



# Crystal structure of a nickel compound comprising two nickel(II) complexes with different ligand environments: $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2][\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$

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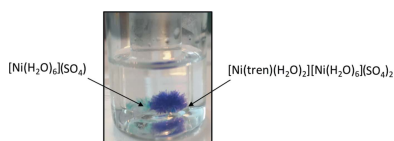
**Keywords:** crystal structure; nickel complexes; tren; tripodal ligand; hydrogen bonding.**CCDC reference:** 1911584**Supporting information:** this article has supporting information at journals.iucr.org/e

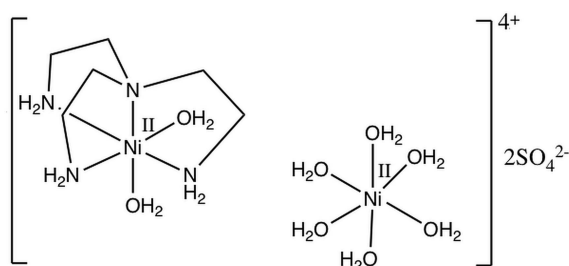
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The title compound, diaqua[tris(2-aminoethyl)amine]nickel(II) hexaaquanickel(II) bis(sulfate),  $[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{H}_2\text{O})_2][\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$  or  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2][\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ , consists of two octahedral nickel complexes within the same unit cell. These metal complexes are formed from the reaction of  $[\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)$  and the ligand tris(2-aminoethyl)amine (tren). The crystals of the title compound are purple, different from those of the starting complex  $[\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)$ , which are turquoise. The reaction was performed both in a 1:1 and 1:2 metal–ligand molar ratio, always yielding the co-precipitation of the two types of crystals. The asymmetric unit of the title compound, which crystallizes in the space group *Pnma*, consists of two half  $\text{Ni}^{\text{II}}$  complexes and a sulfate counter-anion. The mononuclear cationic complex  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]^{2+}$  comprises an Ni ion, the tren ligand and two water molecules, while the mononuclear complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  consists of another Ni ion surrounded by six coordinated water molecules. The  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]$  and  $[\text{Ni}(\text{H}_2\text{O})_6]$  subunits are connected to the  $\text{SO}_4^{2-}$  counter-anions through hydrogen bonding, thus consolidating the crystal structure.

## 1. Chemical context

Tris(2-aminoethyl)amine (tren) has been used extensively as an ancillary tripodal ligand for capping transition metals to form mononuclear and polynuclear complexes. The tren ligand has the capacity to chelate metal ions through its central tertiary amine and through its three terminal amine groups in a spider-like conformation, leaving one or two positions available for additional ligand coordination (Marzotto *et al.*, 1993; Albertin *et al.*, 1975; Blackman, 2005; Brines *et al.*, 2007). Metal complexes with a variety of ligands in which also tren is coordinating to the metal center have been proposed for applications in catalysis (Ruffin *et al.*, 2017), sensors, and as precursors of bioinorganic reactions (Sakai *et al.*, 1996). For instance, Ni(tren) complexes have been proposed for applications in biological systems (Salam & Aoki, 2001) or as a model to study enantioselective synthesis or asymmetric catalysis (Rao *et al.*, 2009), and as coordination polymers in magnetism, electrical conductivity and ion exchange (Park *et al.*, 2001; Tanase *et al.*, 1996).  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]$  was reported previously (Chen *et al.*, 2001; Pedersen *et al.*, 2014); however, to our knowledge, this is the first report of it co-crystallizing with the hexaaquo nickel complex  $[\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)$ .





## 2. Structural commentary

Fig. 1 shows the molecular structure of the title compound, which crystallizes in the space group  $Pnma$ . Its asymmetric unit comprises two half  $\text{Ni}^{\text{II}}$  complexes and a sulfate counteranion. Each Ni complex shows a different ligand environment: (i) the mononuclear cationic complex  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]^{2+}$  includes Ni1, the tren ligand and two water molecules; (ii) the mononuclear complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  consists of Ni2 surrounded by six coordinated water molecules.

