Crystal structure and thermal properties of a square-planar Ni^{II} complex of cyanide and a tricyclic bis-amidine ligand formed *in situ* under solvothermal conditions

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The reaction of *N*¹,*N*^{1'}-(ethane-1,2-diyl)bis(propane-1,3-diamine) (bapen), K₂[Ni(CN)₄]·H₂O and dimethylformamide in the presence of Gd(NO₃)₃·6H₂O under solvothermal conditions yielded yellow crystals of dicyanido(2,3,4,6,7,9,10,11-octahydropyrimido[2',1':3,4]pyrazino[1,2-*a*]pyrimidine)nickel(II) hemihydrate, [Ni(CN)₂(C₁₀H₁₆N₄)]·0.5H₂O, (I), the crystal structure of which is composed of [Ni(CN)₂(pdpm)] molecules (pdpm is 2,3,4,6,7,9,10,11-octahydropyrimido[2',1':3,4]pyrazino[1,2-*a*]pyrimidine) on general positions linked by O—H···N hydrogen bonds to water molecules located on twofold axes. This structural unit is further linked by nonclassical C—H···N interactions to form a warped two-dimensional net perpendicular to the unit-cell *b* axis. The nets are stacked, with C—H···O contacts joining successive units. The Ni^{II} cation is coordinated with square-planar geometry by a chelating pdpm ligand and two cyanide ligands in mutually *cis* positions. Complex (I) is stable up to 360 K, at which point dehydration takes place; the ligands start to decompose at 558 K.

Comment

The formation of new ligands by the reaction of organic compounds in the presence of metal cations, leading to the isolation of new solid coordination compounds, is commonly observed in solvothermal preparations. Examples include the *in situ* reduction of pyridine-2-carbaldehyde to (pyridin-2-yl)methanol during the synthesis of tetranuclear Ni^{II} and dinuclear Fe^{III} complexes (Sun *et al.*, 2011), or the transformation of the mono Schiff base 4-chloro-2-[(3-cyclohexylaminopropyl)iminomethyl]phenol in the presence of Zn^{II}

cations to 4-chloro-2-[[3-(5-chloro-2-hydroxybenzyl)amino-propyl]iminomethyl]phenol with a newly formed C—N single bond (You *et al.*, 2012).

Within our broader studies of 3*d*–4*f* complexes, we have reacted Gd(NO₃)₃·6H₂O, *N*¹,*N*^{1'}-(ethane-1,2-diyl)bis(propane-1,3-diamine) (bapen), K₂[Ni(CN)₄]·H₂O and dimethylformamide (DMF) under solvothermal conditions. The formation of 3*d*–4*f* complexes based on Gd^{III} and [Ni(CN)₄]^{2−} has already been reported (Du *et al.*, 2001), so our goal was to isolate a compound based on Gd^{III}, bapen and [Ni(CN)₄]^{2−}. However, the synthetic procedure unexpectedly produced the title complex, [Ni(CN)₂(pdpm)]·0.5H₂O (pdpm is 2,3,4,6,7,9,10,11-octahydropyrimido[2',1':3,4]pyrazino[1,2-*a*]pyrimidine), (I), the structure of which was established by single-crystal X-ray diffraction. The result indicates that *in situ* formation of the pdpm ligand has occurred. The newly synthesized complex was further characterized by CHN analysis, as well as by its spectroscopic and thermal properties.

The synthesis of (I) itself merits comment. From the system bapen–K₂[Ni(CN)₄]·H₂O–Gd(NO₃)₃·6H₂O (in a 4:3:2 ratio) with DMF (in excess) as solvent under solvothermal conditions, yellow crystals of (I) were isolated in low yield. Crystals of the same compound were obtained after lowering the

Figure 1
The IR spectra of (I) (top) and (Ia) (bottom). See *Comment* for details.

content of the Gd^{III} salt to give ratios of 4:3:0.5. However, in the absence of the Gd^{III} salt, no crystals of (I) were produced, suggesting a possible catalytic role for Gd^{III} . A previously reported preparation of pdpm involved reaction of dithio-oxamide with bapen in absolute ethanol under an N_2 atmosphere, followed by azeotropic distillation with toluene (Li *et al.*, 2010).

