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# Tetraaqua(2,2′-diamino-4,4′-bi-1,3-thiazole-$\kappa^2N^3,N^{3'}$)nickel(II) bis(pyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)nickel(II) trihydrate

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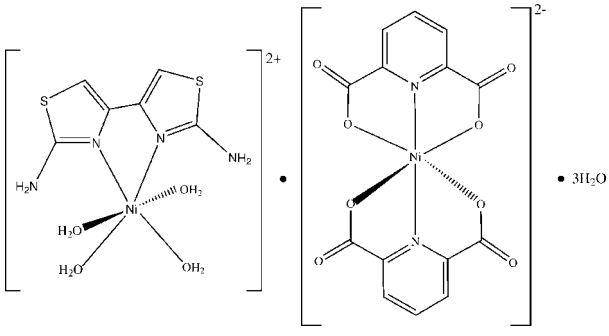
Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.034; $wR$ factor = 0.084; data-to-parameter ratio = 12.3.

The crystal structure of the title compound, $[Ni(C_6H_6N_4S_2)(H_2O)_4][Ni(C_7H_3NO_4)_2]\cdot 3H_2O$, consists of $Ni^{II}$ complex cations, $Ni^{II}$ complex anions and lattice water molecules. The $Ni^{II}$ ions in both the complex cation and anion assume a distorted octahedral coordination geometry. O—H···O, N—H···O and C—H···S hydrogen bonds occur in the crystal structure.

## Related literature

For general background, see: Waring (1981); Fisher *et al.* (1985). For a related structure, see: Liu *et al.* (2003); Zhang *et al.* (2006). For synthesis, see: Erlenmeyer (1948).



## Experimental

### Crystal data

$[Ni(C_6H_6N_4S_2)(H_2O)_4][Ni(C_7H_3NO_4)_2]\cdot 3H_2O$
$M_r$ = 772.01
Triclinic, $P\overline{1}$
$a$ = 11.4756 (13) Å
$b$ = 11.5609 (13) Å
$c$ = 13.2667 (15) Å
$\alpha$ = 65.3590 (10)°
$\beta$ = 82.1140 (11)°
$\gamma$ = 66.0180 (10)°
$V$ = 1460.6 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.51 mm$^{-1}$
$T$ = 295 K
0.23 × 0.18 × 0.15 mm

### Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.710, $T_{max}$ = 0.795
7580 measured reflections
5052 independent reflections
4181 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084
$S$ = 1.05
5052 reflections
412 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.43 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1$A$···O14$^{i}$ | 0.86 | 1.75 | 2.606 (3) | 174 |
| O1—H1$B$···O21$^{ii}$ | 0.82 | 1.92 | 2.747 (3) | 176 |
| O2—H2$A$···O12$^{iii}$ | 0.77 | 2.01 | 2.772 (3) | 169 |
| O2—H2$B$···O22$^{ii}$ | 0.76 | 2.12 | 2.874 (3) | 170 |
| O3—H3$A$···O3$W^{ii}$ | 0.78 | 1.98 | 2.742 (3) | 169 |
| O3—H3$B$···O11$^{iii}$ | 0.75 | 1.94 | 2.683 (3) | 173 |
| O4—H4$A$···O24$^{iv}$ | 0.83 | 1.89 | 2.717 (4) | 179 |
| O4—H4$B$···O1$W$ | 0.74 | 2.16 | 2.820 (4) | 149 |
| O1$W$—H1$WA$···O23$^{iv}$ | 0.91 | 2.01 | 2.907 (4) | 166 |
| O1$W$—H1$WB$···O24$^{iii}$ | 0.75 | 2.41 | 3.150 (5) | 169 |
| O2$W$—H2$WB$···O3$W^{v}$ | 0.72 | 2.41 | 3.104 (4) | 162 |
| O2$W$—H2$WA$···O14 | 0.79 | 2.02 | 2.815 (4) | 174 |
| O3$W$—H3$WA$···O22$^{vi}$ | 0.73 | 2.24 | 2.934 (3) | 158 |
| O3$W$—H3$WB$···O21 | 0.88 | 2.10 | 2.892 (3) | 149 |
| N32—H32$A$···O12 | 0.98 | 1.97 | 2.940 (5) | 169 |
| N32—H32$B$···O2 | 0.95 | 2.19 | 2.996 (5) | 142 |
| N34—H34$A$···O2$W^{vii}$ | 0.92 | 1.98 | 2.886 (4) | 168 |
| N34—H34$B$···O3 | 0.92 | 2.12 | 2.952 (4) | 149 |
| C12—H12···S31 | 0.93 | 2.71 | 3.631 (4) | 170 |

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2461).

