽⁴⁾ and R₄⁽₄⁾(24) types (Fig. 4 and Table 2). Additional O—H_{water}···O_{carbonyl} hydrogen bonds involving the binuclear complexes and solvent water molecules, together with weak C—H···S hydrogen bonds, link the layers to form a supra-molecular framework (Fig. 5).

**Synthesis and crystallization**

The synthesis and crystal structure of the reagent tetra-2,3,5,6-bromomethyl-pyrazine (TBr) have been reported [Ferigo et al., 1994; Assoumatine & Stoeckli-Evans, 2014 (CSD refcode TOJXUN)].

**Synthesis of ligand 2,2',2″,2‴-[[pyrazine-2,3,5,6-tetracyl(tetras(sulfanediyl))tetraacetic acid (H₂L₁): Thioglycolic acid (1.6313 g, 1.77 mol, 4 eq) was dissolved in 50 ml of THF, then NaOH (1.4166 g, 3.54 mol, 8 eq), dissolved in a minimum amount of water (a few ml) was added. The volume was increased to 100 ml adding THF and then the reaction was left to stir under reflux for 1 h. TBr (2 g, 4.42 mol, 1 eq) dissolved in 50 ml of THF, was then added dropwise using an addition funnel. The mixture was stirred under reflux for 6 h. After evaporation of the solvent, the mixture was dissolved in 50 ml of deionized water, and HCl (puriss.) was added dropwise until a clearly acidic pH was
Table 3
Experimental details.

| Crystal data | Chemical formula | [Ni₂(C₁₆H₁₆N₂O₈S₄)(H₂O)₂]·7H₂O |
|--------------|------------------|---------------------------------|
| Mₐ           |                  | 797.11                           |
| Crystal system, space group | Triclinic, Pt | |
| Temperature (K) | 153 | |
| a, b, c (Å) | 8.6799 (8), 11.4092 (10), 14.7210 (13) |
| α, β, γ (°) | 90.308 (7), 103.619 (7), 93.801 (7) |
| V (Å³)       | 1434.2 (2)       |
| Z            | 2                |
| Radiation type | Mo Kα |
| μ (mm⁻¹)     | 1.71             |
| Crystal size (mm) | 0.49 × 0.06 × 0.06 |

Data collection

| Diffractometer | Stoe IPDS 2 |
|----------------|-------------|
| Absorption correction | Empirical (using intensity measurements) (ShxAbs; Spek, 2020) |
| T_min, T_max | 0.261, 0.714 |
| No. of measured, independent and observed | 19974, 7779, 6120 |
| Rint | 0.052 |
| (sin θ/λ)max (Å⁻¹) | 0.693 |

Refinement

| R[F² > 2σ(F²)] | 0.039, 0.096, 1.02 |
| No. of reflections | 7779 |
| No. of parameters | 443 |
| No. of restraints | 2 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³) | 0.74, −0.64 |

Crystal data, data collection and structure refinement details are summarized in Table 3. For complex I, the average HKL measurement multiplicity was low at 2.6, hence an empirical absorption correction was applied.

Acknowledgements

We are extremely grateful to Professor Joan Ribas and members of his group at the Universitat de Barcelona, Departamento de Química Inorgánica, for the magnetic measurements, help in their interpretation and valuable discussions. HSE is grateful to the University of Neuchâtel for their support over the years.

Funding information

Funding for this research was provided by: Swiss National Science Foundation; University of Neuchâtel.