The most prominent feature in the IR spectrum of (I) (Fig. 1, top) is the strong sharp absorption band at 2118 cm^{-1} which, in accord with the literature (Nakamoto, 1997), was assigned to the stretching vibrations of the terminal cyanide groups. A further easily identifiable absorption band is observed at 3500 cm^{-1} , signalling the presence of the interstitial water molecule. Additionally, several weak-to-medium absorption bands observed below 3000 cm^{-1} can be attributed to the $\nu(\text{CH})$ vibrations of the methylene groups. A broad strong absorption due to the $\text{N}=\text{C}-\text{C}=\text{N}$ fragment is observed at 1616 cm^{-1} ; this band was observed at 1601 cm^{-1} in the free pdpm ligand and between 1525 and 1670 cm^{-1} in the spectra of various complexes containing pdpm as a ligand (Li *et al.*, 2010).

Compound (I) forms molecular crystals as a hemihydrate, in which the Ni-centred complex resides on a general position, while the solvent water sits on a crystallographic twofold axis. The central Ni^{II} cation is coordinated in a square-planar fashion (Fig. 2) by two cyanide ligands *cis* to each other and with the two remaining mutually *cis* positions occupied by N atoms of the pdpm ligand. A search of the Cambridge Structural Database (CSD, Version 5.34; Allen, 2002) reveals no square-planar Ni^{II} complexes with mutually *cis* cyanide ligands and two N-bound ligands. Thus, complex (I) is the first example of a square-planar Ni^{II} complex with this coordination set. In contrast, there have been a few examples reported of square-planar Ni^{II} complexes with C_2P_2 donor sets, *e.g.* *cis*-

Figure 2
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The H atoms of the minor disorder component at atoms C4 and C5 have been omitted. The dashed line represents a hydrogen bond.

Figure 3
The $\text{O}-\text{H}\cdots\text{N}(\text{C})$ hydrogen bonds (dashed lines) linking the solvent water molecule and two molecules of the complex. H atoms not involved in hydrogen bonding and one disordered position of atom C5 of the pdpm ligand are not shown. [Symmetry code: (iv) $-x + 1, y, -z + \frac{3}{2}$.]

$[\text{Ni}(\text{CN})_2(\text{dppe})]$ [dppe = 1,2-bis(diphenylphosphanyl)ethene; Oberhauser *et al.*, 1998] or *trans*- $[\text{Ni}(\text{CN})_2(\text{chp})_2]$ (chp = tricyclohexylphosphane; Xia *et al.*, 2002), and with a C_2NS donor set, *e.g.* *cis*- $[\text{Ni}(\text{CN})_2(\text{Htsc})_2]\cdot\text{H}_2\text{O}$ (Htsc = thiosemicarbazide; Dunaj-Jurčo *et al.*, 1992).

The mean $\text{Ni}-\text{C}$ bond length of $1.847(3)\text{ \AA}$ (Table 1) is close to the typical value of $1.859\text{ \AA}$ for this bond in square-planar complexes (Orpen *et al.*, 1989). The other geometric parameters associated with the cyanide ligands are also as expected (Ray *et al.*, 2008). The $\text{Ni}-\text{C}$ distances in (I) are also similar to those found in a five-coordinate Ni complex with a *cis*- $[\text{Ni}(\text{CN})_2\text{N}_3]$ coordination set (Li *et al.*, 2006), but are significantly shorter than those found for a six-coordinate Ni compound with *cis*- $[\text{Ni}(\text{CN})_2\text{N}_4]$ coordination (Jiang *et al.*, 2005). The $\text{Ni}-\text{N}$ bonds to the chelating pdpm ligand [$1.902(2)$ and $1.909(3)\text{ \AA}$] are longer than the $\text{Ni}-\text{C}$ bonds, but similar to the value of $1.923(2)\text{ \AA}$ found for the square-planar complex *cis*- $[\text{Ni}(\text{CN})_2(\text{Htsc})_2]\cdot\text{H}_2\text{O}$ (Dunaj-Jurčo *et al.*, 1992). The geometric parameters associated with the pdpm ligand are similar to those found in analogous complexes, *e.g.* in $[\text{Zn}(\text{pdpm})_3](\text{ClO}_4)_2$ (Li *et al.*, 2010).