Ni1 exhibits an octahedral geometry of the type  $\text{N}_4\text{O}_2$ , with the central N1 atom of the tren ligand occupying one of the axial positions and atoms N2, N3 and N2<sup>i</sup> occupying three of the equatorial positions [symmetry code: (i)  $x, -y + \frac{1}{2}, z$ ]. The remaining two positions, one axial (O2) and one equatorial (O1), are occupied by two oxygen atoms from the two water molecules. The bond lengths are similar for the Ni1–N bonds that are *trans* to oxygen atoms; for instance, Ni1–N1<sub>ax</sub> is 2.064 (2) Å and Ni1–N3<sub>eq</sub> is 2.069 (2) Å; a longer bond distance is observed between Ni1–N2<sub>eq</sub>, 2.122 (2), which is *trans* by symmetry to another nitrogen atom, N2<sup>i</sup>. The nickel–oxygen bond length is shorter for Ni1–O2<sub>ax</sub> at 2.094 (2) Å, in comparison to Ni1–O1<sub>eq</sub>, which is 2.140 (2) Å. The N3 and C3 atoms of the tren ligand lie on a mirror plane perpendicular to [010]. This results in a symmetry-induced disorder of the N3/C4/C3 fragment. The octahedral geometry around the Ni1 ion is reflected by the angles N1–Ni1–O2 = 178.42 (8)°, N2–Ni1–N2<sup>i</sup> = 164.74 (9)°, and N3–Ni1–O1 = 177.27 (8)°.

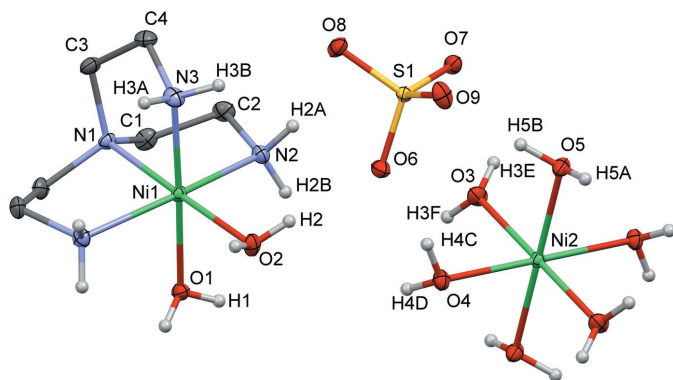


Figure 1

View of the molecular structure of the title compound with displacement ellipsoids drawn at the 20% probability level and labeling scheme for the symmetry-independent atoms. The  $\text{CH}_2$  hydrogen atoms have been omitted for clarity. The symmetry operations generating the equivalent atoms are  $1 - x, 1 - y, 2 - z$  and  $x, \frac{1}{2} - y, z$  for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]^{2+}$ , respectively.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 $\cdots$ O8 <sup>i</sup>	0.78 (2)	2.05 (2)	2.8212 (16)	172 (2)
O2–H2 $\cdots$ O6	0.81 (2)	1.96 (2)	2.7342 (15)	162 (3)
O3–H3E $\cdots$ O9 <sup>ii</sup>	0.81 (2)	1.94 (2)	2.731 (2)	167 (2)
O3–H3F $\cdots$ O7 <sup>i</sup>	0.85 (2)	2.05 (2)	2.8403 (18)	155 (2)
O4–H4C $\cdots$ O6	0.83 (2)	1.91 (2)	2.7249 (18)	171 (2)
O4–H4D $\cdots$ O8 <sup>i</sup>	0.83 (2)	1.95 (2)	2.7810 (18)	179 (2)
O5–H5A $\cdots$ O7 <sup>iii</sup>	0.88	2.02	2.8125 (19)	150
O5–H5B $\cdots$ O7	0.88	1.95	2.7826 (17)	160

Symmetry codes: (i)  $x + \frac{1}{2}, y, -z + \frac{3}{2}$ ; (ii)  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ .

The Ni2 ion of the mononuclear complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  also shows an octahedral geometry. In the asymmetric unit, the atom Ni2 sits on an inversion center on a screw axis along the  $b$ -axis direction. The Ni2–O<sub>water</sub> bond lengths with O3, O4 and O5 range between 2.051 (1) and 2.074 (1) Å, respectively, with angles of 180° due to symmetry.

