Synthesis, characterization and crystal structure of the new pentahydrate of bis(2,2'-bipyridine- κ^2N,N')(oxalato- κ^2O^1,O^2)nickel(II)

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The reaction of NiCl_2 , $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and 2,2'-bipyridine (bpy) in water–ethanol solution at 281 K yields light-purple needles of the new pentahydrate of bis(2,2'-bipyridine)oxalato-nickel(II), $[\text{Ni}(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)_2] \cdot 5\text{H}_2\text{O}$ or $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot 5\text{H}_2\text{O}$, while at room temperature, deep-pink prisms of the previously reported tetrahydrate $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot 4\text{H}_2\text{O}$ [Román, Luque, Guzmán-Miralles & Beitia (1995), *Polyhedron*, **14**, 2863–2869] were gathered. The asymmetric unit in the crystal structure of the new pentahydrate incorporates the discrete molecular complex $[\text{Ni}(\text{ox})(\text{bpy})_2]$ and five solvent water molecules. Within the complex molecule, all three ligands are bonded as chelates. The complex molecules are involved in an extended system of hydrogen bonds with the solvent water molecules. Additionally, π – π interactions also contribute to the stabilization of the extended structure. The dehydration of the pentahydrate starts at 323 K and proceeds in at least two steps as determined by thermal analysis.

Keywords: crystal structure; TGA/DTA analysis; bis(2,2'-bipyridine)(oxalato)nickel(II); pentahydrate; IR spectra; hydrogen bonding; π – π interactions.

1. Introduction

The oxalate dianion is well known as a versatile ligand which can adopt a large range of coordination modes (Castillo, Luque, Lloret & Román, 2001; Liu *et al.*, 2007; Paredes-García *et al.*, 2011). As a bridging ligand it is able to mediate strong exchange interactions between paramagnetic metal ions separated by more than 5 Å, which is the basis for the synthetic and magneto-structural investigations of these

complexes (Keene *et al.*, 2009; Castillo, Luque, Román *et al.*, 2001; Chun *et al.*, 2009; Coronado *et al.*, 2008).

As part of our current research on such compounds we have undertaken a study of the system Ni^{II} –bpy–ox (bpy is 2,2'-bipyridine and H_2ox is oxalic acid). Previously, the mononuclear complex $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot 4\text{H}_2\text{O}$ was isolated and structurally characterized (Román *et al.*, 1995). In addition, with Cu^{II} present during the synthesis, the partially substituted compound $[\text{M}(\text{ox})(\text{bpy})_2] \cdot 4\text{H}_2\text{O}$ ($\text{M} = 0.95\text{Ni}:0.05\text{Cu}$) was also isolated and characterized (Kuchár *et al.*, 2009). We were successful in preparing the title complex, $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot 5\text{H}_2\text{O}$, (I), only by lowering the crystallization temperature to 281 K. The isostructural compounds $[\text{M}(\text{ox})(\text{bpy})_2] \cdot 5\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Zn}$), which have already been reported, were formed at room temperature (Šestan *et al.*, 2004; Šestan Jurić *et al.*, 2006).

2. Experimental

Elemental analysis was performed on a Perkin–Elmer 2400 Series II CHNS/O analyser. IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin–Elmer Spectrum 100 CSI DTGS FT–IR spectrophotometer with a UATR one-bounce KRS-5 accessory. The thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded on a TA 2960 SDT V3.0F instrument under the following conditions: heating rate = 2 K min^{-1} , nitrogen atmosphere, temperature range = 293–973 K, aluminum crucibles.

2.1. Synthesis and crystallization

NiCl_2 , $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, 2,2'-bipyridine and ethanol (96%) were purchased from commercial sources and used as received.

A water solution of NiCl_2 (1 mmol, 129.6 mg in 5 ml) was added dropwise with stirring to a water solution of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (2 mmol, 368.5 g in 7.5 ml), giving a green solution. An ethanol solution of 2,2'-bipyridine (2 mmol, 312.4 mg in 7.5 ml) was added dropwise. Initially, a blue solid was formed, which subsequently dissolved to give a claret-coloured solution. The solution thus formed was mixed for 10 min, filtered and poured into two vessels, where it was left aside for crystallization at different temperatures. Crystallization at 281 K yielded light-purple needles of $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot 5\text{H}_2\text{O}$, (I), in 2 d. If the solution was left undisturbed for a further 2 d, a few deep-pink prisms of $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot$

Table 1

Experimental details.

Crystal data	
Chemical formula	$[\text{Ni}(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)_2] \cdot 5\text{H}_2\text{O}$
M_r	549.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	10.7474 (4), 22.7052 (9), 9.9647 (5)
β (°)	103.390 (4)
V (Å ³)	2365.50 (18)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.88
Crystal size (mm)	0.30 × 0.10 × 0.07
Data collection	
Diffractometer	Agilent Xcalibur Sapphire3 diffractometer
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2012)
$T_{\min}, T_{\max}$	0.779, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21922, 5415, 4730
R_{int}	0.033
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.077, 1.04
No. of reflections	5415
No. of parameters	355
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.29

Computer programs: *CrysAlis PRO* (Agilent, 2012), *DIAMOND* (Brandenburg & Putz, 2008), *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

4H₂O, (II), also appeared. The crystals were isolated by filtration on a glass frit, quickly washed with water and air-dried. The few crystals of the minor phase were removed manually under a microscope [yield for (I): 50%]. In contrast, crystallization at room temperature overnight yielded deep-pink prisms of (II) accompanied by a few purple needles of (I). The crystals were isolated by filtration on a glass frit, quickly washed with water and air-dried. The few crystals of the minor phase were separated manually under a microscope [yield for (II): 55%]. Analysis calculated for C₂₂H₂₆N₄NiO₉: C 48.12, H 4.77, N 10.20%; found: C 47.68, H 5.12, N 9.95%. TGA, water loss: expected 16.4%, observed 14.4%.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. C-bound H atoms were placed at calculated positions, with C—H = 0.95 Å, and refined as riding atoms. The H atoms of the water molecules were located in a difference map and their positions were refined freely. For all H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$.