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# supporting information

*Acta Cryst.* (2009). E**65**, m277–m278 [doi:10.1107/S1600536809004589]

# Tetraaqua(2,2′-diamino-4,4′-bi-1,3-thiazole-$\kappa^2N^3,N^{3'}$)nickel(II) bis(pyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)nickel(II) trihydrate

**Bing-Xin Liu, Yan-Ping Yu, Zen Cao and Liang-Jun Zhang**

## S1. Comment

Transition metal complexes of 2,2′-diamino-4,4′-bi-1,3-thiazole (DABT) have shown potential application in some fields, for example, a $Co^{II}$ complex and a $Ni^{II}$ complex with the DABT ligand have been found to be effective inhibitors of DNA synthesis of tumor cell (Waring, 1981; Fisher *et al.*, 1985). As part of serial structural investigation of metal complexes with DABT, the title $Ni^{II}$ complex was prepared in the laboratory and its X-ray structure is presented here.

The crystal of title compound consists of $Ni^{II}$ complex cations, $Ni^{II}$ complex anions and lattice water molecules (Fig. 1). Within the complex cation, the $Ni^{II}$ ion is coordinated by a DABT ligand and four water molecules in a distorted octahedral geometry. The thiazole rings of DABT are approximately coplanar with the dihedral angle of 6.2 (2)° between thiazole rings. The average of Ni—N bond distance of 2.082 (2) Å is comparable to the Ni—N bond distance of 2.103 (4) Å found in $[Ni(C_6H_6N_4S_2)_2(H_2O)_2][Ni(C_7H_3NO_4)_2].5(H_2O)$ (Zhang *et al.*, 2006) and 2.113 (2) Å found in $[Ni(C_8H_4O_4)(C_6H_6N_4S_2)_2].3.5H_2O$ (Liu *et al.*, 2003).

In the complex anion, the $Ni^{II}$ ion is chelated by two pyridinedicarboxylate (pdc) dianions with a distorted octahedral geometry. Two planar pdc ligands are nearly perpendicular to each other, the dihedral angle being 88.46 (8)°.

The extensive hydrogen bonding between lattice water molecules, complex cainos and complex anions helps to stabilize the crystal structure (Table 1).

## S2. Experimental

The microcrystals of DABT were obtained in the manner reported by Erlenmeyer (1948). An aqueous solution (20 ml) containing DABT (0.20 g, 1 mmol) and $NiCl_2$ (0.13 g, 1 mmol) was mixed with another aqueous solution (10 ml) of 2,6-pyridinedicarboxylic acid (0.17 g, 1 mmol) and NaOH (0.08 g, 2 mmol). The mixture was refluxed for 6 h. The solution was filtered after cooling to room temperature. Green single crystals were obtained from the filtrate after 30 d.

## S3. Refinement

Aromatic H atoms were placed in calculated positions with C—H = 0.93 Å and were included in the final cycles of refinement in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms on N atom of amino group of DABT and on O atom of water molecules were located in a difference Fourier map and also included in the final cycles of refinement in riding mode with $U_{iso}(H) = 1.5U_{eq}(O)$ or $1.2U_{eq}(N)$.

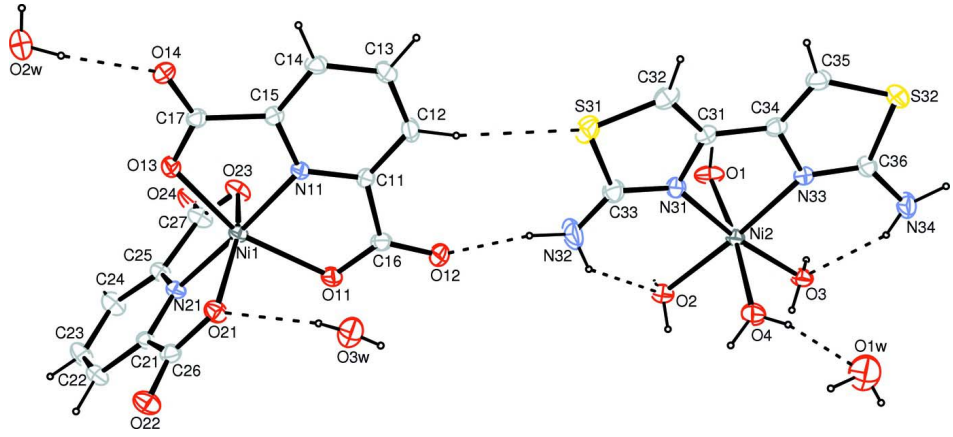


**Figure 1**

The molecular structure of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms), dashed lines showing the hydrogen bonding.