The water molecule does not enter the coordination environment of the Ni^{II} cation, but it nevertheless has an important role in the crystal structure. Each water molecule forms two $\text{O}-\text{H}\cdots\text{N}(\text{C})$ hydrogen bonds (Table 2), linking two molecules of the complex (Fig. 3). Weak $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds link neighbouring units of this aggregate to form a slightly warped two-dimensional net perpendicular to the *b* axis and centred at $y = \frac{1}{4}, \frac{3}{4}$. The net is composed of $R_4^4(25)$ and $R_4^2(16)$ rings (Bernstein *et al.*, 1995) (Fig. 4, denoted A and B). A crystallographic twofold axis parallel to *b* goes through the water molecule at the edge of ring A, while another twofold axis in the same direction goes through the middle of ring B. The three-dimensional structure is completed by stacking of the two-dimensional nets along $[010]$. $\text{C}-\text{H}\cdots\text{O}$

Figure 4

The two-dimensional net in (I), perpendicular to the *b* axis. Ring motifs *A* and *B* are discussed in the *Comment*. [Symmetry codes: (iv) $-x + 1, y, -z + \frac{3}{2}$; (v) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (vi) $-x + \frac{3}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii) $-x + 1, y, -z + \frac{1}{2}$.]

Figure 5

The stacking of layers along the *b* direction in (I), with C—H...O contacts (dashed lines) bridging adjoining layers. [Symmetry code: (viii) $-x + 1, -y + 1, -z + 1$.]

contacts (Table 2 and Fig. 5) stabilize the structure in the third dimension.

In order to study the thermal stability of complex (I), its thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded (see *Supplementary materials*). The complex starts to dehydrate at 360 K and the observed weight loss of 2.7% corresponds well to the calculated value of 2.8% for the water content. The IR spectrum of the dehydrated sample, (Ia) (heated to 423 K) (Fig. 1, bottom), does not show the absorption band due to the $\nu(\text{OH})$ vibration, which appears at 3501 cm^{-1} in the spectrum of the hydrate. The anhydrous complex (Ia) thus formed is stable up to 558 K, at which point a complicated three-step decomposition process takes place. The weight of the solid residue (26.6%) is consistent with any of several interpretations, but it clearly does not contain any species relevant to the characterization of complex (I).

In conclusion, under solvothermal conditions the organic compound bapen reacts to form pdpm, which binds to Ni^{II} giving the title square-planar complex $[\text{Ni}(\text{CN})_2(\text{pdpm})]\cdot 0.5\text{H}_2\text{O}$ as yellow crystals. The present complex is, to the best of our knowledge, the first structurally characterized square-planar Ni^{II} cyanide complex with a *cis*- C_2N_2 donor set. The solvent water molecule is hydrogen bonded to two molecules of the complex (Fig. 3), and C—H...N contacts further unite this structural unit into two-dimensional nets, which are stacked along [010]. The complex is stable up to 360 K, at which point dehydration takes place; the dehydrated product is stable up to 558 K.

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Experimental

$\text{Ni}^{\text{I}}, \text{Ni}^{\text{I'}}$ -(Ethane-1,2-diyl)bis(propene-1,3-diamine) (bapen; 94%, Aldrich), $\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ (Aldrich), $\text{Gd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich) and DMF (99.8%, Aldrich) were used as received.

A mixture of solid $\text{Gd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.914 g, 2 mmol), bapen (0.78 ml, 4 mmol), solid $\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ (0.774 g, 3 mmol) and DMF (5 ml, 65 mmol) was placed in a stainless steel reactor with a Teflon liner. The reactor was heated in a linear manner to 453 K at a rate of 78 K h^{-1} . After 8 h of reaction at 453 K, the reactor was cooled to room temperature at a rate of 11 K h^{-1} . The light-brown powder (0.275 g) which had formed was removed by filtration and the dark-orange filtrate was left for crystallization at room temperature. Yellow crystals of (I) formed within 3 d; these were isolated by filtration, and washed with DMF and hexane (yield: 8%, 0.07 g). Analysis calculated for $\text{C}_{12}\text{H}_{17}\text{N}_6\text{NiO}_{0.5}$: C 46.20, H 5.49, N 26.94%; found: C 46.54, H 5.59, N 26.96%. Thermogravimetric analysis (TA), water: expected 2.7%, calculated 2.8%.