## 3. Supramolecular features

The crystal structure of the title compound is consolidated through intermolecular hydrogen bonding between the water molecules from the  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]$  complex, the sulfate oxygen atoms and the water molecules from the  $[\text{Ni}(\text{H}_2\text{O})_6]$  complex (Fig. 2 and Table 1). In particular, the two water molecules of  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]$  form O1–H1 $\cdots$ O8<sup>i</sup> and O2–H2 $\cdots$ O6 hydrogen bonds of 2.05 (2) and 1.96 (2) Å respectively, involving two neighboring  $\text{SO}_4^{2-}$  anions [symmetry code: (i)  $x + \frac{1}{2}, y, -z + \frac{3}{2}$ ]. The  $[\text{Ni}(\text{H}_2\text{O})_6]$  complex is hydrogen bonded to adjacent  $\text{SO}_4^{2-}$  anions through O3–H3E $\cdots$ O9<sup>ii</sup>, O3–H3F $\cdots$ O7<sup>i</sup>, O4–H4C $\cdots$ O6, O4–H4D $\cdots$ O8<sup>i</sup>, O5–H5B $\cdots$ O7, O5–H5A $\cdots$ O7<sup>iii</sup> contacts [symmetry codes: (ii)  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ ]. These hydrogen-bond distances range from 1.905 (15) to 2.047 (18) Å. Additional weak hydrogen bonds are formed between the hydrogen atoms from the primary amine groups of the tren ligand and the sulfate oxygen atoms.

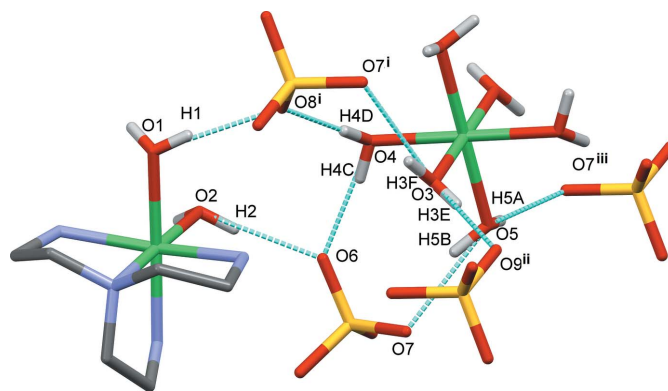


Figure 2

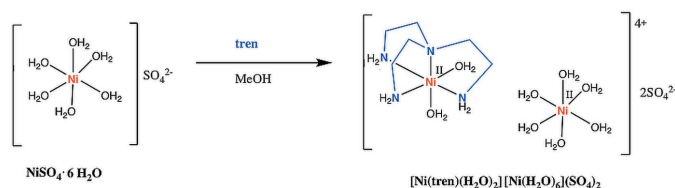
The hydrogen-bonding network (cyan dotted lines) in the title compound. Symmetry codes: (i)  $x + \frac{1}{2}, y, -z + \frac{3}{2}$ ; (ii)  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ .

#### 4. Database survey

A search for tris(2-aminoethyl)aminenickel complexes in the Cambridge Structural Database (CSD version 5.38, updated February 2019; Groom *et al.*, 2016) yielded 222 hits. Among these results, 124 hits contained the ligand tris(2-aminoethyl)amine capping the nickel ion, along with other types of ligands on the remaining coordination sites. Only two hits contain the diaqua[tris(2-aminoethyl)amine]nickel(II) complex, [Ni(tren)(H<sub>2</sub>O)<sub>2</sub>] (LUMVIY; Chen *et al.*, 2001; TIYQAT; Tanase *et al.*, 1996). More precisely, the asymmetric unit in LUMVIY comprises the [Ni(tren)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cation with two independent halves of a 1,5-naphthalenedisulfonate (1,5nds) ligand as counter-anion. A common feature of this structure with the title compound is the hydrogen bond network formed between the water molecules on the Ni(tren) motif with the counter anions. However, in the title compound, also the hydrogen atoms on the primary amine groups form hydrogen bonds with the sulfate anions, albeit quite weak. In TIYQAT, sulfate anions act as counter-ions for the [Ni(tren)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> complex, and uncoordinated water molecules are included in the crystal lattice. The angle between the Ni center and the two oxygen atoms from the coordinated water molecules are 86.52 (5)° (O7–Ni1–O8) and 86.9 (4)° (O5–Ni1–O6) for LUMVIY and TIYQAT, respectively. The corresponding angle O2–Ni–O1 in the title compound has a value of 88.70 (8)°, which is in good agreement with the reported values. The title compound is the first example of a crystal structure of [Ni(tren)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> co-crystallizing with the [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> complex.