## Tetraaqua(2,2′-diamino-4,4′-bi-1,3-thiazole-$\kappa^2N^3,N^{3'}$)nickel(II) bis(pyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)nickel(II) trihydrate

*Crystal data*

$[Ni(C_6H_6N_4S_2)(H_2O)_4][Ni(C_7H_3NO_4)_2]\cdot 3H_2O$
$M_r = 772.01$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 11.4756\ (13)$ Å
$b = 11.5609\ (13)$ Å
$c = 13.2667\ (15)$ Å
$\alpha = 65.359\ (1)°$
$\beta = 82.1140\ (11)°$
$\gamma = 66.018\ (1)°$
$V = 1460.6\ (3)$ Å$^3$
$Z = 2$
$F(000) = 792$
$D_x = 1.755$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4980 reflections
$\theta = 2.0–25.0°$
$\mu = 1.51$ mm$^{-1}$
$T = 295$ K
Prism, green
0.23 × 0.18 × 0.15 mm

*Data collection*

Bruker APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.710$, $T_{max} = 0.795$
7580 measured reflections
5052 independent reflections
4181 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
$h = -13\rightarrow7$
$k = -13\rightarrow13$
$l = -15\rightarrow15$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$
$S = 1.05$
5052 reflections
412 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.7271P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.31$ e Å$^{-3}$
$\Delta\rho_{min} = -0.43$ e Å$^{-3}$

*Special details*

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

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ni1 | 0.16770 (3) | 0.07786 (4) | 0.17826 (3) | 0.02475 (11) |
| Ni2 | 0.23271 (3) | 0.51033 (4) | 0.71455 (3) | 0.02385 (11) |
| O1 | 0.2614 (2) | 0.3223 (2) | 0.84334 (17) | 0.0390 (6) |
| H1A | 0.3396 | 0.2657 | 0.8611 | 0.059* |
| H1B | 0.2134 | 0.3025 | 0.8940 | 0.059* |
| O2 | 0.06240 (19) | 0.4957 (2) | 0.68468 (17) | 0.0343 (5) |
| H2A | −0.0007 | 0.5604 | 0.6691 | 0.051* |
| H2B | 0.0430 | 0.4451 | 0.7356 | 0.051* |
| O3 | 0.13816 (18) | 0.6134 (2) | 0.81574 (16) | 0.0319 (5) |
| H3A | 0.1392 | 0.5667 | 0.8783 | 0.048* |
| H3B | 0.0692 | 0.6533 | 0.7976 | 0.048* |
| O4 | 0.1730 (2) | 0.7000 (2) | 0.58611 (17) | 0.0414 (6) |
| H4A | 0.1238 | 0.7351 | 0.5318 | 0.062* |
| H4B | 0.1773 | 0.7579 | 0.5939 | 0.062* |
| O11 | 0.10601 (19) | 0.2234 (2) | 0.25192 (17) | 0.0337 (5) |
| O12 | 0.1791 (2) | 0.2960 (2) | 0.35197 (18) | 0.0389 (5) |
| O13 | 0.29701 (19) | −0.0576 (2) | 0.11358 (17) | 0.0326 (5) |
| O14 | 0.50368 (19) | −0.1545 (2) | 0.08943 (17) | 0.0349 (5) |
| O21 | 0.10956 (19) | 0.2430 (2) | 0.01530 (16) | 0.0311 (5) |
| O22 | −0.0369 (2) | 0.3366 (2) | −0.12130 (17) | 0.0382 (5) |
| O23 | 0.1450 (2) | −0.0753 (2) | 0.32817 (17) | 0.0362 (5) |
| O24 | 0.0132 (3) | −0.1844 (3) | 0.4064 (2) | 0.0612 (8) |
| N11 | 0.3291 (2) | 0.0700 (2) | 0.21889 (19) | 0.0232 (5) |
| N21 | 0.0100 (2) | 0.0718 (2) | 0.14401 (19) | 0.0239 (5) |
| N31 | 0.3493 (2) | 0.4052 (2) | 0.62139 (19) | 0.0290 (6) |
| N32 | 0.2175 (3) | 0.3633 (4) | 0.5323 (3) | 0.0644 (10) |
| H32A | 0.2169 | 0.3353 | 0.4722 | 0.077* |
| H32B | 0.1419 | 0.4222 | 0.5525 | 0.077* |
| N33 | 0.4079 (2) | 0.5113 (2) | 0.74188 (19) | 0.0257 (5) |
| N34 | 0.3714 (3) | 0.6488 (3) | 0.8419 (2) | 0.0467 (8) |
| H34A | 0.4167 | 0.6570 | 0.8887 | 0.056* |
| H34B | 0.2868 | 0.6592 | 0.8476 | 0.056* |