Crystal data

$[\text{Ni}(\text{CN})_2(\text{C}_{10}\text{H}_{16}\text{N}_4)]\cdot 0.5\text{H}_2\text{O}$
 $M_r = 312.03$
 Orthorhombic, *Pbcn*
 $a = 20.4120(4)\text{ \AA}$
 $b = 7.1730(2)\text{ \AA}$
 $c = 17.8858(4)\text{ \AA}$

$V = 2618.75(11)\text{ \AA}^3$
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 1.48\text{ mm}^{-1}$
 $T = 150\text{ K}$
 $0.19 \times 0.17 \times 0.03\text{ mm}$

Data collection

Agilent Xcalibur Sapphire3
 diffractometer
 Absorption correction: multi-scan
 (*CrysAlis PRO*; Agilent, 2012)
 $T_{\min} = 0.835$, $T_{\max} = 1.000$

42018 measured reflections
 2994 independent reflections
 2304 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.107$
 $S = 1.14$
 2994 reflections
 190 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.54\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.29\text{ e \AA}^{-3}$

Atom C5 of the pdpm ligand was found to be disordered over two positions. The occupancies refined to values of 0.601 (12) for atom C5A and 0.399 (12) for atom C5B, and these were fixed at 0.60 and 0.40, respectively, for the final refinement. H atoms attached to C atoms were placed in calculated positions, with C—H = $0.99\text{ \AA}$, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The pivot atom C4 was assigned two sets of H atoms, corresponding to idealized geometries for the two congeners of C5. The unique H atom of the water molecule, atom O1 of which sits on a twofold axis, was located in a difference Fourier map and refined freely with an isotropic displacement parameter.

Table 1

Selected geometric parameters (Å, °).

Ni1—C11	1.841 (3)	C6—N3	1.469 (4)
Ni1—C12	1.853 (3)	C8—N4	1.473 (4)
Ni1—N1	1.902 (2)	C9—N4	1.298 (3)
Ni1—N4	1.909 (2)	C9—N3	1.336 (3)
C1—N1	1.471 (3)	C9—C10	1.493 (4)
C1—C2	1.518 (4)	C10—N1	1.299 (3)
C3—N2	1.466 (4)	C10—N2	1.329 (4)
N4—C9—C10	114.0 (2)	N6—C12—Ni1	178.5 (3)
N1—C10—N2	127.1 (3)	C10—N1—Ni1	114.64 (19)
N5—C11—Ni1	179.5 (3)	C1—N1—Ni1	129.00 (18)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1W···N6	0.78 (4)	2.18 (4)	2.934 (3)	164 (4)
C2—H2B···N5 ⁱ	0.99	2.60	3.483 (4)	148
C3—H3A···O1 ⁱⁱ	0.99	2.45	3.324 (5)	146
C5A—H5A···N5 ⁱⁱⁱ	0.99	2.57	3.275 (6)	128

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3094). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Crystal structure and thermal properties of a square-planar Ni^{II} complex of cyanide and a tricyclic bis-amidine ligand formed *in situ* under solvothermal conditions

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Dicyanido(2,3,4,6,7,9,10,11-octahydropyrimido[2',1':3,4]pyrazino[1,2-a]pyrimidine)nickel(II) hemihydrate

Crystal data

[Ni(CN)₂(C₁₀H₁₆N₄)]·0.5H₂O

M_r = 312.03

Orthorhombic, *Pbcn*

a = 20.4120 (4) Å

b = 7.1730 (2) Å

c = 17.8858 (4) Å

V = 2618.75 (11) Å³

Z = 8

F(000) = 1304

D_x = 1.583 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 8937 reflections

θ = 4.1–28.8°

μ = 1.48 mm⁻¹

T = 150 K

Plate, yellow

0.19 × 0.17 × 0.03 mm

Data collection

Agilent Xcalibur Sapphire3
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.0655 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2012)

T_{min} = 0.835, *T_{max}* = 1.000

42018 measured reflections

2994 independent reflections

2304 reflections with *I* > 2σ(*I*)

R_{int} = 0.052

θ_{max} = 27.5°, θ_{min} = 4.1°

h = −26→26

k = −9→9

l = −23→23

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.043

wR (*F*²) = 0.107

S = 1.14

2994 reflections

190 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 atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0357*P*)² + 3.9675*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.54 e Å⁻³

Δρ_{min} = −0.29 e Å⁻³

Special details

Experimental. Elemental analyses were performed on a Perkin–Elmer 2400 CHNS instrument. IR spectra were recorded on a Perkin–Elmer Spectrum 100 FT–IR spectrophotometer with UATR accessory in the range of 4000–300 cm^{−1}. The TG and DTG curves were recorded on a 2960 SDT V3.0 F instrument under the following conditions: sample weight = 1.8945 mg, heating rate = 10° min^{−1}, nitrogen atmosphere, temperature range 20–700°C, aluminium crucibles.