3. Results and discussion

The crystal structure of the title complex, (I) (Fig. 1), is molecular and is composed of $[\text{Ni}(\text{ox})(\text{bpy})_2]$ units and five independent uncoordinated water molecules. The isostructural compounds $[\text{M}(\text{ox})(\text{bpy})_2] \cdot 5\text{H}_2\text{O}$ ($M = \text{Co}, \text{Zn}$) have been described previously (Šestan *et al.*, 2004; Šestan Jurić *et*

Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

al., 2006). The central Ni^{II} atom is coordinated by three chelating ligands in a distorted octahedron, with the oxalate ligand bound side-on *via* two O atoms. Although the tris(-chelate) complex is chiral, both enantiomers are present in equal amounts in the crystal structure, which is centrosymmetric. The same situation was observed in the structure of the tetrahydrate, (II) (Román *et al.*, 1995).

The Ni—N bond distances in (I) [2.0720 (13)–2.1001 (13) Å] are slightly longer than the Ni—O distances [2.0359 (11)–2.0673 (12) Å]. The N—Ni—N bite angles are 78.35 (5) and 78.97 (5)°, and the O—Ni—O bite angle is 80.79 (4)°. Similar values for the geometric parameters were found in tetrahydrate (II), *e.g.* the corresponding Ni—N bonds are in the range 2.072 (8)–2.113 (9) Å and the Ni—O bonds are in the range 2.036 (8)–2.070 (8) Å, while the N—Ni—N bite angles are 78.0 (4) and 78.7 (4)°, and the O—Ni—O bite angle is 79.9 (3)° (Román *et al.*, 1995).

The uncoordinated water molecules and oxalate ligands are linked together by an extensive system of hydrogen bonds (Table 2) which plays a key role in the crystal packing. The structure is extended in two dimensions by a hydrophilic two-dimensional hydrogen-bonding network perpendicular to the *a* axis, which contains voids that accommodate the $[\text{Ni}(\text{bpy})_2]$ units. Within this hydrogen-bonded system, which is an unbounded two-dimensional array of fused rings, five ring patterns can be distinguished; their graph-set symbols (Bernstein *et al.*, 1995) are $R_5^3(10)$, $R_4^4(8)$, $R_4^4(10)$, $R_4^4(14)$ and $R_{10}^{10}(26)$ (Fig. 2a; the respective rings are denoted R1–R5). This net can be further divided into two subsystems, namely a chain of R1 and R2 congeners (running vertically through the centre of Fig. 2a) and a broader subsystem consisting of a fused R3/R4 pair alternating with the larger R5 (also running in the vertical direction in Fig. 2a). Ring R5 is centred on a crystallographic

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C4-H4\cdots O8W^i$	0.95	2.55	3.502 (2)	176
$C5-H5\cdots O7W$	0.95	2.60	3.356 (2)	137
$C9-H9\cdots O2^{ii}$	0.95	2.61	3.137 (2)	116
$C10-H10\cdots O1$	0.95	2.65	3.1875 (19)	116
$C10-H10\cdots O2^{ii}$	0.95	2.52	3.106 (2)	120
$C12-H12\cdots O1^{iii}$	0.95	2.48	3.112 (2)	124
$C15-H15\cdots O5W$	0.95	2.46	3.139 (2)	129
$C20-H20\cdots O3$	0.95	2.61	3.164 (2)	118
$O5W-H1O5\cdots O9W^{ii}$	0.84 (2)	1.92 (2)	2.7509 (19)	168 (2)
$O5W-H2O5\cdots O6W$	0.82 (2)	1.94 (2)	2.739 (2)	162 (2)
$O6W-H1O6\cdots O8W^{iv}$	0.85 (3)	1.94 (3)	2.780 (2)	174 (2)
$O6W-H2O6\cdots O7W^{iv}$	0.80 (3)	1.94 (3)	2.739 (2)	175 (2)
$O7W-H1O7\cdots O9W^v$	0.76 (2)	2.05 (3)	2.8107 (19)	177 (3)
$O7W-H2O7\cdots O8W^i$	0.83 (3)	2.14 (3)	2.919 (2)	157 (2)
$O8W-H1O8\cdots O3$	0.77 (2)	2.01 (2)	2.7890 (17)	178 (2)
$O8W-H2O8\cdots O5W^{vi}$	0.83 (2)	1.88 (3)	2.711 (2)	173 (2)
$O9W-H2O9\cdots O2$	0.76 (2)	1.99 (2)	2.7364 (19)	167 (2)
$O9W-H1O9\cdots O4^{vii}$	0.80 (2)	1.97 (2)	2.7658 (18)	173 (2)

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

inversion centre. The bpy ligands containing atoms N3 and N4 (and their symmetry equivalents) extend roughly parallel to [100] and fill the space between the undulating hydrogen-bonded nets. The result is that the structure is segregated into hydrophilic layers and thicker hydrophobic slabs, alternating along the a axis. In contrast, in tetrahydrate (II) a simpler two-dimensional hydrogen-bonded fused-ring net perpendicular to the c axis is formed by only two topologically distinct rings, with graph-set symbols $R_3^3(8)$ and $R_{11}^{10}(28)$ (Fig. 2b, rings R6 and R7). In this case, the large ring R7, which possesses no point symmetry, has just one $[\text{Ni}(\text{bpy})_2]$ fragment projecting into its interior. A further difference between the structures is that in (I) the two $[\text{Ni}(\text{ox})(\text{bpy})_2]$ complex molecules are hydrogen bonded to two common water-molecule bridges (ring R4, Fig. 2a), while in (II) the complex molecules have a lesser degree of proximity (Fig. 2b) (Román *et al.*, 1995).