#### 5. Synthesis and crystallization

The synthesis of the title compound is summarized in the reaction scheme shown in Fig. 3. NiSO<sub>4</sub>·6H<sub>2</sub>O and tris(2-aminoethyl)amine (tren) were used without further purification. A methanolic solution of NiSO<sub>4</sub>·6H<sub>2</sub>O (0.0265 g, 0.1 mmol) was added slowly to a tren (0.0146 g, 0.1 mmol) solution (4 mL MeOH) at room temperature. The resulting solution was stirred for two h and it changed color from light green to purple. The solution was then filtered through celite and evaporated under reduced pressure. Single crystals of the title compound were obtained by vapor diffusion of methanol into 2-propanol. In the crystallization process, two types of crystal were formed: the starting reagent hexahydrate nickel (II) complex (turquoise crystals) and the nickel(II) tren complex (purple crystals, Fig. 4). The reaction was performed both in a 1:1 and 1:2 metal–ligand molar ratio, always yielding



**Figure 3**  
Reaction scheme for the synthesis of [Ni(tren)(H<sub>2</sub>O)<sub>2</sub>][Ni(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>.

**Table 2**  
Experimental details.

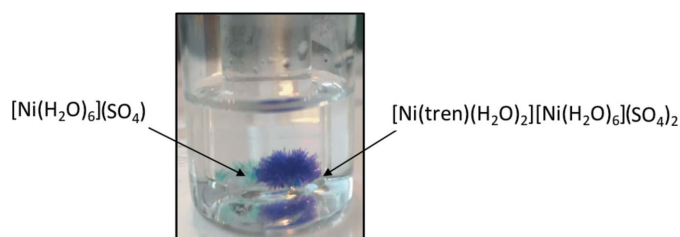
Crystal data	
Chemical formula	[Ni(C <sub>6</sub> H <sub>18</sub> N <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ][Ni(H <sub>2</sub> O) <sub>6</sub> ](SO <sub>4</sub> ) <sub>2</sub>
<i>M<sub>r</sub></i>	599.91
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.8937 (1), 21.3933 (2), 8.4468 (1)
<i>V</i> (Å <sup>3</sup> )	2149.25 (4)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	4.76
Crystal size (mm)	0.28 × 0.21 × 0.09
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Single source at offset/far, HyPix3000
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.353, 0.661
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	17858, 2044, 1996
<i>R<sub>int</sub></i> (sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.023 0.605
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.023, 0.063, 1.12
No. of reflections	2044
No. of parameters	173
No. of restraints	8
H-atom treatment	All H-atom parameters refined
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.37, −0.35

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXL2016* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

the title compound. IR data: 3265 (*m*), 3171 (*m*), 2937 (*w*), 2891 (*w*), 1607 (*m*), 1472 (*w*) 1338 (*w*), 1054 (*s*), 984 (*m*), 885 (*m*), 750 (*w*), 685 (*w*).

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were included in geometrically calculated positions for the alkyl and amine groups using a riding model: C–H = 0.97 Å and N–H = 0.89 Å with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C, N). The hydrogen atoms of the water molecules were located from the difference-Fourier map; they were refined freely in the case of O1 and O2, with a DFIX of 0.85 (2) Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O) in the case of O3 and O4, and riding with O–H = 0.88 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O) in the case of O5.



**Figure 4**  
Crystallization of [Ni(tren)(H<sub>2</sub>O)<sub>2</sub>][Ni(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub> and [Ni(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub> in the same reaction vial.

The N3 and C3 atoms of the tren ligand lie on a mirror plane perpendicular to [010]. This results in a symmetry-induced disorder of the N3/C4/C3 fragment.

### Acknowledgements

We are grateful to the Department of Natural Science at UPR Carolina Campus (Department of Education, grant No. PO31S130068; however, those contents do not necessarily represent the policy of the Department of Education, and you should not assume endorsement by the Federal Government) and the University of Puerto Rico's Molecular Sciences Research Center for the use of the Rigaku XTLab SuperNova diffractometer. Special thanks to Dr Indranil Chakraborty for consultation on the final refinement of the structure.