IR (cm^{−1}): 3501 (*m*), 2981 (*w*), 2931 (*w*), 2874 (*w*), 2118 (*s*), 1616 (*s*), 1530 (*w*), 1484 (*m*), 1428 (*w*), 1385 (*m*), 1360 (*s*), 1317 (*s*), 1219 (*m*), 1201 (*m*), 1172 (*m*), 1127 (*w*), 1105 (*m*), 1082 (*m*), 1017 (*s*), 976 (*w*), 943 (*m*), 801 (*w*), 764 (*m*), 577 (*m*), 568 (*m*), 511 (*s*), 411 (*s*), 394 (*s*), 337 (*m*), 298 (*m*).

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1	0.720296 (16)	0.74617 (5)	0.557303 (19)	0.02275 (13)	
C1	0.78102 (14)	0.6524 (4)	0.70851 (16)	0.0280 (6)	
H1A	0.7808	0.5149	0.7135	0.034*	
H1B	0.7389	0.7002	0.7281	0.034*	
C2	0.83706 (14)	0.7328 (4)	0.75409 (16)	0.0297 (6)	
H2A	0.8352	0.8706	0.7528	0.036*	
H2B	0.8331	0.6921	0.8068	0.036*	
C3	0.90153 (14)	0.6671 (5)	0.72241 (16)	0.0305 (7)	
H3A	0.9380	0.7367	0.7459	0.037*	
H3B	0.9076	0.5329	0.7333	0.037*	
C4	0.96506 (15)	0.7087 (7)	0.60409 (19)	0.0505 (11)	
H4A	0.9976	0.7597	0.6396	0.061*	0.60
H4B	0.9792	0.5809	0.5907	0.061*	0.60
H4C	0.9845	0.8321	0.6150	0.061*	0.40
H4D	0.9943	0.6132	0.6261	0.061*	0.40
C5A	0.9654 (2)	0.8212 (10)	0.5378 (3)	0.0360 (12)	0.60
H5A	1.0062	0.7968	0.5093	0.043*	0.60
H5B	0.9652	0.9545	0.5521	0.043*	0.60
C5B	0.9644 (4)	0.6831 (16)	0.5237 (4)	0.038 (2)	0.40
H5C	0.9615	0.5484	0.5121	0.045*	0.40
H5D	1.0057	0.7313	0.5022	0.045*	0.40
C6	0.91205 (15)	0.8205 (6)	0.40855 (18)	0.0424 (9)	
H6A	0.9497	0.7523	0.3869	0.051*	
H6B	0.9192	0.9555	0.4004	0.051*	
C7	0.85057 (16)	0.7615 (5)	0.37072 (17)	0.0376 (7)	
H7A	0.8491	0.6237	0.3683	0.045*	
H7B	0.8504	0.8097	0.3189	0.045*	
C8	0.79102 (14)	0.8313 (5)	0.41094 (16)	0.0323 (7)	
H8A	0.7885	0.9686	0.4058	0.039*	
H8B	0.7514	0.7773	0.3876	0.039*	
C9	0.84943 (13)	0.7647 (4)	0.52216 (16)	0.0244 (6)	