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full crystallographic data

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\((\mu-2',2'',2''-\{[\text{Pyrazine}-2,3,5,6-\text{tetracyltetakis(methylene)]tetrakis(sulfanediyl)}\text{tetraacetato}\}\text{bis[aquanickel(II)] heptahydrate}}\)

Crystal data

\[\text{[Ni}_2(\text{C}_16\text{H}_{16}\text{N}_2\text{O}_8\text{S}_4)(\text{H}_2\text{O})_2]\cdot7\text{H}_2\text{O}\]

\[M_r = 772.11\]

Triclinic, \(\overline{P}\)

\[a = 8.6799 (8) \text{ Å}\]

\[b = 11.4092 (10) \text{ Å}\]

\[c = 14.7210 (13) \text{ Å}\]

\[\alpha = 90.308 (7)^\circ\]

\[\beta = 103.619 (7)^\circ\]

\[\gamma = 93.801 (7)^\circ\]

\[V = 1413.4 (2) \text{ Å}^3\]

Data collection

STOE IPDS 2 diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

\(\phi + \omega\) scans

Absorption correction: empirical (using intensity measurements)

\((\text{ShxAbs; Spek, 2020})\)

\(T_{\text{min}} = 0.261, T_{\text{max}} = 0.714\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\[R(F^2) = 0.039\]

\[wR(F^2) = 0.096\]

\[S = 1.02\]

7779 reflections

443 parameters

2 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

Extinction correction: (\text{SHELXL-2018/3; Sheldrick, 2015}), \(\text{Fc}^o = \text{kFc}[1+0.001x\text{Fc}^o\lambda^3/\sin(2\theta)]^{1/4}\), Extinction coefficient: 0.0029 (6)
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.

**Refinement.** H atoms of coordinated and non-coordinated water molecules were all located from difference-Fourier maps and freely refined. The C-bound H atoms were included in calculated positions and treated as riding on their parent C atom: C—H = 0.97 - 0.99 Å with $U_	ext{iso}$(H) = 1.2 $U_	ext{eq}$(C).

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\overline{\text{Å}}^2$)