| | | | | |
|---|---|---|---|---|
| S31 | 0.47085 (9) | 0.26783 (9) | 0.50388 (7) | 0.0432 (2) |
| S32 | 0.61255 (8) | 0.50673 (9) | 0.80414 (8) | 0.0412 (2) |
| C11 | 0.3283 (3) | 0.1372 (3) | 0.2798 (2) | 0.0248 (6) |
| C12 | 0.4413 (3) | 0.1217 (3) | 0.3184 (3) | 0.0343 (7) |
| H12 | 0.4412 | 0.1698 | 0.3597 | 0.041* |
| C13 | 0.5547 (3) | 0.0337 (3) | 0.2948 (3) | 0.0360 (8) |
| H13 | 0.6320 | 0.0210 | 0.3209 | 0.043* |
| C14 | 0.5528 (3) | −0.0360 (3) | 0.2316 (3) | 0.0297 (7) |
| H14 | 0.6284 | −0.0953 | 0.2148 | 0.036* |
| C15 | 0.4374 (3) | −0.0157 (3) | 0.1945 (2) | 0.0238 (6) |
| C16 | 0.1940 (3) | 0.2267 (3) | 0.2975 (2) | 0.0279 (7) |
| C17 | 0.4124 (3) | −0.0821 (3) | 0.1264 (2) | 0.0263 (6) |
| C21 | −0.0484 (3) | 0.1524 (3) | 0.0445 (2) | 0.0238 (6) |
| C22 | −0.1516 (3) | 0.1387 (3) | 0.0152 (2) | 0.0316 (7) |
| H22 | −0.1932 | 0.1958 | −0.0540 | 0.038* |
| C23 | −0.1914 (3) | 0.0377 (4) | 0.0917 (3) | 0.0384 (8) |
| H23 | −0.2598 | 0.0254 | 0.0737 | 0.046* |
| C24 | −0.1295 (3) | −0.0449 (3) | 0.1947 (3) | 0.0356 (8) |
| H24 | −0.1557 | −0.1127 | 0.2467 | 0.043* |
| C25 | −0.0284 (3) | −0.0246 (3) | 0.2186 (2) | 0.0279 (7) |
| C26 | 0.0113 (3) | 0.2535 (3) | −0.0281 (2) | 0.0267 (7) |
| C27 | 0.0489 (3) | −0.1018 (3) | 0.3268 (3) | 0.0361 (8) |
| C31 | 0.4781 (3) | 0.3740 (3) | 0.6331 (2) | 0.0270 (7) |
| C32 | 0.5566 (3) | 0.3003 (3) | 0.5773 (3) | 0.0382 (8) |
| H32 | 0.6450 | 0.2712 | 0.5783 | 0.046* |
| C33 | 0.3309 (3) | 0.3552 (3) | 0.5550 (3) | 0.0364 (8) |
| C34 | 0.5109 (3) | 0.4281 (3) | 0.7014 (2) | 0.0281 (7) |
| C35 | 0.6263 (3) | 0.4128 (3) | 0.7279 (3) | 0.0372 (8) |
| H35 | 0.7033 | 0.3589 | 0.7079 | 0.045* |
| C36 | 0.4474 (3) | 0.5613 (3) | 0.7966 (3) | 0.0307 (7) |
| O1W | 0.1949 (3) | 0.9552 (3) | 0.5228 (2) | 0.0749 (9) |
| H1WA | 0.1810 | 0.9596 | 0.4548 | 0.112* |
| H1WB | 0.1411 | 1.0142 | 0.5309 | 0.112* |
| O2W | 0.5287 (2) | −0.3045 (3) | −0.0391 (2) | 0.0537 (7) |
| H2WB | 0.5946 | −0.3508 | −0.0270 | 0.081* |
| H2WA | 0.5167 | −0.2587 | −0.0049 | 0.081* |
| O3W | 0.1763 (2) | 0.4471 (2) | 0.03785 (18) | 0.0483 (6) |
| H3WA | 0.1475 | 0.4837 | 0.0745 | 0.072* |
| H3WB | 0.1492 | 0.3796 | 0.0574 | 0.072* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.0183 (2) | 0.0276 (2) | 0.0284 (2) | −0.00704 (16) | −0.00210 (15) | −0.01206 (16) |
| Ni2 | 0.0214 (2) | 0.0248 (2) | 0.0232 (2) | −0.00605 (16) | −0.00041 (15) | −0.00997 (16) |
| O1 | 0.0254 (12) | 0.0335 (12) | 0.0358 (12) | −0.0041 (10) | 0.0056 (10) | −0.0017 (10) |
| O2 | 0.0263 (11) | 0.0338 (12) | 0.0377 (12) | −0.0071 (10) | −0.0021 (9) | −0.0130 (10) |
| O3 | 0.0244 (11) | 0.0359 (12) | 0.0290 (11) | −0.0038 (9) | −0.0016 (9) | −0.0138 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O4 | 0.0510 (15) | 0.0320 (12) | 0.0317 (12) | −0.0134 (11) | −0.0126 (11) | −0.0025 (10) |
| O11 | 0.0204 (11) | 0.0401 (12) | 0.0423 (13) | −0.0039 (10) | −0.0023 (10) | −0.0245 (10) |
| O12 | 0.0338 (13) | 0.0422 (13) | 0.0471 (14) | −0.0064 (10) | −0.0004 (10) | −0.0312 (11) |
| O13 | 0.0244 (12) | 0.0385 (12) | 0.0417 (13) | −0.0083 (10) | −0.0025 (9) | −0.0247 (10) |
| O14 | 0.0282 (12) | 0.0351 (12) | 0.0417 (13) | −0.0035 (10) | 0.0006 (10) | −0.0239 (10) |
| O21 | 0.0299 (12) | 0.0327 (11) | 0.0303 (11) | −0.0160 (10) | −0.0016 (9) | −0.0077 (9) |
| O22 | 0.0388 (13) | 0.0392 (12) | 0.0274 (12) | −0.0171 (11) | −0.0044 (10) | −0.0013 (10) |
| O23 | 0.0287 (12) | 0.0432 (13) | 0.0308 (12) | −0.0153 (10) | −0.0064 (9) | −0.0060 (10) |
| O24 | 0.0633 (18) | 0.0762 (19) | 0.0344 (14) | −0.0482 (16) | −0.0134 (12) | 0.0120 (13) |
| N11 | 0.0191 (12) | 0.0251 (12) | 0.0261 (13) | −0.0069 (10) | −0.0008 (10) | −0.0117 (10) |
| N21 | 0.0195 (12) | 0.0266 (13) | 0.0228 (13) | −0.0079 (10) | −0.0002 (10) | −0.0080 (10) |
| N31 | 0.0305 (14) | 0.0314 (14) | 0.0260 (13) | −0.0096 (12) | 0.0009 (11) | −0.0147 (11) |
| N32 | 0.048 (2) | 0.098 (3) | 0.077 (2) | −0.0195 (19) | −0.0009 (18) | −0.070 (2) |
| N33 | 0.0242 (13) | 0.0241 (12) | 0.0262 (13) | −0.0080 (11) | 0.0006 (10) | −0.0090 (10) |
| N34 | 0.0357 (16) | 0.0591 (19) | 0.067 (2) | −0.0165 (15) | 0.0037 (15) | −0.0468 (17) |
| S31 | 0.0550 (6) | 0.0434 (5) | 0.0343 (5) | −0.0156 (4) | 0.0099 (4) | −0.0242 (4) |
| S32 | 0.0301 (5) | 0.0451 (5) | 0.0524 (5) | −0.0159 (4) | −0.0051 (4) | −0.0198 (4) |
| C11 | 0.0259 (16) | 0.0219 (14) | 0.0279 (15) | −0.0099 (12) | −0.0002 (12) | −0.0103 (12) |
| C12 | 0.0332 (18) | 0.0415 (18) | 0.0411 (19) | −0.0174 (15) | −0.0003 (15) | −0.0250 (16) |
| C13 | 0.0225 (16) | 0.0424 (19) | 0.050 (2) | −0.0126 (15) | −0.0024 (14) | −0.0234 (16) |
| C14 | 0.0181 (15) | 0.0298 (16) | 0.0389 (18) | −0.0074 (13) | 0.0012 (13) | −0.0136 (14) |
| C15 | 0.0224 (15) | 0.0229 (14) | 0.0261 (15) | −0.0097 (12) | 0.0024 (12) | −0.0092 (12) |
| C16 | 0.0262 (16) | 0.0251 (15) | 0.0264 (16) | −0.0051 (13) | −0.0019 (13) | −0.0088 (13) |
| C17 | 0.0281 (17) | 0.0217 (15) | 0.0257 (16) | −0.0074 (13) | −0.0010 (13) | −0.0079 (12) |
| C21 | 0.0186 (15) | 0.0260 (15) | 0.0254 (15) | −0.0061 (12) | −0.0004 (12) | −0.0111 (12) |
| C22 | 0.0252 (16) | 0.0406 (18) | 0.0270 (16) | −0.0118 (14) | −0.0045 (13) | −0.0107 (14) |
| C23 | 0.0301 (18) | 0.057 (2) | 0.0347 (18) | −0.0252 (17) | −0.0010 (14) | −0.0162 (16) |
| C24 | 0.0324 (18) | 0.0446 (19) | 0.0312 (17) | −0.0242 (16) | 0.0031 (14) | −0.0081 (15) |
| C25 | 0.0269 (16) | 0.0309 (16) | 0.0237 (15) | −0.0112 (13) | −0.0014 (13) | −0.0081 (13) |
| C26 | 0.0226 (16) | 0.0248 (15) | 0.0304 (17) | −0.0061 (13) | 0.0004 (13) | −0.0116 (13) |
| C27 | 0.0306 (18) | 0.0411 (19) | 0.0297 (18) | −0.0144 (15) | −0.0036 (14) | −0.0058 (15) |
| C31 | 0.0276 (16) | 0.0228 (15) | 0.0264 (16) | −0.0089 (13) | 0.0051 (13) | −0.0079 (12) |
| C32 | 0.0375 (19) | 0.0330 (17) | 0.0402 (19) | −0.0105 (15) | 0.0101 (15) | −0.0167 (15) |
| C33 | 0.042 (2) | 0.0367 (18) | 0.0312 (17) | −0.0121 (16) | 0.0003 (15) | −0.0164 (15) |
| C34 | 0.0264 (16) | 0.0223 (15) | 0.0301 (16) | −0.0086 (13) | 0.0020 (13) | −0.0066 (12) |
| C35 | 0.0270 (18) | 0.0326 (17) | 0.047 (2) | −0.0073 (14) | 0.0024 (15) | −0.0152 (15) |
| C36 | 0.0271 (17) | 0.0320 (17) | 0.0353 (17) | −0.0139 (14) | 0.0002 (13) | −0.0130 (14) |
| O1W | 0.108 (3) | 0.0634 (19) | 0.0524 (17) | −0.0390 (18) | −0.0031 (17) | −0.0143 (15) |
| O2W | 0.0598 (17) | 0.0577 (16) | 0.0551 (16) | −0.0190 (14) | −0.0104 (13) | −0.0327 (13) |
| O3W | 0.0644 (17) | 0.0424 (14) | 0.0417 (14) | −0.0231 (13) | 0.0052 (12) | −0.0187 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—N11 | 1.956 (2) | N33—C34 | 1.394 (4) |
| Ni1—N21 | 1.960 (2) | N34—C36 | 1.339 (4) |
| Ni1—O13 | 2.067 (2) | N34—H34A | 0.9184 |
| Ni1—O23 | 2.110 (2) | N34—H34B | 0.9241 |
| Ni1—O11 | 2.121 (2) | S31—C32 | 1.711 (4) |