Face-to-face π - π interactions are also present in (I). The bpy fragments containing atoms N1 (centroid Cg1) and N2 (Cg2) interact, mediating the formation of a zigzag chain parallel to the c axis [Fig. 3a; $\text{Cg1}\cdots\text{Cg2}^i = 3.6025(10)$ Å, dihedral angle = $1.91(8)^\circ$]. This chain is roughly eclipsed by, and parallel to, the hydrogen-bonded fused-ring substructure $\cdots R2/R1 \cdots$ that runs vertically through the centre of Fig. 2(a). The neighbouring bpy ligands that include atoms N3 (Cg3) and N4 (Cg4) are coplanar and are also involved in weaker stacking interactions. The normal distance from Cg3 to the plane containing Cg4ⁱⁱⁱ is 3.4520 (7) Å, while the corresponding distance from Cg4ⁱⁱⁱ to the plane of the ring containing Cg3 is 3.4740 (7) Å; the distance between Cg3 and Cg4ⁱⁱⁱ is 4.0266 (10) Å. In (II), only one type of stacking interaction was found ($\text{Cg}\cdots\text{Cg} = 3.75$ Å), forming a zigzag chain-like arrangement of the complex molecules (Fig. 3b; Román *et al.*, 1995). The same motif of π - π interactions as in (I) was found in $[\text{Co}(\text{ox})(\text{bpy})_2]\cdot 5\text{H}_2\text{O}$ and the geometric parameters for the first type of π - π interaction are similar to those observed in (I) [3.536 (2) Å and 1.71°]. However, the

Figure 2

(a) The hydrogen-bonding system of (I) (dashed lines) [symmetry codes: (ii) $-x + 1, -y, -z + 2$; (v) $-x, -y, -z + 1$; (vi) $x - 1, y, z$; (vii) $-x, -y, -z + 2$; (viii) $x, y, z + 1$]. (b) The hydrogen-bonding system of (II) (dashed lines). The ring motifs R1–R5 are discussed in the text.

$\text{Cg}\cdots\text{Cg}$ distance for the second type is shorter [3.880 (2) Å] than in (I) (Šestan *et al.*, 2004).

In the structure of tetrahydrate (II), some additional weak $\text{C}-\text{H}\cdots\text{O}$ interactions contribute to the packing forces; the important geometric parameters are in the ranges 2.75 (1)–3.39 (1) Å for $\text{C}\cdots\text{O}$ distances and 120 – 179° for $\text{C}-\text{H}\cdots\text{O}$ angles (Román *et al.*, 1995). On the other hand, in pentahydrate (I) the importance of the observed $\text{C}-\text{H}\cdots\text{O}$ interactions is considerably lower, as can be deduced from the corresponding geometric parameters; the $\text{C}\cdots\text{O}$ distances are in the range 3.106 (2)–3.502 (2) Å, while the $\text{C}-\text{H}\cdots\text{O}$ angles span the range 116 – 176° (Table 2).

Both (I) and (II) crystallize in the same monoclinic space group $P2_1/c$ [the structure of (II) was reported in the $P2_1/n$ setting; Román *et al.*, 1995]. The different temperatures [100 K for (I) and 293 K for (II)] used for the respective data collections do not allow a closer comparison of the unit-cell dimensions and cell volumes [2365.50 (18) and 2442.4 (6) Å³

Figure 3

(a) The two-dimensional network of π - π interactions in (I) (dashed lines) [symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, -y, -z + 1$]. (b) The zigzag chain-like pattern of π - π interactions in (II) (dashed lines) [symmetry codes: (ix) $-x, -y, -z - \frac{1}{2}$].

for (I) and (II), respectively]. Nevertheless, the comparison of the two hydrates suggests that the structures are not related topotactically and the structural rearrangement from pentahydrate to tetrahydrate would require considerable structural changes.

The measured IR spectrum of (I) (Fig. 4) agrees very well with that of $[\text{Zn}(\text{ox})(\text{bpy})_2] \cdot 5\text{H}_2\text{O}$ (Šestan Jurić *et al.*, 2006), as well as with those of the above-mentioned tetrahydrate complexes (Román *et al.*, 1995; Kuchár *et al.*, 2009). The existence of a broad absorption band near 3300 cm^{-1} reflects the presence of solvent water molecules. The presence of bpy ligands is proved by several weak absorption bands for $\nu(\text{C}_{\text{ar}}-\text{H})$ valence vibrations observed in the range 3130 – 3080 cm^{-1} , and by the sharp weak-to-medium bands of C–C and C–N stretching vibrations located in the 1605 – 1439 cm^{-1} region. The strongest absorption band in the IR spectrum at 1641 cm^{-1} was assigned to $\nu_{\text{asym}}(\text{CO})$ vibrations of the

Figure 4

The IR spectrum of (I).

Figure 5
Thermogravimetric (TG, black) and differential thermal analysis (DTA, red) curves for (I).

Figure 6
Photographs of single crystals of (I) (left) and (II) (right).

bidentate oxalate ligand. The medium sharp absorption bands for $\nu_{\text{sym}}(\text{CO})$ vibrations appear at 1421 and 1285 cm^{-1} . In the IR spectrum of (II), the bands corresponding to these oxalate vibrations appeared at 1670, 1645, 1425, 1290 and 770 cm^{-1} , respectively (Román *et al.*, 1995).

