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# *trans*-Diaquabis(L-phenylalaninato-$\kappa^2N,O$)nickel(II)

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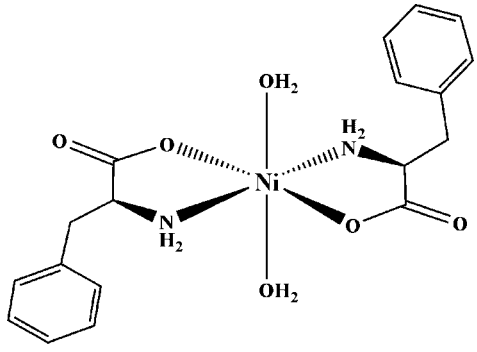
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.023; $wR$ factor = 0.058; data-to-parameter ratio = 12.6.

In the title compound, $[Ni(C_9H_{10}NO_2)_2(H_2O)_2]$, the coordination geometry around the $Ni^{II}$ ion can be described as distorted octahedral, with two N atoms and two O atoms from phenylalaninate ligands in the basal plane and two aqua O atoms at the axial sites. The crystal packing is stabilized by intermolecular O—H···O and N—H···O hydrogen bonds.

## Related literature

For background to amino acid complexes, see: Thanavelan *et al.* (2011). For related structures, see: Rombach *et al.* (2002); Marandi & Shahbakhsh (2007). For similar hydrogen-bonded networks, see: Cao *et al.* (2011). For details of $\pi$–$\pi$ stacking interactions, see: Janiak (2000).




## Experimental

### Crystal data

$[Ni(C_9H_{10}NO_2)_2(H_2O)_2]$
$M_r$ = 423.10
Monoclinic, $P2_1$
$a$ = 4.8272 (5) Å
$b$ = 32.617 (4) Å
$c$ = 6.0585 (7) Å
$\beta$ = 105.995 (1)°
$V$ = 916.97 (18) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.10 mm$^{-1}$
$T$ = 100 K
0.46 × 0.15 × 0.15 mm

### Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.633, $T_{max}$ = 0.853
8826 measured reflections
3214 independent reflections
3157 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.058
$S$ = 1.06
3214 reflections
256 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.22 e Å$^{-3}$
Absolute structure: Flack (1983), 1567 Friedel pairs
Flack parameter: −0.003 (10)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O13—H13$A$···O1$^{i}$ | 0.84 (2) | 1.95 (2) | 2.747 (2) | 159 (2) |
| O13—H13$B$···O23$^{ii}$ | 0.86 (2) | 1.88 (2) | 2.658 (2) | 150 (3) |
| O33—H33$A$···O3$^{iii}$ | 0.83 (2) | 1.88 (2) | 2.691 (2) | 163 (3) |
| O33—H33$B$···O21$^{iv}$ | 0.83 (2) | 1.97 (2) | 2.748 (2) | 156 (2) |
| N5—H5$B$···O1$^{i}$ | 0.92 | 2.49 | 3.359 (2) | 157 |
| N5—H5$A$···O3$^{iii}$ | 0.92 | 2.39 | 3.193 (3) | 147 |
| N25—H25$A$···O13$^{iv}$ | 0.92 | 2.57 | 3.148 (2) | 122 |
| N25—H25$A$···O21$^{iv}$ | 0.92 | 2.47 | 3.310 (2) | 153 |
| N25—H25$B$···O23$^{ii}$ | 0.92 | 2.36 | 3.181 (3) | 149 |

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2191).

## References

Bruker (2008). *SADABS*. Bruker AXS inc., Madison, Wisconsin, USA.
Bruker (2010). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cao, Y., Zhao, H., Bai, F., Xing, V., Wei, D., Niu, S. & Shi, S. (2011). *Inorg. Chim. Acta*, **368**, 223–230.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
Marandi, F. & Shahbakhsh, N. (2007). *Z. Anorg. Allg. Chem.* **6333**, 1137–1139.
Rombach, M., Gelinsky, M. & Vahrenkamp, M. (2002). *Inorg. Chim. Acta*, **334**, 25–33.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Thanavelan, R., Ramalingam, G., Manikandan, G. & Thanikachalam, V. (2011). *J. Saudi Chem. Soc.* http://dx.doi.org/10.1016/j.jscs.2011.06.016.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

# supporting information

*Acta Cryst.* (2012). E**68**, m446 [https://doi.org/10.1107/S160053681201080X]