| Atom | x     | y     | z     | $U_	ext{eq}$/$U_	ext{eq}$ |
|------|-------|-------|-------|-------------------------------|
| Ni1  | 0.53221 (4) | 0.24084 (3) | 0.38618 (2) | 0.01578 (8) |
| S1   | 0.80929 (7)  | 0.27577 (5)  | 0.45193 (4)  | 0.01770 (12) |
| S2   | 0.25256 (8)  | 0.24883 (6)  | 0.32588 (5)  | 0.01966 (13) |
| O1   | 0.6527 (3)   | 0.09177 (18) | 0.64400 (14) | 0.0260 (4)   |
| O2   | 0.5239 (2)   | 0.15751 (16) | 0.50754 (13) | 0.0189 (3)   |
| O3   | 0.4421 (3)   | 0.4074 (2)   | 0.13485 (16) | 0.0374 (5)   |
| O4   | 0.5504 (2)   | 0.31920 (17) | 0.26639 (13) | 0.0218 (4)   |
| O1W  | 0.5614 (2)   | 0.07971 (17) | 0.33656 (14) | 0.0214 (4)   |
| H1WA | 0.493 (5)    | 0.021 (4)    | 0.347 (3)    | 0.044 (12)*  |
| H1WB | 0.562 (5)    | 0.074 (4)    | 0.280 (4)    | 0.049 (13)*  |
| N1   | 0.5120 (2)   | 0.39964 (18) | 0.45117 (14) | 0.0150 (4)   |
| C1   | 0.6427 (3)   | 0.4640 (2)   | 0.49454 (16) | 0.0150 (4)   |
| C2   | 0.8013 (3)   | 0.4274 (2)   | 0.48542 (19) | 0.0187 (5)   |
| H2A  | 0.878607     | 0.443243     | 0.546080     | 0.022*       |
| H2B  | 0.836764     | 0.477764     | 0.438614     | 0.022*       |
| C3   | 0.8088 (3)   | 0.1985 (2)   | 0.5586 (2)   | 0.0243 (5)   |
| H3A  | 0.881017     | 0.134074     | 0.562820     | 0.029*       |
| H3B  | 0.854011     | 0.253460     | 0.611882     | 0.029*       |
| C4   | 0.6478 (3)   | 0.1460 (2)   | 0.57012 (18) | 0.0186 (5)   |
| C5   | 0.3695 (3)   | 0.4333 (2)   | 0.45563 (17) | 0.0157 (4)   |
| C6   | 0.2232 (3)   | 0.3583 (2)   | 0.40844 (18) | 0.0191 (5)   |
| H6A  | 0.142444     | 0.410319     | 0.375290     | 0.023*       |
| H6B  | 0.179663     | 0.317800     | 0.457218     | 0.023*       |
| C7   | 0.2684 (3)   | 0.3386 (3)   | 0.22634 (19) | 0.0267 (6)   |
| H7A  | 0.195741     | 0.302037     | 0.169739     | 0.032*       |
| H7B  | 0.230429     | 0.416684     | 0.235880     | 0.032*       |
| C8   | 0.4334 (3)   | 0.3569 (3)   | 0.20767 (19) | 0.0233 (5)   |
| Ni2  | 0.08393 (4)  | 0.76880 (3)  | 0.11162 (2)  | 0.01682 (8)  |
| S3   | −0.17445 (8) | 0.74194 (6)  | 0.13855 (4)  | 0.01891 (13) |
| S4   | 0.33203 (7)  | 0.76930 (6)  | 0.07086 (4)  | 0.01819 (12) |
| O5   | −0.2463 (2)  | 0.9086 (2)   | −0.09705 (16) | 0.0298 (5)  |
| O6   | −0.0227 (2)  | 0.85094 (17) | −0.00750 (13) | 0.0211 (4) |
| O7   | 0.4137 (2)   | 0.62254 (19) | 0.31716 (15) | 0.0272 (4)   |
| O8   | 0.1895 (2)   | 0.67823 (17) | 0.22496 (13) | 0.0208 (4)   |
| O2W  | 0.1272 (3)   | 0.92039 (18) | 0.18933 (14) | 0.0230 (4)   |
| H2WA | 0.159 (6)    | 0.984 (4)    | 0.162 (3)    | 0.052 (13)*  |
|    | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$  | $U_{13}$  | $U_{23}$  |
|----|-----------|-----------|-----------|-----------|-----------|-----------|
| Ni1| 0.01756 (15) | 0.01571 (15) | 0.01319 (15) | 0.00010 (11) | 0.00220 (11) | −0.00087 (11) |
| S1 | 0.0181 (3)  | 0.0171 (3)  | 0.0182 (3)  | 0.0016 (2)  | 0.0048 (2)  | −0.0015 (2)  |
| S2 | 0.0195 (3)  | 0.0176 (3)  | 0.0199 (3)  | −0.0013 (2) | 0.0015 (2)  | −0.0045 (2)  |
| O1 | 0.0324 (10) | 0.0244 (10) | 0.0177 (9)  | −0.0046 (8) | 0.0007 (8)  | 0.0025 (8)   |
| O2 | 0.0206 (8)  | 0.0201 (9)  | 0.0149 (8)  | −0.0013 (7) | 0.0026 (7)  | 0.0003 (7)   |
### Geometric parameters (Å, °)

| Bond                  | Distance  | Angle     |
|-----------------------|-----------|-----------|
| Ni1—O1W               | 2.0276 (19)| S3—C10   | 1.810 (3) |
| Ni1—O2                | 2.0423 (18)| S4—C15   | 1.805 (3) |
| Ni1—O4                | 2.0158 (19)| S4—C14   | 1.814 (3) |
| Ni1—N1                | 2.081 (2)  | O5—C12   | 1.248 (3) |
| Ni1—S1                | 2.3775 (7) | O6—C12   | 1.260 (3) |
| Ni1—S2                | 2.3883 (8) | O7—C16   | 1.236 (3) |
| S1—C3                 | 1.805 (3)  | O8—C16   | 1.281 (3) |
| S1—C2                 | 1.806 (3)  | O2W—H2WA | 0.88 (5)  |
| S2—C6                 | 1.809 (3)  | O2W—H2WB | 0.88 (6)  |