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## supporting information

*Acta Cryst.* (2020). E76, 314-317 [https://doi.org/10.1107/S2056989020001358]

## Crystal structure of a nickel compound comprising two nickel(II) complexes with different ligand environments: $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2][\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$

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### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *olex2.solve* (Bourhis *et al.*, 2015); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### Diaqua[tris(2-aminoethyl)amine]nickel(II) hexaaquanickel(II) bis(sulfate)

#### Crystal data

$[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{H}_2\text{O})_2][\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$

$M_r = 599.91$

Orthorhombic, *Pnma*

$a = 11.8937$  (1) Å

$b = 21.3933$  (2) Å

$c = 8.4468$  (1) Å

$V = 2149.25$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 1256$

$D_x = 1.854$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 14387 reflections

$\theta = 3.7\text{--}68.8^\circ$

$\mu = 4.76$  mm<sup>-1</sup>

$T = 293$  K

Block, clear violet

$0.28 \times 0.21 \times 0.09$  mm

#### Data collection

Rigaku Oxford Diffraction SuperNova, Single source at offset/far, HyPix3000 diffractometer

$\omega$  scans

Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)

$T_{\min} = 0.353$ ,  $T_{\max} = 0.661$

17858 measured reflections

2044 independent reflections

1996 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 68.9^\circ$ ,  $\theta_{\min} = 4.1^\circ$

$h = -14 \rightarrow 14$

$k = -25 \rightarrow 25$

$l = -10 \rightarrow 10$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.063$

$S = 1.12$

2044 reflections

173 parameters

8 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 1.2986P]$

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

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

$\Delta\rho_{\max} = 0.37$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

Extinction correction: SHELXL2016 (Sheldrick, 2015),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00044 (5)