In order to study the thermal stability of complex (I), its thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded (Fig. 5). Thermal decomposition starts with the elimination of uncoordinated water molecules; a weight loss of 14.4% is observed up to a temperature of 363 K. A weight loss of 16.4% calculated for five water molecules is higher than that observed (which corresponds to 4.4 H_2O molecules), but the discrepancy is acceptable taking into account the low temperature used for preparation and possible partial dehydration of the compound during sample preparation for thermal analysis. As suggested by the DTA curve, the endothermic dehydration is at least a two-step process. This dehydration was followed by IR spectroscopy

and the spectrum of the dehydrated sample does not show the $\nu(\text{OH})$ absorption band at 3300 cm^{-1} . A very weak endothermic effect centred at 453 K may correspond to a release of one molecule of bpy (observed weight loss 27.9%, calculated 28.4%). Further heating beyond 613 K causes a very strong exothermic effect (maximum at 648 K) with a continuous weight loss of 43.6% (calculated 44.4% for the second bpy and oxalate).

In conclusion, from the aqueous–ethanolic Ni^{II} –bpy–ox system, light-purple needles of the new pentahydrate of the mononuclear complex, *viz.* $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot 5\text{H}_2\text{O}$, were obtained by slow evaporation at 281 K, while at room temperature pink prisms of the previously reported $[\text{Ni}(\text{ox})(\text{bpy})_2] \cdot 4\text{H}_2\text{O}$ complex were gathered. The colours of the two complexes clearly differ (Fig. 6), even though the chromophores are chemically identical. Two-dimensional hydrogen-bonding systems exist in both (I) and (II), but they differ in their patterns of supramolecular aggregation.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: FN3166).

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supplementary materials

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Synthesis, characterization and crystal structure of the new pentahydrate of bis-(2,2'-bipyridine- κ^2N,N')(oxalato- κ^2O^1,O^2)nickel(II)

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXL97* (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* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

Bis(2,2'-bipyridine- κ^2N,N')(oxalato- κ^2O^1,O^2)nickel(II) pentahydrate

Crystal data

[Ni(C₂O₄)(C₁₀H₈N₂)₂] $\cdot$ 5H₂O

$M_r = 549.18$

Monoclinic, $P2_1/c$

$a = 10.7474$ (4) Å

$b = 22.7052$ (9) Å

$c = 9.9647$ (5) Å

$\beta = 103.390$ (4)°

$V = 2365.50$ (18) Å³

$Z = 4$

$F(000) = 1144$

$D_x = 1.542$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4223 reflections

$\theta = 0.8$ – 1.0 °

$\mu = 0.88$ mm⁻¹

$T = 100$ K

Needle, light purple

$0.30 \times 0.10 \times 0.07$ 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)

$T_{\min} = 0.779$, $T_{\max} = 1.000$

21922 measured reflections

5415 independent reflections

4730 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 4.2$ °

$h = -13 \rightarrow 13$

$k = -29 \rightarrow 29$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.077$

$S = 1.04$

5415 reflections

355 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

$$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 1.1619P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. Elemental analysis was performed on CHNOS Elemental Analyzer vario MICRO instrument. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrophotometer with UATR accessory in the range of 4000–400 cm⁻¹. The TG and DTA curves were recorded on a 2960 SDT V3.0 F instrument under the following conditions: sample weight = 5.7873 mg, heating rate = 2 °/min, nitrogen atmosphere, temperature range 20–700°C, aluminium crucibles. IR (in cm⁻¹): 3285(*m*); 3105(*w*); 3088(*w*); 1718(*w*); 1641(*s*); 1601(*m*); 1595(*m*); 1573(*m*); 1566(*m*); 1489(*w*); 1470(*m*); 1438(*m*); 1421(*m*); 1309(*w*); 1284(*m*); 1248(*w*); 1224(*w*); 1168(*w*); 1155(*w*); 1119(*w*); 1100(*w*); 1072(*w*); 1043(*w*); 1022(*w*); 1016(*w*); 976(*w*); 903 (*w*); 863(*w*); 816(*w*); 763(*m*); 734(*m*); 649(*m*); 629(*m*); 549(*m*); 507(*m*); 461(*m*); 439(*m*); 415(*m*).

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.345086 (18)	0.110379 (8)	0.70079 (2)	0.01229 (7)
C1	0.36811 (15)	0.23795 (7)	0.72976 (16)	0.0137 (3)
C2	0.34379 (16)	0.29781 (7)	0.70734 (17)	0.0185 (3)
H2	0.3859	0.3260	0.7728	0.022*
C3	0.25757 (17)	0.31585 (7)	0.58880 (18)	0.0208 (4)
H3	0.2393	0.3565	0.5723	0.025*
C4	0.19833 (16)	0.27409 (7)	0.49473 (18)	0.0204 (3)
H4	0.1400	0.2855	0.4118	0.024*
C5	0.22589 (15)	0.21518 (7)	0.52392 (17)	0.0169 (3)
H5	0.1844	0.1864	0.4597	0.020*
C6	0.45835 (14)	0.21456 (7)	0.85440 (16)	0.0135 (3)
C7	0.53731 (16)	0.25026 (7)	0.95159 (17)	0.0183 (3)
H7	0.5366	0.2918	0.9397	0.022*
C8	0.61699 (16)	0.22460 (7)	1.06586 (18)	0.0197 (3)
H8	0.6707	0.2483	1.1340	0.024*
C9	0.61720 (15)	0.16393 (7)	1.07940 (17)	0.0179 (3)
H9	0.6710	0.1453	1.1569	0.021*
C10	0.53734 (15)	0.13084 (7)	0.97768 (17)	0.0158 (3)
H10	0.5380	0.0892	0.9867	0.019*
C11	0.45342 (16)	0.07516 (7)	0.46851 (16)	0.0164 (3)
C12	0.54106 (17)	0.06554 (7)	0.38764 (18)	0.0216 (4)
H12	0.5137	0.0494	0.2976	0.026*
C13	0.66829 (18)	0.07965 (8)	0.43941 (19)	0.0240 (4)
H13	0.7290	0.0742	0.3847	0.029*
C14	0.70614 (17)	0.10188 (7)	0.57218 (19)	0.0222 (4)
H14	0.7932	0.1114	0.6106	0.027*