## *trans*-Diaquabis(L-phenylalaninato-$\kappa^2N,O$)nickel(II)

**Massomeh Ghorbanloo, Nahid Shahbakhsh and Duane Choquesillo-Lazarte**

### S1. Comment

Amino acids are of special importance among the other chemical substances since they form the basic constituents of living organisms. It is imperative to know the properties of amino acids in order to understand and explain their behavior and the synthesis of peptides, proteins and enzymes in living organisms. Also they are widely applied in food, cosmetic, pharmaceutical and chemical industry. It is known that the reactions of peptides, proteins and enzymes with metal ions are of biochemical importance but they are yet to be thoroughly understood (Thanavelan *et al.*, 2011). The explanation of these phenomena in the biological systems can be possible only by the determination of structure of amino acids.

Because of the importance the characterization of amino acid derivatives, here, we report the synthesis and crystal structure of Trans-diaqua-bis[(L-phenylalanine)-$\kappa^2$N,O]nickel(II). In the title compound, $[Ni(OH_2)_2(C_{18}H_{20}N_2O_4)_2]$, the coordination geometry around the nickel(II) can be described as a distored octahedral which is shown in Fig. 1. In the title compound, the amino acid ligands form equatorial plane and axial positions are occupied by the oxygen atoms from aqua ligands. The oxygen atoms of the amino acid ligands are located *trans* to each other. Moreover, the nitrogen atom of the amino acid ligand (N5) is located *trans* to the nitrogen atom of the other amino acid (N25). In the title compound the amino acid ligands form two five–membered chelate rings.

The carboxylate groups of the amino acids in the title compound are involved in anti–anti bidentate bridging coordination. The amino acid is N,O-chelated, forming a five-membered ring. Unlike our complex, most of aminoacid complexes with this kind of O,N chelation form coordination polymers held together by bridging carboxylate ligands (Rombach *et al.*, 2002).

This configuration is stabilized by four intermolecular hydrogen bonds of the types O—H···O=C—O and O—H···O—C=O and five hydrogen bonds of the type N—H···O=C—O and N—H···O—C=O (Fig. 2). The carboxylate groups are the acceptors of all hydrogen bonds. Really, this structure as composed of molecules linked by hydrogen bonded into layers leading to 1D network.

### S2. Experimental

All reagents were commercially available and used as received. For preparing the title compound a methanol (10 ml) solution of L-phenylalanine (2 mmol) and NaOH (2mmol) were added to a methanol solution (10 ml) of $Ni(NO_3)_2.6H_2O$ (1 mmol), and the mixture was refluxed for 6 h.

The X-ray quality blue crystals of the title compound were obtained by slow solvent evaporation during 5 days. Yield: 68%, mp > 400 °C. IR ($cm^{-1}$): 3357 (broad, $H_2O$), 1594 (vs, $\nu$as(COO)), 1497 (s, $\nu$s(COO)), 1404 (s, $\delta$-$NH_2$), 450 (w), 546 (w), 575 (w).

## S3. Refinement

H atoms were located in difference Fourier maps and included in the refinement as constrained idealized atoms riding on the parent atom, with C-H = 0.95 Å (aromatic groups), 1.00 Å (CH–N groups), 0.99 Å ($CH_2$–Ph groups) or 0.92 Å ($–NH_2$ groups) and with $U_{iso}$(H) = 1.2$U_{eq}$(C,N). The H atoms of the aqua ligands were refined as semi-free with a distance restraint, and with $U_{iso}$(H) = 1.2$U_{eq}$(O).