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1	0.31517 (3)	0.250000	0.58049 (4)	0.01987 (12)	
O1	0.49430 (15)	0.250000	0.5573 (2)	0.0285 (4)	
H1	0.523 (2)	0.2795 (11)	0.592 (3)	0.042 (7)*	
O2	0.33527 (17)	0.250000	0.8268 (2)	0.0315 (4)	
H2	0.304 (2)	0.2795 (11)	0.867 (3)	0.056 (8)*	
N1	0.29062 (16)	0.250000	0.3386 (2)	0.0237 (4)	
N2	0.32729 (13)	0.34830 (7)	0.55183 (18)	0.0291 (3)	
H2A	0.275056	0.367313	0.609911	0.035*	
H2B	0.394537	0.361563	0.583583	0.035*	
N3	0.14137 (18)	0.250000	0.5913 (3)	0.0330 (5)	
H3A	0.116429	0.211740	0.613150	0.040*	0.5
H3B	0.118127	0.275722	0.667351	0.040*	0.5
C1	0.34686 (17)	0.30780 (9)	0.2826 (2)	0.0336 (4)	
H1A	0.327506	0.315269	0.172689	0.040*	
H1B	0.427761	0.302752	0.289509	0.040*	
C2	0.31074 (17)	0.36314 (9)	0.3821 (2)	0.0362 (4)	
H2C	0.354856	0.399608	0.353854	0.043*	
H2D	0.232177	0.372476	0.362353	0.043*	
C3	0.1684 (2)	0.250000	0.3008 (3)	0.0344 (6)	
H3C	0.145952	0.208172	0.269741	0.041*	0.5
H3D	0.154994	0.277594	0.211689	0.041*	0.5
C4	0.0975 (3)	0.27067 (19)	0.4375 (5)	0.0384 (10)	0.5
H4A	0.092804	0.315934	0.437065	0.046*	0.5
H4B	0.022018	0.254369	0.424014	0.046*	0.5
Ni2	0.500000	0.500000	1.000000	0.02058 (12)	
O3	0.46413 (12)	0.51163 (6)	0.76229 (15)	0.0337 (3)	
H3E	0.4398 (19)	0.5433 (9)	0.723 (2)	0.051*	
H3F	0.5103 (18)	0.4984 (11)	0.693 (2)	0.051*	
O4	0.47512 (11)	0.40611 (6)	0.96546 (16)	0.0291 (3)	
H4C	0.4079 (14)	0.3972 (9)	0.956 (3)	0.044*	
H4D	0.5051 (17)	0.3935 (9)	0.883 (2)	0.044*	
O5	0.33269 (10)	0.51618 (6)	1.05567 (15)	0.0309 (3)	
H5A	0.320545	0.510448	1.156884	0.046*	
H5B	0.288625	0.490680	1.003402	0.046*	
S1	0.14894 (3)	0.39419 (2)	0.92733 (4)	0.02016 (12)	
O6	0.26060 (10)	0.36508 (6)	0.92041 (16)	0.0339 (3)	
O7	0.15935 (10)	0.46130 (5)	0.88353 (15)	0.0297 (3)	
O8	0.07525 (11)	0.36247 (6)	0.81077 (16)	0.0341 (3)	
O9	0.10124 (13)	0.38801 (6)	1.08500 (15)	0.0408 (4)	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.0238 (2)	0.0199 (2)	0.0160 (2)	0.000	-0.00128 (15)	0.000
O1	0.0262 (9)	0.0235 (9)	0.0357 (10)	0.000	-0.0058 (8)	0.000
O2	0.0465 (11)	0.0277 (10)	0.0203 (9)	0.000	-0.0002 (8)	0.000
N1	0.0257 (10)	0.0280 (10)	0.0172 (9)	0.000	-0.0027 (8)	0.000
N2	0.0326 (8)	0.0234 (7)	0.0313 (8)	0.0027 (6)	-0.0018 (6)	-0.0024 (6)
N3	0.0275 (11)	0.0381 (12)	0.0335 (12)	0.000	0.0076 (9)	0.000
C1	0.0396 (10)	0.0397 (11)	0.0214 (9)	-0.0057 (8)	0.0016 (8)	0.0098 (8)
C2	0.0439 (10)	0.0254 (9)	0.0392 (11)	-0.0015 (8)	-0.0059 (9)	0.0115 (8)
C3	0.0316 (13)	0.0423 (15)	0.0292 (13)	0.000	-0.0114 (11)	0.000
C4	0.0252 (16)	0.046 (2)	0.044 (2)	0.0077 (14)	-0.0074 (15)	-0.0045 (16)
Ni2	0.0226 (2)	0.0206 (2)	0.0185 (2)	-0.00029 (15)	-0.00085 (15)	-0.00050 (15)
O3	0.0442 (8)	0.0364 (7)	0.0206 (6)	0.0102 (6)	-0.0007 (6)	0.0031 (5)
O4	0.0297 (6)	0.0264 (6)	0.0312 (7)	-0.0037 (5)	0.0030 (6)	-0.0036 (5)
O5	0.0258 (6)	0.0392 (7)	0.0279 (6)	-0.0029 (5)	0.0000 (5)	-0.0073 (6)
S1	0.0224 (2)	0.0187 (2)	0.0193 (2)	-0.00018 (14)	-0.00065 (14)	0.00073 (14)
O6	0.0255 (6)	0.0294 (7)	0.0468 (8)	0.0032 (5)	-0.0021 (6)	-0.0059 (6)
O7	0.0369 (7)	0.0207 (6)	0.0316 (7)	-0.0039 (5)	-0.0083 (5)	0.0049 (5)
O8	0.0378 (7)	0.0280 (6)	0.0364 (7)	-0.0079 (5)	-0.0130 (6)	0.0017 (5)
O9	0.0594 (9)	0.0344 (7)	0.0284 (7)	0.0040 (7)	0.0168 (6)	0.0024 (6)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ni1—O1	2.1395 (18)	C2—H2D	0.9700
Ni1—O2	2.0940 (19)	C3—H3C	0.9700
Ni1—N1	2.0640 (19)	C3—H3C <sup>i</sup>	0.9700
Ni1—N2	2.1217 (15)	C3—H3D	0.9700
Ni1—N2 <sup>i</sup>	2.1217 (15)	C3—H3D <sup>i</sup>	0.9700
Ni1—N3	2.069 (2)	C3—C4	1.496 (4)
O1—H1	0.78 (2)	C4—H4A	0.9700
O1—H1 <sup>i</sup>	0.78 (2)	C4—H4B	0.9700
O2—H2	0.81 (2)	Ni2—O3 <sup>ii</sup>	2.0678 (13)
O2—H2 <sup>i</sup>	0.81 (2)	Ni2—O3	2.0678 (13)
N1—C1	1.483 (2)	Ni2—O4 <sup>ii</sup>	2.0511 (13)
N1—C1 <sup>i</sup>	1.483 (2)	Ni2—O4	2.0511 (13)
N1—C3	1.488 (3)	Ni2—O5	2.0739 (12)
N2—H2A	0.8900	Ni2—O5 <sup>ii</sup>	2.0739 (12)
N2—H2B	0.8900	O3—H3E	0.808 (15)
N2—C2	1.481 (2)	O3—H3F	0.851 (15)
N3—H3A <sup>i</sup>	0.8900	O4—H4C	0.826 (15)
N3—H3A	0.8900	O4—H4D	0.830 (15)
N3—H3B	0.8900	O5—H5A	0.8756
N3—H3B <sup>i</sup>	0.8900	O5—H5B	0.8759
N3—C4	1.468 (4)	S1—O6	1.4679 (13)
C1—H1A	0.9700	S1—O7	1.4878 (12)
C1—H1B	0.9700	S1—O8	1.4826 (12)