C15	0.61423 (16)	0.10999 (7)	0.64778 (18)	0.0189 (3)
H15	0.6403	0.1250	0.7390	0.023*
C16	0.31527 (16)	0.06224 (7)	0.42106 (17)	0.0174 (3)
C17	0.26045 (18)	0.03938 (7)	0.29108 (18)	0.0226 (4)
H17	0.3122	0.0310	0.2280	0.027*
C18	0.13049 (19)	0.02897 (8)	0.25457 (19)	0.0259 (4)
H18	0.0917	0.0133	0.1664	0.031*
C19	0.05756 (18)	0.04166 (8)	0.34862 (18)	0.0244 (4)
H19	−0.0322	0.0352	0.3260	0.029*
C20	0.11801 (16)	0.06401 (7)	0.47631 (18)	0.0210 (4)
H20	0.0678	0.0726	0.5407	0.025*
C21	0.28064 (15)	0.01334 (7)	0.84458 (16)	0.0160 (3)
C22	0.17847 (15)	0.06133 (7)	0.85287 (16)	0.0147 (3)
N1	0.30859 (12)	0.19701 (6)	0.63873 (14)	0.0137 (3)
N2	0.45918 (12)	0.15531 (6)	0.86708 (13)	0.0133 (3)
N3	0.49052 (13)	0.09766 (6)	0.59778 (14)	0.0156 (3)
N4	0.24424 (13)	0.07409 (6)	0.51318 (14)	0.0163 (3)
O1	0.37284 (10)	0.03031 (5)	0.79495 (12)	0.0161 (2)
O2	0.26399 (12)	−0.03711 (5)	0.88283 (15)	0.0296 (3)
O3	0.18687 (11)	0.10853 (5)	0.78563 (12)	0.0150 (2)
O4	0.09914 (12)	0.05107 (5)	0.92132 (13)	0.0223 (3)
O5W	0.81514 (12)	0.19349 (6)	0.83438 (14)	0.0246 (3)
H1O5	0.836 (2)	0.1682 (10)	0.897 (2)	0.029*
H2O5	0.826 (2)	0.2258 (11)	0.873 (2)	0.029*
O6W	0.85321 (14)	0.30956 (6)	0.90721 (16)	0.0297 (3)
H1O6	0.898 (2)	0.3122 (10)	0.989 (3)	0.036*
H2O6	0.899 (2)	0.3135 (11)	0.855 (3)	0.036*
O7W	0.01231 (14)	0.18470 (7)	0.22899 (15)	0.0292 (3)
H1O7	−0.014 (2)	0.1626 (11)	0.172 (2)	0.035*
H2O7	0.013 (2)	0.2179 (11)	0.195 (2)	0.035*
O8W	−0.00803 (13)	0.18857 (6)	0.67982 (13)	0.0227 (3)
H1O8	0.046 (2)	0.1663 (10)	0.708 (2)	0.027*
H2O8	−0.060 (2)	0.1872 (9)	0.730 (2)	0.027*
O9W	0.09388 (13)	−0.10459 (6)	0.98145 (14)	0.0225 (3)
H2O9	0.136 (2)	−0.0817 (10)	0.959 (2)	0.027*
H1O9	0.039 (2)	−0.0912 (10)	1.014 (2)	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01480 (11)	0.01073 (11)	0.01161 (11)	−0.00078 (7)	0.00363 (8)	−0.00061 (7)
C1	0.0154 (7)	0.0143 (7)	0.0133 (7)	−0.0004 (6)	0.0070 (6)	−0.0005 (6)
C2	0.0240 (8)	0.0137 (8)	0.0186 (9)	−0.0010 (6)	0.0065 (7)	−0.0012 (6)
C3	0.0270 (9)	0.0152 (8)	0.0220 (9)	0.0040 (6)	0.0089 (7)	0.0054 (7)
C4	0.0211 (8)	0.0215 (8)	0.0182 (8)	0.0024 (6)	0.0039 (7)	0.0071 (7)
C5	0.0185 (8)	0.0182 (8)	0.0139 (8)	−0.0016 (6)	0.0034 (6)	0.0017 (6)
C6	0.0147 (7)	0.0138 (7)	0.0132 (7)	−0.0004 (6)	0.0058 (6)	−0.0015 (6)
C7	0.0205 (8)	0.0136 (7)	0.0206 (8)	−0.0016 (6)	0.0046 (7)	−0.0036 (6)
C8	0.0184 (8)	0.0210 (8)	0.0182 (8)	−0.0014 (6)	0.0010 (6)	−0.0065 (7)
C9	0.0166 (8)	0.0224 (8)	0.0140 (8)	0.0035 (6)	0.0026 (6)	−0.0001 (6)