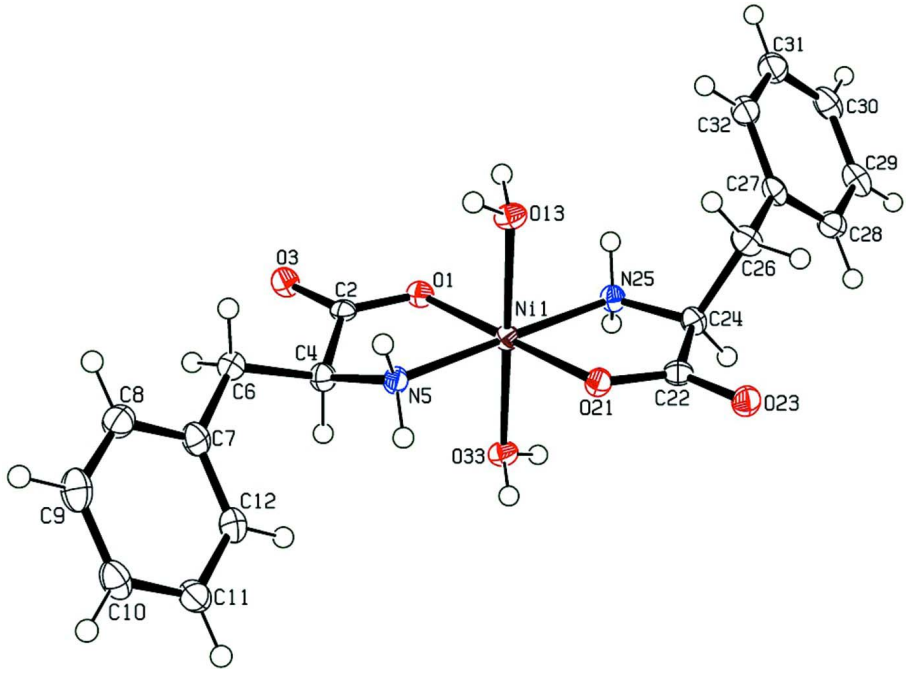


**Figure 1**

The molecular structure of the title compound, with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level) for non-H atoms.

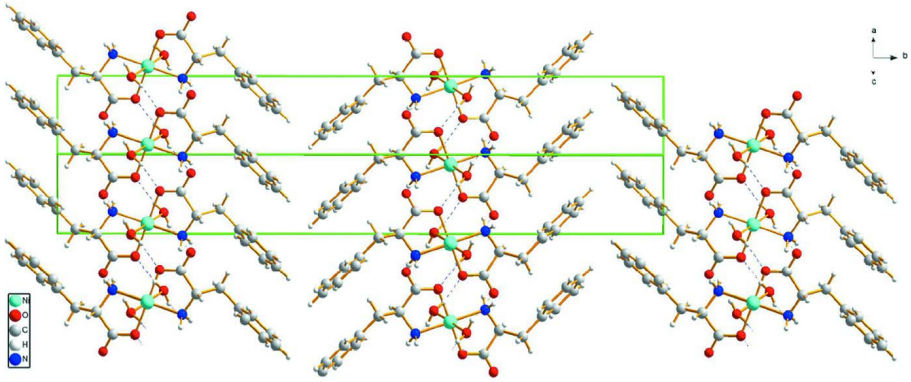

**Figure 2**

The packing diagram of the title compound which O–H···O hydrogen bonds shown as blue dashed lines.

**trans-Diaquabis(*L*-phenylalaninato-$\kappa^2N,O$)nickel(II)**

*Crystal data*

$[Ni(C_9H_{10}NO_2)_2(H_2O)_2]$
$M_r = 423.10$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 4.8272$ (5) Å
$b = 32.617$ (4) Å
$c = 6.0585$ (7) Å
$\beta = 105.995$ (1)°
$V = 916.97$ (18) Å$^3$
$Z = 2$
$F(000) = 444$
$D_x = 1.532$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7357 reflections
$\theta = 2.5$–$27.8°$
$\mu = 1.10$ mm$^{-1}$
$T = 100$ K
Block, pale blue
0.46 × 0.15 × 0.15 mm

*Data collection*

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.633$, $T_{max} = 0.853$
8826 measured reflections
3214 independent reflections
3157 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.3°$
$h = -5 \rightarrow 5$
$k = -38 \rightarrow 38$
$l = -7 \rightarrow 7$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.058$
$S = 1.06$
3214 reflections
256 parameters
5 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 0.0026P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{min} = -0.22$ e Å$^{-3}$
Absolute structure: Flack (1983), 1567 Friedel pairs
Absolute structure parameter: −0.003 (10)