C10	0.84659 (13)	0.7184 (4)	0.60346 (16)	0.0239 (6)
C11	0.65737 (14)	0.7888 (4)	0.48561 (17)	0.0284 (6)
C12	0.65114 (14)	0.7112 (4)	0.62294 (17)	0.0285 (6)
N1	0.78732 (11)	0.7029 (3)	0.62914 (13)	0.0236 (5)
N2	0.90211 (11)	0.6977 (4)	0.64140 (13)	0.0288 (6)
N3	0.90782 (11)	0.7820 (4)	0.48908 (14)	0.0317 (6)
N4	0.79239 (11)	0.7818 (3)	0.49086 (13)	0.0257 (5)
N5	0.61745 (13)	0.8148 (4)	0.44083 (15)	0.0381 (7)
N6	0.60749 (13)	0.6917 (4)	0.66256 (16)	0.0409 (7)
O1	0.5000	0.5297 (6)	0.7500	0.0529 (11)
H1W	0.5254 (18)	0.592 (6)	0.729 (2)	0.054 (13)*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01569 (18)	0.0297 (2)	0.0229 (2)	−0.00265 (15)	−0.00032 (13)	0.00025 (15)
C1	0.0240 (15)	0.0376 (16)	0.0224 (14)	−0.0016 (12)	0.0023 (12)	0.0033 (12)
C2	0.0309 (15)	0.0369 (16)	0.0213 (13)	0.0008 (13)	−0.0010 (12)	−0.0005 (13)
C3	0.0227 (15)	0.0463 (18)	0.0226 (15)	−0.0014 (13)	−0.0041 (12)	0.0024 (13)
C4	0.0196 (15)	0.101 (3)	0.0304 (18)	0.0060 (18)	0.0020 (13)	0.0058 (19)
C5A	0.017 (2)	0.060 (4)	0.031 (3)	−0.003 (3)	−0.004 (2)	0.000 (3)
C5B	0.014 (4)	0.073 (6)	0.025 (4)	−0.002 (4)	0.002 (3)	−0.009 (4)
C6	0.0264 (16)	0.073 (2)	0.0279 (17)	−0.0014 (16)	0.0068 (13)	0.0106 (17)
C7	0.0403 (18)	0.0493 (19)	0.0231 (15)	−0.0022 (16)	0.0018 (13)	0.0039 (15)
C8	0.0243 (15)	0.0492 (19)	0.0233 (15)	−0.0082 (13)	−0.0029 (12)	0.0066 (14)
C9	0.0195 (13)	0.0276 (14)	0.0259 (14)	−0.0029 (12)	0.0002 (11)	−0.0016 (12)
C10	0.0194 (13)	0.0277 (15)	0.0246 (14)	−0.0009 (11)	0.0000 (11)	−0.0003 (11)
C11	0.0204 (14)	0.0349 (17)	0.0300 (15)	−0.0052 (12)	0.0040 (12)	0.0000 (12)
C12	0.0239 (15)	0.0339 (16)	0.0278 (15)	0.0006 (12)	−0.0029 (12)	−0.0016 (12)
N1	0.0192 (12)	0.0310 (13)	0.0205 (12)	−0.0022 (9)	0.0004 (9)	0.0004 (9)
N2	0.0186 (12)	0.0448 (15)	0.0230 (12)	0.0002 (10)	−0.0022 (10)	0.0013 (11)
N3	0.0185 (12)	0.0535 (18)	0.0232 (13)	−0.0065 (11)	0.0013 (9)	0.0032 (11)
N4	0.0200 (12)	0.0355 (14)	0.0215 (12)	−0.0057 (10)	−0.0015 (9)	0.0016 (10)
N5	0.0200 (13)	0.0593 (18)	0.0349 (15)	−0.0057 (12)	−0.0023 (11)	0.0059 (13)
N6	0.0249 (14)	0.0549 (18)	0.0428 (17)	−0.0008 (12)	0.0103 (13)	0.0016 (14)
O1	0.039 (2)	0.052 (2)	0.067 (3)	0.000	0.026 (2)	0.000

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

Ni1—C11	1.841 (3)	C5A—H5B	0.9900
Ni1—C12	1.853 (3)	C5B—N3	1.490 (9)
Ni1—N1	1.902 (2)	C5B—H5C	0.9900
Ni1—N4	1.909 (2)	C5B—H5D	0.9900
C1—N1	1.471 (3)	C6—N3	1.469 (4)
C1—C2	1.518 (4)	C6—C7	1.487 (4)
C1—H1A	0.9900	C6—H6A	0.9900
C1—H1B	0.9900	C6—H6B	0.9900
C2—C3	1.508 (4)	C7—C8	1.499 (4)
C2—H2A	0.9900	C7—H7A	0.9900
C2—H2B	0.9900	C7—H7B	0.9900