C10	0.0160 (7)	0.0151 (7)	0.0169 (8)	0.0028 (6)	0.0046 (6)	0.0008 (6)
C11	0.0256 (8)	0.0099 (7)	0.0151 (8)	−0.0004 (6)	0.0074 (6)	0.0008 (6)
C12	0.0330 (10)	0.0159 (8)	0.0183 (8)	0.0030 (7)	0.0110 (7)	0.0000 (6)
C13	0.0297 (9)	0.0197 (9)	0.0279 (10)	0.0033 (7)	0.0177 (8)	0.0021 (7)
C14	0.0211 (8)	0.0183 (8)	0.0296 (10)	−0.0013 (6)	0.0106 (7)	0.0011 (7)
C15	0.0222 (8)	0.0161 (8)	0.0189 (8)	−0.0013 (6)	0.0059 (7)	−0.0003 (6)
C16	0.0269 (9)	0.0105 (7)	0.0148 (8)	−0.0006 (6)	0.0046 (7)	0.0008 (6)
C17	0.0358 (10)	0.0168 (8)	0.0158 (8)	−0.0015 (7)	0.0070 (7)	−0.0007 (6)
C18	0.0374 (10)	0.0184 (8)	0.0173 (9)	−0.0049 (7)	−0.0031 (7)	0.0003 (7)
C19	0.0251 (9)	0.0216 (9)	0.0227 (9)	−0.0048 (7)	−0.0025 (7)	0.0011 (7)
C20	0.0224 (8)	0.0187 (8)	0.0210 (9)	−0.0031 (6)	0.0033 (7)	0.0006 (7)
C21	0.0171 (7)	0.0152 (7)	0.0147 (8)	−0.0008 (6)	0.0016 (6)	0.0001 (6)
C22	0.0161 (7)	0.0148 (7)	0.0127 (8)	−0.0027 (6)	0.0022 (6)	−0.0036 (6)
N1	0.0152 (6)	0.0135 (6)	0.0132 (7)	−0.0002 (5)	0.0046 (5)	0.0015 (5)
N2	0.0136 (6)	0.0131 (6)	0.0141 (7)	0.0004 (5)	0.0048 (5)	−0.0007 (5)
N3	0.0199 (7)	0.0124 (6)	0.0158 (7)	−0.0002 (5)	0.0065 (5)	0.0001 (5)
N4	0.0220 (7)	0.0117 (6)	0.0140 (7)	−0.0011 (5)	0.0020 (5)	−0.0004 (5)
O1	0.0177 (6)	0.0129 (5)	0.0187 (6)	0.0010 (4)	0.0064 (4)	−0.0002 (4)
O2	0.0264 (7)	0.0177 (6)	0.0474 (9)	0.0015 (5)	0.0143 (6)	0.0122 (6)
O3	0.0162 (5)	0.0126 (5)	0.0173 (6)	0.0006 (4)	0.0060 (4)	0.0003 (4)
O4	0.0241 (6)	0.0232 (6)	0.0234 (6)	−0.0021 (5)	0.0133 (5)	−0.0004 (5)
O5W	0.0265 (7)	0.0270 (7)	0.0194 (7)	0.0003 (5)	0.0036 (5)	0.0007 (6)
O6W	0.0327 (8)	0.0372 (8)	0.0202 (7)	0.0046 (6)	0.0079 (6)	−0.0021 (6)
O7W	0.0405 (8)	0.0245 (7)	0.0228 (7)	−0.0046 (6)	0.0079 (6)	−0.0031 (6)
O8W	0.0218 (7)	0.0269 (7)	0.0200 (7)	0.0067 (5)	0.0061 (5)	0.0030 (5)
O9W	0.0249 (7)	0.0191 (6)	0.0267 (7)	−0.0008 (5)	0.0127 (5)	0.0008 (5)

Geometric parameters (Å, °)

Ni1—O1	2.0359 (11)	C13—C14	1.386 (3)
Ni1—O3	2.0673 (12)	C13—H13	0.9500
Ni1—N1	2.0720 (13)	C14—C15	1.386 (2)
Ni1—N3	2.0793 (14)	C14—H14	0.9500
Ni1—N2	2.0854 (13)	C15—N3	1.337 (2)
Ni1—N4	2.1001 (13)	C15—H15	0.9500
C1—N1	1.352 (2)	C16—N4	1.350 (2)
C1—C2	1.392 (2)	C16—C17	1.393 (2)
C1—C6	1.486 (2)	C17—C18	1.380 (3)
C2—C3	1.384 (2)	C17—H17	0.9500
C2—H2	0.9500	C18—C19	1.384 (3)
C3—C4	1.381 (2)	C18—H18	0.9500
C3—H3	0.9500	C19—C20	1.384 (2)
C4—C5	1.386 (2)	C19—H19	0.9500
C4—H4	0.9500	C20—N4	1.340 (2)
C5—N1	1.341 (2)	C20—H20	0.9500
C5—H5	0.9500	C21—O2	1.233 (2)
C6—N2	1.351 (2)	C21—O1	1.266 (2)
C6—C7	1.391 (2)	C21—C22	1.563 (2)
C7—C8	1.385 (2)	C22—O4	1.231 (2)
C7—H7	0.9500	C22—O3	1.2781 (19)