*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**. 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 | 0.28611 (5) | 0.648490 (11) | 0.40794 (4) | 0.01552 (8) |
| O1 | 0.4353 (3) | 0.62803 (5) | 0.1433 (3) | 0.0176 (3) |
| C2 | 0.3680 (5) | 0.59137 (6) | 0.0787 (4) | 0.0154 (5) |

| | | | | |
|---|---|---|---|---|
| O3 | 0.4153 (4) | 0.57545 (5) | −0.0940 (3) | 0.0208 (4) |
| C4 | 0.2425 (5) | 0.56442 (7) | 0.2377 (4) | 0.0187 (5) |
| H4 | 0.4108 | 0.5512 | 0.3495 | 0.022* |
| N5 | 0.1012 (4) | 0.59095 (5) | 0.3755 (3) | 0.0166 (4) |
| H5A | 0.1239 | 0.5796 | 0.5184 | 0.020* |
| H5B | −0.0929 | 0.5929 | 0.3038 | 0.020* |
| C6 | 0.0588 (5) | 0.52992 (7) | 0.1089 (4) | 0.0213 (5) |
| H6A | 0.1709 | 0.5153 | 0.0189 | 0.026* |
| H6B | −0.1116 | 0.5421 | −0.0019 | 0.026* |
| C7 | −0.0470 (5) | 0.49844 (7) | 0.2534 (4) | 0.0212 (5) |
| C8 | −0.2788 (5) | 0.47360 (8) | 0.1455 (4) | 0.0245 (5) |
| H8 | −0.3693 | 0.4773 | −0.0136 | 0.029* |
| C9 | −0.3811 (6) | 0.44351 (9) | 0.2643 (5) | 0.0285 (6) |
| H9 | −0.5387 | 0.4268 | 0.1864 | 0.034* |
| C10 | −0.2533 (6) | 0.43785 (8) | 0.4970 (5) | 0.0262 (6) |
| H10 | −0.3241 | 0.4175 | 0.5794 | 0.031* |
| C11 | −0.0218 (6) | 0.46217 (7) | 0.6083 (4) | 0.0249 (5) |
| H11 | 0.0675 | 0.4584 | 0.7675 | 0.030* |
| C12 | 0.0812 (5) | 0.49241 (7) | 0.4865 (4) | 0.0233 (5) |
| H12 | 0.2402 | 0.5089 | 0.5640 | 0.028* |
| O13 | −0.0828 (4) | 0.67531 (5) | 0.1807 (3) | 0.0190 (3) |
| H13A | −0.231 (4) | 0.6608 (7) | 0.133 (4) | 0.023* |
| H13B | −0.042 (6) | 0.6837 (8) | 0.059 (3) | 0.023* |
| O21 | 0.1315 (3) | 0.66878 (5) | 0.6664 (3) | 0.0173 (3) |
| C22 | 0.2192 (5) | 0.70390 (7) | 0.7484 (4) | 0.0170 (5) |
| O23 | 0.1545 (4) | 0.72004 (5) | 0.9143 (3) | 0.0215 (4) |
| C24 | 0.4021 (5) | 0.72964 (7) | 0.6278 (4) | 0.0177 (5) |
| H24 | 0.5846 | 0.7379 | 0.7437 | 0.021* |
| N25 | 0.4761 (4) | 0.70600 (5) | 0.4425 (3) | 0.0169 (4) |
| H25A | 0.6730 | 0.7032 | 0.4760 | 0.020* |
| H25B | 0.4138 | 0.7200 | 0.3060 | 0.020* |
| C26 | 0.2290 (5) | 0.76835 (7) | 0.5355 (4) | 0.0218 (5) |
| H26A | 0.0524 | 0.7601 | 0.4164 | 0.026* |
| H26B | 0.1680 | 0.7813 | 0.6623 | 0.026* |
| C27 | 0.3862 (5) | 0.80002 (7) | 0.4338 (4) | 0.0198 (5) |
| C28 | 0.6211 (5) | 0.82146 (7) | 0.5734 (4) | 0.0220 (5) |
| H28 | 0.6866 | 0.8153 | 0.7326 | 0.026* |
| C29 | 0.7596 (6) | 0.85182 (8) | 0.4812 (5) | 0.0255 (6) |
| H29 | 0.9187 | 0.8662 | 0.5773 | 0.031* |
| C30 | 0.6654 (6) | 0.86095 (8) | 0.2499 (5) | 0.0274 (7) |
| H30 | 0.7605 | 0.8815 | 0.1868 | 0.033* |
| C31 | 0.4317 (6) | 0.84014 (8) | 0.1094 (4) | 0.0278 (6) |
| H31 | 0.3651 | 0.8467 | −0.0492 | 0.033* |
| C32 | 0.2955 (5) | 0.80967 (7) | 0.2019 (4) | 0.0239 (5) |
| H32 | 0.1377 | 0.7952 | 0.1046 | 0.029* |
| O33 | 0.6519 (4) | 0.62138 (5) | 0.6364 (3) | 0.0187 (3) |
| H33A | 0.592 (6) | 0.6108 (8) | 0.740 (4) | 0.022* |
| H33B | 0.792 (4) | 0.6368 (6) | 0.684 (4) | 0.022* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.01495 (13) | 0.01567 (13) | 0.01611 (13) | −0.00181 (13) | 0.00456 (9) | 0.00010 (13) |