C1—C2	1.514 (3)	S1—O9	1.4537 (13)
C2—H2C	0.9700		
O2—Ni1—O1	88.70 (8)	C1—C2—H2D	109.8
O2—Ni1—N2	96.06 (4)	H2C—C2—H2D	108.2
O2—Ni1—N2 <sup>i</sup>	96.06 (4)	N1—C3—H3C <sup>i</sup>	109.06 (3)
N1—Ni1—O1	92.87 (8)	N1—C3—H3C	109.1
N1—Ni1—O2	178.42 (8)	N1—C3—H3D <sup>i</sup>	109.07 (10)
N1—Ni1—N2 <sup>i</sup>	84.07 (4)	N1—C3—H3D	109.1
N1—Ni1—N2	84.07 (4)	N1—C3—C4	112.6 (2)
N1—Ni1—N3	84.39 (9)	H3C—C3—H3C <sup>i</sup>	134.6
N2 <sup>i</sup> —Ni1—O1	85.52 (4)	H3C <sup>i</sup> —C3—H3D <sup>i</sup>	107.8
N2—Ni1—O1	85.52 (4)	H3C—C3—H3D	107.8
N2 <sup>i</sup> —Ni1—N2	164.74 (9)	H3C—C3—H3D <sup>i</sup>	35.2
N3—Ni1—O1	177.27 (8)	H3D—C3—H3C <sup>i</sup>	35.2
N3—Ni1—O2	94.03 (9)	H3D—C3—H3D <sup>i</sup>	75.0
N3—Ni1—N2 <sup>i</sup>	94.18 (4)	C4—C3—H3C	109.1
N3—Ni1—N2	94.18 (4)	C4—C3—H3C <sup>i</sup>	77.37 (16)
Ni1—O1—H1 <sup>i</sup>	113.6 (18)	C4—C3—H3D <sup>i</sup>	133.34 (17)
Ni1—O1—H1	113.6 (18)	C4—C3—H3D	109.1
H1—O1—H1 <sup>i</sup>	109 (3)	N3—C4—H3A <sup>i</sup>	34.21 (10)
Ni1—O2—H2	111.3 (19)	N3—C4—C3	113.2 (3)
Ni1—O2—H2 <sup>i</sup>	111.3 (19)	N3—C4—H4A	108.9
H2—O2—H2 <sup>i</sup>	103 (4)	N3—C4—H4B	108.9
C1 <sup>i</sup> —N1—Ni1	104.58 (11)	C3—C4—H3A <sup>i</sup>	136.9 (3)
C1—N1—Ni1	104.58 (11)	C3—C4—H4A	108.9
C1—N1—C1 <sup>i</sup>	113.0 (2)	C3—C4—H4B	108.9
C1—N1—C3	111.85 (12)	H4A—C4—H3A <sup>i</sup>	76.7
C1 <sup>i</sup> —N1—C3	111.85 (12)	H4A—C4—H4B	107.8
C3—N1—Ni1	110.50 (15)	H4B—C4—H3A <sup>i</sup>	109.6
Ni1—N2—H2A	110.0	O3 <sup>ii</sup> —Ni2—O3	180.0
Ni1—N2—H2B	110.0	O3 <sup>ii</sup> —Ni2—O5	89.88 (5)
H2A—N2—H2B	108.4	O3—Ni2—O5	90.12 (5)
C2—N2—Ni1	108.29 (11)	O3 <sup>ii</sup> —Ni2—O5 <sup>ii</sup>	90.12 (5)
C2—N2—H2A	110.0	O3—Ni2—O5 <sup>ii</sup>	89.88 (5)
C2—N2—H2B	110.0	O4—Ni2—O3 <sup>ii</sup>	92.87 (5)
Ni1—N3—H3A	110.0	O4 <sup>ii</sup> —Ni2—O3	92.87 (5)
Ni1—N3—H3A <sup>i</sup>	110.008 (12)	O4—Ni2—O3	87.13 (5)
Ni1—N3—H3B <sup>i</sup>	110.01 (5)	O4 <sup>ii</sup> —Ni2—O3 <sup>ii</sup>	87.13 (5)
Ni1—N3—H3B	110.0	O4 <sup>ii</sup> —Ni2—O4	180.0
H3A—N3—H3A <sup>i</sup>	133.8	O4 <sup>ii</sup> —Ni2—O5 <sup>ii</sup>	93.28 (5)
H3A—N3—H3B	108.4	O4 <sup>ii</sup> —Ni2—O5	86.72 (5)
H3A—N3—H3B <sup>i</sup>	34.7	O4—Ni2—O5 <sup>ii</sup>	86.72 (5)
H3A <sup>i</sup> —N3—H3B <sup>i</sup>	108.4	O4—Ni2—O5	93.28 (5)
H3B—N3—H3A <sup>i</sup>	34.7	O5—Ni2—O5 <sup>ii</sup>	180.00 (7)
H3B—N3—H3B <sup>i</sup>	76.4	Ni2—O3—H3E	124.9 (15)
C4—N3—Ni1	108.42 (19)	Ni2—O3—H3F	119.7 (15)
C4—N3—H3A	110.0	H3E—O3—H3F	103 (2)