C8—C9	1.384 (2)	O5W—H1O5	0.84 (2)
C8—H8	0.9500	O5W—H2O5	0.82 (2)
C9—C10	1.388 (2)	O6W—H1O6	0.85 (3)
C9—H9	0.9500	O6W—H2O6	0.80 (3)
C10—N2	1.342 (2)	O7W—H1O7	0.76 (2)
C10—H10	0.9500	O7W—H2O7	0.83 (3)
C11—N3	1.357 (2)	O8W—H1O8	0.77 (2)
C11—C12	1.391 (2)	O8W—H2O8	0.83 (2)
C11—C16	1.480 (2)	O9W—H2O9	0.76 (2)
C12—C13	1.383 (3)	O9W—H1O9	0.80 (2)
C12—H12	0.9500		
O1—Ni1—O3	80.79 (4)	C11—C12—H12	120.3
O1—Ni1—N1	169.33 (5)	C12—C13—C14	119.13 (16)
O3—Ni1—N1	91.41 (5)	C12—C13—H13	120.4
O1—Ni1—N3	93.26 (5)	C14—C13—H13	120.4
O3—Ni1—N3	169.30 (5)	C13—C14—C15	118.58 (17)
N1—Ni1—N3	95.54 (5)	C13—C14—H14	120.7
O1—Ni1—N2	94.25 (5)	C15—C14—H14	120.7
O3—Ni1—N2	94.19 (5)	N3—C15—C14	122.82 (16)
N1—Ni1—N2	78.97 (5)	N3—C15—H15	118.6
N3—Ni1—N2	95.12 (5)	C14—C15—H15	118.6
O1—Ni1—N4	92.88 (5)	N4—C16—C17	121.50 (16)
O3—Ni1—N4	92.99 (5)	N4—C16—C11	115.27 (14)
N1—Ni1—N4	94.81 (5)	C17—C16—C11	123.23 (16)
N3—Ni1—N4	78.35 (5)	C18—C17—C16	119.56 (17)
N2—Ni1—N4	170.60 (5)	C18—C17—H17	120.2
N1—C1—C2	121.43 (14)	C16—C17—H17	120.2
N1—C1—C6	115.53 (13)	C17—C18—C19	118.89 (16)
C2—C1—C6	123.03 (14)	C17—C18—H18	120.6
C3—C2—C1	119.32 (15)	C19—C18—H18	120.6
C3—C2—H2	120.3	C20—C19—C18	118.68 (17)
C1—C2—H2	120.3	C20—C19—H19	120.7
C4—C3—C2	119.25 (15)	C18—C19—H19	120.7
C4—C3—H3	120.4	N4—C20—C19	122.98 (17)
C2—C3—H3	120.4	N4—C20—H20	118.5
C3—C4—C5	118.53 (15)	C19—C20—H20	118.5
C3—C4—H4	120.7	O2—C21—O1	125.89 (15)
C5—C4—H4	120.7	O2—C21—C22	118.51 (14)
N1—C5—C4	122.90 (15)	O1—C21—C22	115.58 (13)
N1—C5—H5	118.6	O4—C22—O3	126.24 (15)
C4—C5—H5	118.6	O4—C22—C21	118.85 (14)
N2—C6—C7	121.69 (14)	O3—C22—C21	114.90 (14)
N2—C6—C1	115.03 (13)	C5—N1—C1	118.56 (14)
C7—C6—C1	123.28 (14)	C5—N1—Ni1	126.09 (11)
C8—C7—C6	119.27 (15)	C1—N1—Ni1	115.15 (10)
C8—C7—H7	120.4	C10—N2—C6	118.59 (13)
C6—C7—H7	120.4	C10—N2—Ni1	126.25 (11)
C9—C8—C7	119.05 (15)	C6—N2—Ni1	115.01 (10)

C9—C8—H8	120.5	C15—N3—C11	118.74 (15)
C7—C8—H8	120.5	C15—N3—Ni1	125.69 (11)
C8—C9—C10	118.74 (15)	C11—N3—Ni1	115.57 (11)
C8—C9—H9	120.6	C20—N4—C16	118.39 (14)
C10—C9—H9	120.6	C20—N4—Ni1	126.29 (12)
N2—C10—C9	122.65 (15)	C16—N4—Ni1	115.28 (11)
N2—C10—H10	118.7	C21—O1—Ni1	114.05 (10)
C9—C10—H10	118.7	C22—O3—Ni1	113.33 (10)
N3—C11—C12	121.29 (15)	H1O5—O5W—H2O5	106 (2)
N3—C11—C16	115.50 (14)	H1O6—O6W—H2O6	109 (2)
C12—C11—C16	123.20 (15)	H1O7—O7W—H2O7	109 (2)
C13—C12—C11	119.41 (16)	H1O8—O8W—H2O8	108 (2)
C13—C12—H12	120.3	H2O9—O9W—H1O9	114 (2)
N1—C1—C2—C3	−0.5 (2)	O3—Ni1—N2—C10	92.16 (13)
C6—C1—C2—C3	−179.55 (15)	N1—Ni1—N2—C10	−177.22 (14)
C1—C2—C3—C4	−0.5 (3)	N3—Ni1—N2—C10	−82.56 (13)
C2—C3—C4—C5	1.1 (3)	N4—Ni1—N2—C10	−128.1 (3)
C3—C4—C5—N1	−0.8 (3)	O1—Ni1—N2—C6	−173.55 (11)
N1—C1—C6—N2	−6.5 (2)	O3—Ni1—N2—C6	−92.49 (11)
C2—C1—C6—N2	172.62 (15)	N1—Ni1—N2—C6	−1.88 (11)
N1—C1—C6—C7	173.22 (15)	N3—Ni1—N2—C6	92.79 (11)
C2—C1—C6—C7	−7.7 (2)	N4—Ni1—N2—C6	47.2 (4)
N2—C6—C7—C8	−1.4 (2)	C14—C15—N3—C11	1.3 (2)
C1—C6—C7—C8	178.96 (15)	C14—C15—N3—Ni1	−178.25 (12)
C6—C7—C8—C9	0.9 (3)	C12—C11—N3—C15	−0.8 (2)
C7—C8—C9—C10	0.0 (2)	C16—C11—N3—C15	179.53 (14)
C8—C9—C10—N2	−0.5 (3)	C12—C11—N3—Ni1	178.83 (12)
N3—C11—C12—C13	−0.6 (2)	C16—C11—N3—Ni1	−0.86 (17)
C16—C11—C12—C13	179.08 (15)	O1—Ni1—N3—C15	−86.83 (13)
C11—C12—C13—C14	1.4 (2)	O3—Ni1—N3—C15	−142.6 (2)
C12—C13—C14—C15	−0.9 (2)	N1—Ni1—N3—C15	87.11 (13)
C13—C14—C15—N3	−0.5 (3)	N2—Ni1—N3—C15	7.74 (14)
N3—C11—C16—N4	−0.5 (2)	N4—Ni1—N3—C15	−179.11 (14)
C12—C11—C16—N4	179.78 (14)	O1—Ni1—N3—C11	93.58 (11)
N3—C11—C16—C17	179.57 (15)	O3—Ni1—N3—C11	37.8 (3)
C12—C11—C16—C17	−0.1 (2)	N1—Ni1—N3—C11	−92.47 (11)
N4—C16—C17—C18	0.6 (2)	N2—Ni1—N3—C11	−171.85 (11)
C11—C16—C17—C18	−179.55 (15)	N4—Ni1—N3—C11	1.31 (11)
C16—C17—C18—C19	0.1 (3)	C19—C20—N4—C16	0.5 (2)
C17—C18—C19—C20	−0.4 (3)	C19—C20—N4—Ni1	177.82 (13)
C18—C19—C20—N4	0.1 (3)	C17—C16—N4—C20	−0.8 (2)
O2—C21—C22—O4	14.3 (2)	C11—C16—N4—C20	179.28 (14)
O1—C21—C22—O4	−167.41 (14)	C17—C16—N4—Ni1	−178.46 (12)
O2—C21—C22—O3	−165.80 (15)	C11—C16—N4—Ni1	1.65 (17)
O1—C21—C22—O3	12.5 (2)	O1—Ni1—N4—C20	88.23 (13)
C4—C5—N1—C1	−0.3 (2)	O3—Ni1—N4—C20	7.31 (13)
C4—C5—N1—Ni1	174.35 (13)	N1—Ni1—N4—C20	−84.35 (14)
C2—C1—N1—C5	0.9 (2)	N3—Ni1—N4—C20	−179.03 (14)