| O1 | 0.0157 (8) | 0.0181 (8) | 0.0192 (8) | −0.0020 (6) | 0.0051 (6) | 0.0016 (7) |
| C2 | 0.0127 (11) | 0.0169 (12) | 0.0149 (12) | 0.0017 (9) | 0.0011 (9) | 0.0025 (9) |
| O3 | 0.0238 (9) | 0.0194 (8) | 0.0224 (9) | −0.0007 (7) | 0.0120 (7) | 0.0004 (7) |
| C4 | 0.0191 (12) | 0.0182 (12) | 0.0197 (12) | −0.0010 (9) | 0.0067 (10) | −0.0008 (9) |
| N5 | 0.0181 (10) | 0.0161 (10) | 0.0156 (9) | −0.0020 (8) | 0.0044 (8) | −0.0015 (7) |
| C6 | 0.0250 (13) | 0.0195 (12) | 0.0186 (12) | −0.0010 (10) | 0.0048 (10) | −0.0007 (9) |
| C7 | 0.0235 (13) | 0.0177 (12) | 0.0253 (13) | 0.0015 (10) | 0.0118 (10) | −0.0026 (9) |
| C8 | 0.0250 (13) | 0.0251 (13) | 0.0228 (13) | 0.0014 (10) | 0.0054 (10) | −0.0018 (10) |
| C9 | 0.0239 (15) | 0.0243 (14) | 0.0378 (16) | −0.0079 (11) | 0.0092 (12) | −0.0063 (12) |
| C10 | 0.0332 (16) | 0.0180 (13) | 0.0329 (15) | −0.0034 (11) | 0.0184 (13) | −0.0009 (11) |
| C11 | 0.0310 (14) | 0.0197 (12) | 0.0251 (13) | 0.0021 (11) | 0.0098 (11) | 0.0016 (10) |
| C12 | 0.0234 (13) | 0.0182 (12) | 0.0279 (13) | −0.0034 (10) | 0.0065 (11) | −0.0037 (10) |
| O13 | 0.0169 (8) | 0.0235 (9) | 0.0168 (9) | −0.0037 (7) | 0.0051 (7) | 0.0035 (7) |
| O21 | 0.0198 (8) | 0.0170 (8) | 0.0162 (8) | −0.0034 (7) | 0.0069 (7) | −0.0011 (6) |
| C22 | 0.0131 (11) | 0.0197 (12) | 0.0174 (12) | 0.0010 (9) | 0.0030 (9) | 0.0026 (9) |
| O23 | 0.0298 (10) | 0.0194 (9) | 0.0180 (9) | −0.0024 (7) | 0.0111 (7) | 0.0001 (7) |
| C24 | 0.0178 (12) | 0.0155 (11) | 0.0207 (12) | −0.0008 (9) | 0.0068 (10) | −0.0002 (9) |
| N25 | 0.0171 (10) | 0.0159 (10) | 0.0184 (10) | −0.0017 (8) | 0.0064 (8) | −0.0004 (7) |
| C26 | 0.0200 (12) | 0.0211 (12) | 0.0260 (12) | 0.0023 (10) | 0.0093 (10) | 0.0026 (10) |
| C27 | 0.0215 (12) | 0.0148 (11) | 0.0253 (13) | 0.0037 (10) | 0.0101 (10) | −0.0005 (9) |
| C28 | 0.0233 (12) | 0.0212 (12) | 0.0221 (12) | 0.0036 (10) | 0.0076 (10) | 0.0026 (9) |
| C29 | 0.0227 (14) | 0.0170 (13) | 0.0383 (16) | 0.0007 (11) | 0.0108 (12) | 0.0000 (12) |
| C30 | 0.0340 (16) | 0.0176 (13) | 0.0367 (17) | 0.0022 (11) | 0.0200 (13) | 0.0041 (11) |
| C31 | 0.0401 (16) | 0.0232 (13) | 0.0238 (13) | 0.0040 (11) | 0.0153 (12) | 0.0032 (10) |
| C32 | 0.0292 (13) | 0.0198 (12) | 0.0236 (13) | 0.0010 (10) | 0.0086 (11) | 0.0000 (10) |
| O33 | 0.0164 (8) | 0.0219 (9) | 0.0175 (8) | −0.0040 (7) | 0.0042 (7) | 0.0027 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—O21 | 2.0223 (16) | C12—H12 | 0.9500 |
| Ni1—O1 | 2.0421 (16) | O13—H13A | 0.839 (17) |
| Ni1—N5 | 2.0642 (18) | O13—H13B | 0.861 (17) |
| Ni1—N25 | 2.0731 (18) | O21—C22 | 1.274 (3) |
| Ni1—O33 | 2.1139 (17) | C22—O23 | 1.249 (3) |
| Ni1—O13 | 2.1171 (17) | C22—C24 | 1.541 (3) |
| O1—C2 | 1.272 (3) | C24—N25 | 1.484 (3) |
| C2—O3 | 1.245 (3) | C24—C26 | 1.532 (3) |
| C2—C4 | 1.546 (3) | C24—H24 | 1.0000 |
| C4—N5 | 1.492 (3) | N25—H25A | 0.9200 |
| C4—C6 | 1.510 (3) | N25—H25B | 0.9200 |
| C4—H4 | 1.0000 | C26—C27 | 1.510 (3) |
| N5—H5A | 0.9200 | C26—H26A | 0.9900 |
| N5—H5B | 0.9200 | C26—H26B | 0.9900 |
| C6—C7 | 1.526 (3) | C27—C32 | 1.388 (3) |