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|---|---|---|---|
| Ni1—O21 | 2.164 (2) | S31—C33 | 1.736 (3) |
| Ni2—O4 | 2.041 (2) | S32—C35 | 1.720 (3) |
| Ni2—O1 | 2.056 (2) | S32—C36 | 1.740 (3) |
| Ni2—N31 | 2.067 (2) | C11—C12 | 1.375 (4) |
| Ni2—O3 | 2.0695 (19) | C11—C16 | 1.519 (4) |
| Ni2—N33 | 2.096 (2) | C12—C13 | 1.380 (4) |
| Ni2—O2 | 2.131 (2) | C12—H12 | 0.9300 |
| O1—H1A | 0.8609 | C13—C14 | 1.390 (4) |
| O1—H1B | 0.8248 | C13—H13 | 0.9300 |
| O2—H2A | 0.7732 | C14—C15 | 1.371 (4) |
| O2—H2B | 0.7640 | C14—H14 | 0.9300 |
| O3—H3A | 0.7774 | C15—C17 | 1.523 (4) |
| O3—H3B | 0.7478 | C21—C22 | 1.381 (4) |
| O4—H4A | 0.8275 | C21—C26 | 1.515 (4) |
| O4—H4B | 0.7402 | C22—C23 | 1.386 (4) |
| O11—C16 | 1.267 (4) | C22—H22 | 0.9300 |
| O12—C16 | 1.236 (3) | C23—C24 | 1.383 (4) |
| O13—C17 | 1.257 (3) | C23—H23 | 0.9300 |
| O14—C17 | 1.235 (3) | C24—C25 | 1.373 (4) |
| O21—C26 | 1.276 (3) | C24—H24 | 0.9300 |
| O22—C26 | 1.234 (3) | C25—C27 | 1.510 (4) |
| O23—C27 | 1.263 (4) | C31—C32 | 1.344 (4) |
| O24—C27 | 1.247 (4) | C31—C34 | 1.453 (4) |
| N11—C11 | 1.332 (4) | C32—H32 | 0.9300 |
| N11—C15 | 1.337 (3) | C34—C35 | 1.340 (4) |
| N21—C21 | 1.330 (3) | C35—H35 | 0.9300 |
| N21—C25 | 1.333 (4) | O1W—H1WA | 0.9140 |
| N31—C33 | 1.314 (4) | O1W—H1WB | 0.7473 |
| N31—C31 | 1.387 (4) | O2W—H2WB | 0.7194 |
| N32—C33 | 1.335 (4) | O2W—H2WA | 0.7934 |
| N32—H32A | 0.9783 | O3W—H3WA | 0.7332 |
| N32—H32B | 0.9467 | O3W—H3WB | 0.8837 |
| N33—C36 | 1.312 (4) | | |