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**O3** 0.0421 (13) 0.0489 (14) 0.0205 (10) 0.0069 (11) 0.0048 (9) 0.0131 (10)

**O4** 0.0244 (9) 0.0253 (9) 0.0157 (8) 0.0010 (7) 0.0050 (7) 0.0047 (7)

**O1W** 0.0266 (9) 0.0174 (9) 0.0198 (9) −0.0006 (7) 0.0052 (8) −0.0035 (7)

**N1** 0.0163 (9) 0.0135 (9) 0.0143 (9) −0.0011 (7) 0.0027 (7) −0.0014 (7)

**C1** 0.0169 (10) 0.0150 (10) 0.0127 (10) 0.0012 (8) 0.0026 (8) 0.0007 (8)

**C2** 0.0157 (11) 0.0177 (11) 0.0223 (12) 0.0001 (9) 0.0040 (9) −0.0017 (9)

**C3** 0.0232 (13) 0.0220 (12) 0.0256 (13) 0.0001 (10) 0.0021 (10) 0.0045 (10)

**C4** 0.0230 (12) 0.0168 (11) 0.0144 (11) −0.0009 (9) 0.0021 (9) −0.0011 (9)

**C5** 0.0173 (10) 0.0153 (10) 0.0136 (10) −0.0011 (8) 0.0025 (8) 0.0000 (8)

**C6** 0.0190 (11) 0.0203 (12) 0.0167 (11) −0.0003 (9) 0.0020 (9) −0.0029 (9)

**C7** 0.0271 (13) 0.0351 (15) 0.0164 (12) 0.0059 (11) 0.0011 (10) −0.0008 (11)

**C8** 0.0281 (13) 0.0262 (13) 0.0142 (11) 0.0017 (10) 0.0020 (10) 0.0005 (10)

**Ni2** 0.0178 (15) 0.01761 (16) 0.01431 (15) 0.00035 (11) 0.00256 (11) −0.00098 (11)

**S3** 0.0210 (3) 0.0200 (3) 0.0168 (3) 0.0014 (2) 0.0069 (2) −0.0016 (2)

**S4** 0.0185 (3) 0.0189 (3) 0.0162 (3) −0.0023 (2) 0.0031 (2) −0.0005 (2)

**O3W** 0.0268 (11) 0.0366 (13) 0.0473 (14) 0.0028 (9) 0.0113 (10) 0.0092 (11)

**O4W** 0.0258 (10) 0.0272 (10) 0.0281 (11) −0.0019 (8) 0.0052 (8) 0.0017 (8)

**O5W** 0.0287 (11) 0.0321 (11) 0.0239 (10) 0.0034 (9) 0.0058 (8) −0.0033 (9)

**O6W** 0.0272 (11) 0.0402 (13) 0.0276 (11) 0.0041 (9) 0.0066 (9) 0.0044 (10)

**O7W** 0.0386 (13) 0.0311 (12) 0.0462 (14) −0.0009 (10) 0.0208 (11) −0.0050 (11)

**O8W** 0.0367 (14) 0.0421 (15) 0.061 (2) −0.0031 (11) 0.0130 (14) 0.0098 (14)

**O9W** 0.0352 (12) 0.0336 (12) 0.0345 (12) −0.0043 (10) 0.0132 (10) −0.0071 (10)
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S2—C7 1.819 (3) N2—C13 1.337 (3)
O1—C4 1.248 (3) N2—C9 1.338 (3)
O2—C4 1.255 (3) C9—C13 1.405 (3)
O3—C8 1.235 (3) C10—H10A 0.9900
O4—C8 1.270 (3) C10—H10B 0.9900
O1W—H1WA 0.90 (5) C11—C12 1.515 (4)
O1W—H1WB 0.83 (5) C9—C13 ii 1.405 (3)
N1—C1 1.333 (3) C11—H11A 0.9900
N1—C5 1.335 (3) C11—H11B 0.9900
C1—C5 1.403 (3) C13—C14 1.503 (3)
C1—C2 1.500 (3) C9—C10 1.502 (3)
C2—H2A 0.9900 C14—H14A 0.9900
C2—H2B 0.9900 C14—H14B 0.9900