| | | | |
|---|---|---|---|
| C6—H6A | 0.9900 | C27—C28 | 1.401 (3) |
| C6—H6B | 0.9900 | C28—C29 | 1.395 (4) |
| C7—C8 | 1.390 (3) | C28—H28 | 0.9500 |
| C7—C12 | 1.391 (3) | C29—C30 | 1.381 (4) |
| C8—C9 | 1.386 (4) | C29—H29 | 0.9500 |
| C8—H8 | 0.9500 | C30—C31 | 1.389 (4) |
| C9—C10 | 1.386 (4) | C30—H30 | 0.9500 |
| C9—H9 | 0.9500 | C31—C32 | 1.392 (3) |
| C10—C11 | 1.385 (4) | C31—H31 | 0.9500 |
| C10—H10 | 0.9500 | C32—H32 | 0.9500 |
| C11—C12 | 1.402 (3) | O33—H33A | 0.833 (17) |
| C11—H11 | 0.9500 | O33—H33B | 0.829 (17) |

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| O21—Ni1—O1 | 179.03 (7) | C12—C11—H11 | 119.9 |
| O21—Ni1—N5 | 97.42 (7) | C7—C12—C11 | 120.7 (2) |
| O1—Ni1—N5 | 82.24 (7) | C7—C12—H12 | 119.6 |
| O21—Ni1—N25 | 82.71 (7) | C11—C12—H12 | 119.6 |
| O1—Ni1—N25 | 97.64 (7) | Ni1—O13—H13A | 118.2 (18) |
| N5—Ni1—N25 | 179.38 (8) | Ni1—O13—H13B | 109.7 (18) |
| O21—Ni1—O33 | 92.85 (6) | H13A—O13—H13B | 105 (2) |
| O1—Ni1—O33 | 88.04 (7) | C22—O21—Ni1 | 116.26 (14) |
| N5—Ni1—O33 | 86.75 (7) | O23—C22—O21 | 124.3 (2) |
| N25—Ni1—O33 | 92.64 (7) | O23—C22—C24 | 117.1 (2) |
| O21—Ni1—O13 | 86.82 (6) | O21—C22—C24 | 118.5 (2) |
| O1—Ni1—O13 | 92.29 (6) | N25—C24—C26 | 111.88 (18) |
| N5—Ni1—O13 | 92.84 (7) | N25—C24—C22 | 111.37 (18) |
| N25—Ni1—O13 | 87.77 (7) | C26—C24—C22 | 107.21 (18) |
| O33—Ni1—O13 | 179.43 (7) | N25—C24—H24 | 108.8 |
| C2—O1—Ni1 | 115.66 (14) | C26—C24—H24 | 108.8 |
| O3—C2—O1 | 124.1 (2) | C22—C24—H24 | 108.8 |
| O3—C2—C4 | 118.74 (19) | C24—N25—Ni1 | 110.76 (14) |
| O1—C2—C4 | 116.99 (19) | C24—N25—H25A | 109.5 |
| N5—C4—C6 | 115.3 (2) | Ni1—N25—H25A | 109.5 |
| N5—C4—C2 | 109.68 (17) | C24—N25—H25B | 109.5 |
| C6—C4—C2 | 112.15 (19) | Ni1—N25—H25B | 109.5 |
| N5—C4—H4 | 106.4 | H25A—N25—H25B | 108.1 |
| C6—C4—H4 | 106.4 | C27—C26—C24 | 115.33 (19) |
| C2—C4—H4 | 106.4 | C27—C26—H26A | 108.4 |
| C4—N5—Ni1 | 109.17 (14) | C24—C26—H26A | 108.4 |