| | | | |
|---|---|---|---|
| N11—Ni1—N21 | 175.99 (9) | C35—S32—C36 | 89.37 (15) |
| N11—Ni1—O13 | 79.07 (9) | N11—C11—C12 | 120.2 (3) |
| N21—Ni1—O13 | 99.01 (9) | N11—C11—C16 | 112.4 (2) |
| N11—Ni1—O23 | 97.79 (9) | C12—C11—C16 | 127.4 (3) |
| N21—Ni1—O23 | 78.84 (9) | C11—C12—C13 | 119.0 (3) |
| O13—Ni1—O23 | 95.95 (9) | C11—C12—H12 | 120.5 |
| N11—Ni1—O11 | 77.57 (8) | C13—C12—H12 | 120.5 |
| N21—Ni1—O11 | 104.53 (9) | C12—C13—C14 | 119.6 (3) |
| O13—Ni1—O11 | 156.33 (8) | C12—C13—H13 | 120.2 |
| O23—Ni1—O11 | 90.94 (9) | C14—C13—H13 | 120.2 |
| N11—Ni1—O21 | 106.47 (9) | C15—C14—C13 | 118.9 (3) |
| N21—Ni1—O21 | 77.05 (8) | C15—C14—H14 | 120.6 |
| O13—Ni1—O21 | 92.33 (8) | C13—C14—H14 | 120.6 |
| O23—Ni1—O21 | 155.44 (8) | N11—C15—C14 | 120.2 (3) |