C3—N2	1.466 (4)	C8—N4	1.473 (4)
C3—H3A	0.9900	C8—H8A	0.9900
C3—H3B	0.9900	C8—H8B	0.9900
C4—C5A	1.435 (7)	C9—N4	1.298 (3)
C4—C5B	1.449 (9)	C9—N3	1.336 (3)
C4—N2	1.450 (4)	C9—C10	1.493 (4)
C4—H4A	0.9900	C10—N1	1.299 (3)
C4—H4B	0.9900	C10—N2	1.329 (4)
C4—H4C	0.9900	C11—N5	1.158 (4)
C4—H4D	0.9900	C12—N6	1.147 (4)
C5A—N3	1.490 (6)	O1—H1W ⁱ	0.78 (4)
C5A—H5A	0.9900	O1—H1W	0.78 (4)
C11—Ni1—C12	86.12 (13)	C4—C5B—H5D	109.4
C11—Ni1—N1	178.27 (11)	N3—C5B—H5D	109.4
C12—Ni1—N1	95.61 (11)	H5C—C5B—H5D	108.0
C11—Ni1—N4	94.70 (11)	N3—C6—C7	110.1 (3)
C12—Ni1—N4	179.17 (11)	N3—C6—H6A	109.7
N1—Ni1—N4	83.57 (10)	C7—C6—H6A	109.7
N1—C1—C2	111.0 (2)	N3—C6—H6B	109.7
N1—C1—H1A	109.4	C7—C6—H6B	109.7
C2—C1—H1A	109.4	H6A—C6—H6B	108.2
N1—C1—H1B	109.4	C6—C7—C8	111.8 (3)
C2—C1—H1B	109.4	C6—C7—H7A	109.3
H1A—C1—H1B	108.0	C8—C7—H7A	109.3
C3—C2—C1	109.7 (2)	C6—C7—H7B	109.3
C3—C2—H2A	109.7	C8—C7—H7B	109.3
C1—C2—H2A	109.7	H7A—C7—H7B	107.9
C3—C2—H2B	109.7	N4—C8—C7	111.7 (2)
C1—C2—H2B	109.7	N4—C8—H8A	109.3
H2A—C2—H2B	108.2	C7—C8—H8A	109.3
N2—C3—C2	109.4 (2)	N4—C8—H8B	109.3
N2—C3—H3A	109.8	C7—C8—H8B	109.3
C2—C3—H3A	109.8	H8A—C8—H8B	107.9
N2—C3—H3B	109.8	N4—C9—N3	126.9 (3)
C2—C3—H3B	109.8	N4—C9—C10	114.0 (2)
H3A—C3—H3B	108.2	N3—C9—C10	119.1 (2)
C5A—C4—N2	114.6 (3)	N1—C10—N2	127.1 (3)
C5B—C4—N2	116.2 (4)	N1—C10—C9	113.6 (2)
C5A—C4—H4A	108.6	N2—C10—C9	119.3 (2)
N2—C4—H4A	108.6	N5—C11—Ni1	179.5 (3)
C5A—C4—H4B	108.6	N6—C12—Ni1	178.5 (3)
N2—C4—H4B	108.6	C10—N1—C1	116.4 (2)
H4A—C4—H4B	107.6	C10—N1—Ni1	114.64 (19)
C5B—C4—H4C	108.2	C1—N1—Ni1	129.00 (18)
N2—C4—H4C	108.2	C10—N2—C4	121.0 (2)
C5B—C4—H4D	108.2	C10—N2—C3	121.0 (2)
N2—C4—H4D	108.2	C4—N2—C3	118.1 (2)
H4C—C4—H4D	107.4	C9—N3—C6	120.3 (2)

C4—C5A—N3	111.9 (4)	C9—N3—C5A	117.6 (3)
C4—C5A—H5A	109.2	C6—N3—C5A	119.4 (3)
N3—C5A—H5A	109.2	C9—N3—C5B	117.5 (4)
C4—C5A—H5B	109.2	C6—N3—C5B	116.8 (4)
N3—C5A—H5B	109.2	C9—N4—C8	117.3 (2)
H5A—C5A—H5B	107.9	C9—N4—Ni1	114.24 (19)
C4—C5B—N3	111.1 (6)	C8—N4—Ni1	128.45 (18)
C4—C5B—H5C	109.4	H1W ⁱ —O1—H1W	110 (6)
N3—C5B—H5C	109.4		

Symmetry code: (i) $-x+1, y, -z+3/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1W ⁱ ...N6	0.78 (4)	2.18 (4)	2.934 (3)	164 (4)
C2—H2B...N5 ⁱⁱ	0.99	2.60	3.483 (4)	148
C3—H3A...O1 ⁱⁱⁱ	0.99	2.45	3.324 (5)	146
C5A—H5A...N5 ^{iv}	0.99	2.57	3.275 (6)	128

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