C3—C4 1.531 (4) C15—C16 1.521 (4)
C3—H3A 0.9900 C15—H15A 0.9900
C3—H3B 0.9900 C15—H15B 0.9900
O4—Ni1—O1W 92.71 (8) O2W—Ni2—N2 175.03 (9)
O4—Ni1—O2 177.15 (8) O6—Ni2—N2 85.30 (6)
O1W—Ni1—O2 85.47 (8) O8—Ni2—S4 93.64 (6)
O4—Ni1—N1 92.73 (8) O2W—Ni2—S4 97.60 (6)
O1W—Ni1—N1 173.94 (8) O6—Ni2—S4 94.92 (6)
O2—Ni1—N1 88.99 (8) N2—Ni2—S4 85.63 (6)
O4—Ni1—S1 91.86 (6) N2—Ni2—S3 85.28 (6)
O1W—Ni1—S1 92.11 (6) O2W—Ni2—S3 91.04 (6)
O2—Ni1—S1 86.03 (6) O6—Ni2—S3 84.63 (6)
N1—Ni1—S1 85.03 (6) N2—Ni2—S3 85.28 (6)
O4—Ni1—S2 84.80 (6) S4—Ni2—S3 171.37 (3)
O1W—Ni1—S2 99.55 (6) C11—S3—C10 102.65 (14)
O2—Ni1—S2 97.65 (6) C11—S3—Ni2 93.29 (10)
N1—Ni1—S2 92.73 (8) C10—S3—Ni2 98.05 (8)
S1—Ni1—S2 167.99 (3) C15—S4—C14 101.74 (13)
C3—S1—C2 103.12 (13) C15—S4—Ni2 93.14 (9)
C3—S1—Ni1 95.52 (9) C14—S4—Ni2 97.06 (8)
C2—S1—Ni1 96.06 (8) C12—O6—Ni2 119.89 (17)
| Bond/Angle | Value (E) |
|------------|-----------|
| C6—S2—C7  | 101.48 (13) |
| C6—S2—Ni1 | 96.67 (9)    |
| C7—S2—Ni1 | 95.58 (10)   |
| C4—O2—Ni1 | 121.22 (17)  |
| C8—O4—Ni1 | 123.77 (18)  |
| Ni1—O1W—H1WA | 116 (3)   |
| Ni1—O1W—H1WB | 117 (3) |
| H1WA—O1W—H1WB | 106 (4) |
| C1—N1—C5  | 119.7 (2)    |
| C1—N1—Ni1 | 119.71 (16)  |
| C5—N1—Ni1 | 120.41 (16)  |
| N1—C1—C5  | 120.2 (2)    |
| C5—C1—C2  | 118.9 (2)    |
| C5—C1—C2  | 120.9 (2)    |
| C1—C2—S1  | 116.34 (18)  |
| C1—C2—H2A | 108.2        |
| S1—C2—H2A | 108.2        |
| C1—C2—H2B | 108.2        |
| S1—C2—H2B | 108.2        |
| H2A—C2—H2B| 107.4        |
| C4—C3—S1  | 116.69 (19)  |
| C4—C3—H3A | 108.1        |
| S1—C3—H3A | 108.1        |
| C4—C3—H3B | 108.1        |
| S1—C3—H3B | 108.1        |
| H3A—C3—H3B| 107.3        |
| O1—C4—O2  | 124.7 (2)    |
| O1—C4—C3  | 114.8 (2)    |
| O2—C4—C3  | 120.5 (2)    |
| N1—C5—C1  | 120.1 (2)    |
| N1—C5—C6  | 119.1 (2)    |
| C1—C5—C6  | 120.7 (2)    |
| C5—C6—S2  | 115.43 (17)  |
| C5—C6—H6A | 108.4        |
| S2—C6—H6A | 108.4        |
| C5—C6—H6B | 108.4        |
| S2—C6—H6B | 108.4        |
| H6A—C6—H6B| 107.5        |
| C8—C7—S2  | 116.14 (19)  |
| C8—C7—H7A | 108.3        |
| S2—C7—H7A | 108.3        |
| C8—C7—H7B | 108.3        |
| S2—C7—H7B | 108.3        |
| H7A—C7—H7B| 107.4        |
| O3—C8—O4  | 124.9 (3)    |
| O3—C8—C7  | 116.4 (3)    |
| O4—C8—C7  | 118.7 (2)    |
| O8—Ni2—O2W| 90.24 (8)    |