| C4—N5—H5A | 109.8 | C27—C26—H26B | 108.4 |
| Ni1—N5—H5A | 109.8 | C24—C26—H26B | 108.4 |
| C4—N5—H5B | 109.8 | H26A—C26—H26B | 107.5 |
| Ni1—N5—H5B | 109.8 | C32—C27—C28 | 118.4 (2) |
| H5A—N5—H5B | 108.3 | C32—C27—C26 | 121.0 (2) |
| C4—C6—C7 | 116.5 (2) | C28—C27—C26 | 120.6 (2) |
| C4—C6—H6A | 108.2 | C29—C28—C27 | 120.7 (2) |
| C7—C6—H6A | 108.2 | C29—C28—H28 | 119.7 |
| C4—C6—H6B | 108.2 | C27—C28—H28 | 119.7 |

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|---|---|---|---|
| C7—C6—H6B | 108.2 | C30—C29—C28 | 119.9 (3) |
| H6A—C6—H6B | 107.3 | C30—C29—H29 | 120.0 |
| C8—C7—C12 | 118.1 (2) | C28—C29—H29 | 120.0 |
| C8—C7—C6 | 118.4 (2) | C29—C30—C31 | 120.1 (2) |
| C12—C7—C6 | 123.5 (2) | C29—C30—H30 | 120.0 |
| C9—C8—C7 | 121.6 (2) | C31—C30—H30 | 120.0 |
| C9—C8—H8 | 119.2 | C30—C31—C32 | 119.8 (2) |
| C7—C8—H8 | 119.2 | C30—C31—H31 | 120.1 |
| C8—C9—C10 | 120.0 (3) | C32—C31—H31 | 120.1 |
| C8—C9—H9 | 120.0 | C27—C32—C31 | 121.2 (2) |
| C10—C9—H9 | 120.0 | C27—C32—H32 | 119.4 |
| C11—C10—C9 | 119.5 (2) | C31—C32—H32 | 119.4 |
| C11—C10—H10 | 120.3 | Ni1—O33—H33A | 105.4 (19) |
| C9—C10—H10 | 120.3 | Ni1—O33—H33B | 115.5 (17) |
| C10—C11—C12 | 120.1 (2) | H33A—O33—H33B | 114 (3) |
| C10—C11—H11 | 119.9 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O13—H13*A*···O1$^{i}$ | 0.84 (2) | 1.95 (2) | 2.747 (2) | 159 (2) |
| O13—H13*B*···O23$^{ii}$ | 0.86 (2) | 1.88 (2) | 2.658 (2) | 150 (3) |
| O33—H33*A*···O3$^{iii}$ | 0.83 (2) | 1.88 (2) | 2.691 (2) | 163 (3) |
| O33—H33*B*···O21$^{iv}$ | 0.83 (2) | 1.97 (2) | 2.748 (2) | 156 (2) |
| N5—H5*B*···O1$^{i}$ | 0.92 | 2.49 | 3.359 (2) | 157 |
| N5—H5*A*···O3$^{iii}$ | 0.92 | 2.39 | 3.193 (3) | 147 |
| N25—H25*A*···O13$^{iv}$ | 0.92 | 2.57 | 3.148 (2) | 122 |
| N25—H25*A*···O21$^{iv}$ | 0.92 | 2.47 | 3.310 (2) | 153 |
| N25—H25*B*···O23$^{ii}$ | 0.92 | 2.36 | 3.181 (3) | 149 |

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