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|---|---|---|---|
| O11—Ni1—O21 | 90.65 (8) | N11—C15—C17 | 111.9 (2) |
| O4—Ni2—O1 | 170.27 (9) | C14—C15—C17 | 127.9 (3) |
| O4—Ni2—N31 | 95.55 (9) | O12—C16—O11 | 126.0 (3) |
| O1—Ni2—N31 | 88.13 (9) | O12—C16—C11 | 119.3 (3) |
| O4—Ni2—O3 | 86.23 (8) | O11—C16—C11 | 114.7 (2) |
| O1—Ni2—O3 | 91.32 (8) | O14—C17—O13 | 125.6 (3) |
| N31—Ni2—O3 | 172.35 (9) | O14—C17—C15 | 119.2 (3) |
| O4—Ni2—N33 | 94.86 (9) | O13—C17—C15 | 115.2 (2) |
| O1—Ni2—N33 | 94.67 (9) | N21—C21—C22 | 120.8 (3) |
| N31—Ni2—N33 | 79.68 (9) | N21—C21—C26 | 113.1 (2) |
| O3—Ni2—N33 | 92.77 (9) | C22—C21—C26 | 126.1 (3) |
| O4—Ni2—O2 | 87.35 (9) | C21—C22—C23 | 118.2 (3) |
| O1—Ni2—O2 | 83.27 (8) | C21—C22—H22 | 120.9 |
| N31—Ni2—O2 | 96.50 (9) | C23—C22—H22 | 120.9 |
| O3—Ni2—O2 | 91.00 (8) | C24—C23—C22 | 120.1 (3) |
| N33—Ni2—O2 | 175.75 (8) | C24—C23—H23 | 119.9 |
| Ni2—O1—H1A | 116.2 | C22—C23—H23 | 119.9 |
| Ni2—O1—H1B | 128.2 | C25—C24—C23 | 118.5 (3) |
| H1A—O1—H1B | 111.8 | C25—C24—H24 | 120.7 |
| Ni2—O2—H2A | 119.6 | C23—C24—H24 | 120.7 |
| Ni2—O2—H2B | 112.6 | N21—C25—C24 | 120.9 (3) |
| H2A—O2—H2B | 100.9 | N21—C25—C27 | 112.8 (3) |
| Ni2—O3—H3A | 115.4 | C24—C25—C27 | 126.3 (3) |
| Ni2—O3—H3B | 109.9 | O22—C26—O21 | 126.0 (3) |
| H3A—O3—H3B | 105.8 | O22—C26—C21 | 119.1 (3) |
| Ni2—O4—H4A | 132.5 | O21—C26—C21 | 114.8 (2) |
| Ni2—O4—H4B | 118.2 | O24—C27—O23 | 125.7 (3) |
| H4A—O4—H4B | 106.3 | O24—C27—C25 | 118.3 (3) |
| C16—O11—Ni1 | 115.03 (18) | O23—C27—C25 | 116.1 (3) |
| C17—O13—Ni1 | 115.52 (18) | C32—C31—N31 | 115.6 (3) |
| C26—O21—Ni1 | 114.41 (18) | C32—C31—C34 | 128.2 (3) |
| C27—O23—Ni1 | 113.85 (19) | N31—C31—C34 | 116.2 (2) |
| C11—N11—C15 | 122.1 (2) | C31—C32—S31 | 110.3 (3) |
| C11—N11—Ni1 | 119.51 (19) | C31—C32—H32 | 124.8 |
| C15—N11—Ni1 | 117.94 (19) | S31—C32—H32 | 124.8 |
| C21—N21—C25 | 121.5 (2) | N31—C33—N32 | 124.3 (3) |
| C21—N21—Ni1 | 120.25 (19) | N31—C33—S31 | 113.6 (3) |
| C25—N21—Ni1 | 117.90 (19) | N32—C33—S31 | 122.0 (3) |
| C33—N31—C31 | 110.7 (3) | C35—C34—N33 | 115.4 (3) |
| C33—N31—Ni2 | 134.9 (2) | C35—C34—C31 | 129.0 (3) |
| C31—N31—Ni2 | 114.33 (19) | N33—C34—C31 | 115.5 (3) |
| C33—N32—H32A | 114.5 | C34—C35—S32 | 110.6 (2) |
| C33—N32—H32B | 119.9 | C34—C35—H35 | 124.7 |
| H32A—N32—H32B | 121.6 | S32—C35—H35 | 124.7 |
| C36—N33—C34 | 110.7 (3) | N33—C36—N34 | 125.1 (3) |
| C36—N33—Ni2 | 135.7 (2) | N33—C36—S32 | 113.9 (2) |
| C34—N33—Ni2 | 113.26 (19) | N34—C36—S32 | 121.0 (2) |
| C36—N34—H34A | 111.4 | H1WA—O1W—H1WB | 107.0 |