| Bond                  | Value     | Bond                  | Value     |
|----------------------|-----------|----------------------|-----------|
| O8—Ni2—O6           | 176.47(8) | H8WA—O8W—H8WB        | 120(7)    |
| O2W—Ni2—O6          | 93.24(8)  | H9WA—O9W—H9WB        | 109(5)    |
| O8—Ni2—N2           | 86.76(8)  |                      |           |
| N1—C1—C2—S1        | −20.9(3)  | Ni1—S2—C7—C8        | 9.7(2)    |
| N1—C5—C6—S2        | −14.8(3)  | Ni1—O4—C8—O3        | 178.4(2)  |
| S1—C3—C4—O2        | −0.1(3)   | Ni1—O4—C8—C7        | −2.2(4)   |
| S2—C7—C8—O4        | −6.7(4)   | S2—C7—C8—O3         | 172.7(2)  |
| N2—C13—C14—S4      | −1.3(3)   | C13—N2—C9—C13       | −0.6(4)   |
| N2—C9—C10—S3       | −7.0(3)   | Ni2—N2—C9—C13       | −176.41(18) |
| S4—C15—C16—O8      | −21.9(3)  | C13—N2—C9—C10       | 179.5(2)  |
| S3—C11—C12—O6      | −27.6(4)  | Ni2—N2—C9—C10       | 3.7(3)    |
| C5—N1—C1—C5i       | −0.2(4)   | C13ii—C9—C10—S3     | 173.09(19) |
| Ni1—N1—C1—C5i      | −175.32(17) | C11—S3—C10—C9     | 101.2(2)  |
| C5—N1—C1—C2        | −177.5(2) | Ni2—S3—C10—C9       | 6.0(2)    |
| Ni1—N1—C1—C2       | 7.4(3)    | C10—S3—C11—C12      | −72.7(3)  |
| C5i—C1—C2—S1       | 161.87(19)| Ni2—S3—C11—C12      | 26.3(2)   |
| C3—S1—C2—C1        | −76.6(2)  | Ni2—O6—C12—O5       | −172.1(2) |
| Ni1—S1—C2—C1       | 20.51(19) | Ni2—O6—C12—C11      | 9.8(3)    |
| C2—S1—C3—C4        | 96.0(2)   | S3—C11—C12—O5       | 154.2(2)  |
| Ni1—S1—C3—C4       | −1.6(2)   | C9—N2—C13—C9         | 0.6(4)    |
| Ni1—O2—C4—O1       | −176.6(2) | Ni2—N2—C13—C9ii     | 176.44(18) |
| Ni1—O2—C4—C3       | 2.3(3)    | C9—N2—C13—C14       | −179.6(2) |
| S1—C3—C4—O1        | 178.92(19)| Ni2—N2—C13—C14      | −3.7(3)   |
| C1—N1—C5—C1i       | 0.2(4)    | C9i—C13—C14—S4      | 178.57(19) |
| Ni1—N1—C5—C1i      | 175.29(17)| C15—S4—C14—C13     | 99.1(2)   |
| C1—N1—C5—C6        | −178.5(2) | Ni2—S4—C14—C13      | 4.4(2)    |
| Ni1—N1—C5—C6       | −3.4(3)   | Ni2—S4—C14—C13      | 4.4(2)    |
| C1i—C5—C6—S2       | 166.52(19)| Ni2—S4—C15—C16      | 26.7(2)   |
| C7—S2—C6—C5        | −75.9(2)  | Ni2—O8—C16—O7       | 178.7(2)  |
| Ni1—S2—C6—C5       | 21.24(19) | Ni2—O8—C16—C15      | 0.2(3)    |
| C6—S2—C7—C8        | 107.7(2)  | S4—C15—C16—O7       | 159.5(2)  |