C4—N3—H3A <sup>i</sup>	77.77 (16)	Ni2—O4—H4C	112.3 (14)
C4—N3—H3B	110.0	Ni2—O4—H4D	112.1 (14)
C4—N3—H3B <sup>i</sup>	135.62 (17)	H4C—O4—H4D	105 (2)
N1—C1—H1A	109.6	Ni2—O5—H5A	110.9
N1—C1—H1B	109.6	Ni2—O5—H5B	110.8
N1—C1—C2	110.31 (15)	H5A—O5—H5B	107.8
H1A—C1—H1B	108.1	O6—S1—O7	108.92 (8)
C2—C1—H1A	109.6	O6—S1—O8	108.32 (8)
C2—C1—H1B	109.6	O8—S1—O7	109.01 (7)
N2—C2—C1	109.38 (14)	O9—S1—O6	110.55 (9)
N2—C2—H2C	109.8	O9—S1—O7	110.37 (8)
N2—C2—H2D	109.8	O9—S1—O8	109.63 (8)
C1—C2—H2C	109.8		
Ni1—N1—C1—C2	-48.90 (17)	N1—C3—C4—N3	-35.8 (3)
Ni1—N1—C3—C4	18.68 (18)	C1 <sup>i</sup> —N1—C1—C2	-162.01 (12)
Ni1—N2—C2—C1	-27.22 (18)	C1—N1—C3—C4	-97.4 (2)
Ni1—N3—C4—C3	34.2 (3)	C1 <sup>i</sup> —N1—C3—C4	134.7 (2)
N1—C1—C2—N2	52.2 (2)	C3—N1—C1—C2	70.7 (2)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O8 <sup>iii</sup>	0.78 (2)	2.05 (2)	2.8212 (16)	172 (2)
O2—H2 $\cdots$ O6	0.81 (2)	1.96 (2)	2.7342 (15)	162 (3)
O3—H3E $\cdots$ O9 <sup>iv</sup>	0.81 (2)	1.94 (2)	2.731 (2)	167 (2)
O3—H3F $\cdots$ O7 <sup>iii</sup>	0.85 (2)	2.05 (2)	2.8403 (18)	155 (2)
O4—H4C $\cdots$ O6	0.83 (2)	1.91 (2)	2.7249 (18)	171 (2)
O4—H4D $\cdots$ O8 <sup>iii</sup>	0.83 (2)	1.95 (2)	2.7810 (18)	179 (2)
O5—H5A $\cdots$ O7 <sup>v</sup>	0.88	2.02	2.8125 (19)	150
O5—H5B $\cdots$ O7	0.88	1.95	2.7826 (17)	160

Symmetry codes: (iii)  $x+1/2, y, -z+3/2$ ; (iv)  $-x+1/2, -y+1, z-1/2$ ; (v)  $-x+1/2, -y+1, z+1/2$ .