| | | | |
|---|---|---|---|
| C36—N34—H34B | 116.1 | H2WB—O2W—H2WA | 104.5 |
| H34A—N34—H34B | 126.2 | H3WA—O3W—H3WB | 107.6 |
| C32—S31—C33 | 89.77 (16) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*A*···O14$^{i}$ | 0.86 | 1.75 | 2.606 (3) | 174 |
| O1—H1*B*···O21$^{ii}$ | 0.82 | 1.92 | 2.747 (3) | 176 |
| O2—H2*A*···O12$^{iii}$ | 0.77 | 2.01 | 2.772 (3) | 169 |
| O2—H2*B*···O22$^{ii}$ | 0.76 | 2.12 | 2.874 (3) | 170 |
| O3—H3*A*···O3*W*$^{ii}$ | 0.78 | 1.98 | 2.742 (3) | 169 |
| O3—H3*B*···O11$^{iii}$ | 0.75 | 1.94 | 2.683 (3) | 173 |
| O4—H4*A*···O24$^{iv}$ | 0.83 | 1.89 | 2.717 (4) | 179 |
| O4—H4*B*···O1*W* | 0.74 | 2.16 | 2.820 (4) | 149 |
| O1*W*—H1*WA*···O23$^{iv}$ | 0.91 | 2.01 | 2.907 (4) | 166 |
| O1*W*—H1*WB*···O24$^{iii}$ | 0.75 | 2.41 | 3.150 (5) | 169 |
| O2*W*—H2*WB*···O3*W*$^{v}$ | 0.72 | 2.41 | 3.104 (4) | 162 |
| O2*W*—H2*WA*···O14 | 0.79 | 2.02 | 2.815 (4) | 174 |
| O3*W*—H3*WA*···O22$^{vi}$ | 0.73 | 2.24 | 2.934 (3) | 158 |
| O3*W*—H3*WB*···O21 | 0.88 | 2.10 | 2.892 (3) | 149 |
| N32—H32*A*···O12 | 0.98 | 1.97 | 2.940 (5) | 169 |
| N32—H32*B*···O2 | 0.95 | 2.19 | 2.996 (5) | 142 |
| N34—H34*A*···O2*W*$^{vii}$ | 0.92 | 1.98 | 2.886 (4) | 168 |
| N34—H34*B*···O3 | 0.92 | 2.12 | 2.952 (4) | 149 |
| C12—H12···S31 | 0.93 | 2.71 | 3.631 (4) | 170 |

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