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, −y+1, −z.

Hydrogen-bond geometry (Å, °)

| Bond                  | Value     | Bond                  | Value     |
|----------------------|-----------|----------------------|-----------|
| O1W—H1WA···O1ii      | 0.90(5)   | H2—H8WA···O8Wii      | 1.78(5)   |
| O1W—H1WB···O5W       | 0.83(5)   | H2WA—H8WA···O8W      | 1.85(5)   |
| O2W—H2WA···O5v       | 0.88(5)   | H2WB—H8WB···O8W      | 1.80(5)   |
| O2W—H2WB···O1i       | 0.88(6)   | H2WB—H8WB···O8W      | 1.88(6)   |
| O3W—H3WA···O2        | 0.87(4)   | H3WA···O8W           | 2.02(4)   |
| O3W—H3WB···O8Wii     | 0.98(7)   | H3WB···O8W           | 1.87(7)   |
| O4W—H4WA···O8v       | 0.91(5)   | H4WA···O8W           | 1.83(5)   |
| O4W—H4WB···O6W       | 0.86(5)   | H4WB···O6W           | 1.88(5)   |
| O5W—H5WA···O7W       | 0.97(7)   | H5WA···O7W           | 1.88(7)   |
| O5W—H5WB···O5ii      | 0.80(5)   | H5WB···O5W           | 2.06(5)   |

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| Bond/Symmetry   | d (Å) | E (Å⁻¹) | D (Å⁻¹) | ϕ (°) |
|----------------|-------|---------|---------|-------|
| O6W—H6WA···O7  | 0.83  | 1.98    | 2.814   | 178   |
| O6W—H6WB···O3W  | 0.87  | 1.98    | 2.849   | 173   |
| O7W—H7WA···O9W  | 0.86  | 1.85    | 2.698   | 169   |
| O7W—H7WB···O6W  | 0.97  | 1.94    | 2.899   | 174   |
| O8W—H8WA···O7W  | 0.85  | 2.32    | 3.159   | 173   |
| O8W—H8WB···O3W  | 0.86  | 2.19    | 3.019   | 164   |
| O9W—H9WA···O4   | 0.82  | 1.93    | 2.752   | 174   |
| O9W—H9WB···O4W  | 0.84  | 1.90    | 2.731   | 171   |
| C2—H2A···O4W  | 0.99  | 2.35    | 3.324   | 167   |
| C2—H2B···O6W  | 0.99  | 2.55    | 3.308   | 133   |
| C3—H3A···O8W  | 0.99  | 2.55    | 3.488   | 159   |
| C6—H6A···O4W  | 0.99  | 2.43    | 3.413   | 173   |
| C6—H6B···O3W  | 0.99  | 2.60    | 3.365   | 134   |
| C6—H6B···O6W  | 0.99  | 2.58    | 3.334   | 133   |
| C10—H10B···O3W | 0.99  | 2.27    | 3.150   | 148   |
| C11—H11B···O5W | 0.99  | 2.52    | 3.303   | 136   |
| C11—H11B···O7W | 0.99  | 2.58    | 3.516   | 158   |
| C14—H14A···O9W | 0.99  | 2.45    | 3.260   | 139   |
| C14—H14B···O3  | 0.99  | 2.29    | 3.169   | 148   |
| C15—H15A···S3V | 0.99  | 2.84    | 3.609   | 135   |

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