C6—C1—N1—C5	−179.98 (14)	N2—Ni1—N4—C20	−132.5 (3)
C2—C1—N1—Ni1	−174.29 (12)	O1—Ni1—N4—C16	−94.35 (11)
C6—C1—N1—Ni1	4.82 (17)	O3—Ni1—N4—C16	−175.27 (11)
O1—Ni1—N1—C5	−125.3 (2)	N1—Ni1—N4—C16	93.07 (11)
O3—Ni1—N1—C5	−82.55 (13)	N3—Ni1—N4—C16	−1.61 (11)
N3—Ni1—N1—C5	89.30 (14)	N2—Ni1—N4—C16	45.0 (4)
N2—Ni1—N1—C5	−176.54 (14)	O2—C21—O1—Ni1	165.63 (14)
N4—Ni1—N1—C5	10.57 (14)	C22—C21—O1—Ni1	−12.57 (16)
O1—Ni1—N1—C1	49.5 (3)	O3—Ni1—O1—C21	7.69 (10)
O3—Ni1—N1—C1	92.24 (11)	N1—Ni1—O1—C21	51.2 (3)
N3—Ni1—N1—C1	−95.91 (11)	N3—Ni1—O1—C21	−163.36 (11)
N2—Ni1—N1—C1	−1.75 (11)	N2—Ni1—O1—C21	101.25 (11)
N4—Ni1—N1—C1	−174.63 (11)	N4—Ni1—O1—C21	−84.88 (11)
C9—C10—N2—C6	0.0 (2)	O4—C22—O3—Ni1	174.34 (13)
C9—C10—N2—Ni1	175.21 (12)	C21—C22—O3—Ni1	−5.60 (16)
C7—C6—N2—C10	0.9 (2)	O1—Ni1—O3—C22	−0.40 (10)
C1—C6—N2—C10	−179.38 (14)	N1—Ni1—O3—C22	−173.08 (10)
C7—C6—N2—Ni1	−174.81 (12)	N3—Ni1—O3—C22	56.4 (3)
C1—C6—N2—Ni1	4.89 (17)	N2—Ni1—O3—C22	−94.04 (10)
O1—Ni1—N2—C10	11.10 (13)	N4—Ni1—O3—C22	92.03 (10)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C4—H4 $\cdots$ O8 <i>W</i> ⁱ	0.95	2.55	3.502 (2)	176
C5—H5 $\cdots$ O7 <i>W</i>	0.95	2.60	3.356 (2)	137
C9—H9 $\cdots$ O2 ⁱⁱ	0.95	2.61	3.137 (2)	116
C10—H10 $\cdots$ O1	0.95	2.65	3.1875 (19)	116
C10—H10 $\cdots$ O2 ⁱⁱ	0.95	2.52	3.106 (2)	120
C12—H12 $\cdots$ O1 ⁱⁱⁱ	0.95	2.48	3.112 (2)	124
C15—H15 $\cdots$ O5 <i>W</i>	0.95	2.46	3.139 (2)	129
C20—H20 $\cdots$ O3	0.95	2.61	3.164 (2)	118
O5 <i>W</i> —H1O5 $\cdots$ O9 <i>W</i> ⁱⁱ	0.84 (2)	1.92 (2)	2.7509 (19)	168 (2)
O5 <i>W</i> —H2O5 $\cdots$ O6 <i>W</i>	0.82 (2)	1.94 (2)	2.739 (2)	162 (2)
O6 <i>W</i> —H1O6 $\cdots$ O8 <i>W</i> ^{iv}	0.85 (3)	1.94 (3)	2.780 (2)	174 (2)
O6 <i>W</i> —H2O6 $\cdots$ O7 <i>W</i> ^{iv}	0.80 (3)	1.94 (3)	2.739 (2)	175 (2)
O7 <i>W</i> —H1O7 $\cdots$ O9 <i>W</i> ^v	0.76 (2)	2.05 (3)	2.8107 (19)	177 (3)
O7 <i>W</i> —H2O7 $\cdots$ O8 <i>W</i> ⁱ	0.83 (3)	2.14 (3)	2.919 (2)	157 (2)
O8 <i>W</i> —H1O8 $\cdots$ O3	0.77 (2)	2.01 (2)	2.7890 (17)	178 (2)
O8 <i>W</i> —H2O8 $\cdots$ O5 <i>W</i> ^{vi}	0.83 (2)	1.88 (3)	2.711 (2)	173 (2)
O9 <i>W</i> —H2O9 $\cdots$ O2	0.76 (2)	1.99 (2)	2.7364 (19)	167 (2)
O9 <i>W</i> —H1O9 $\cdots$ O4 ^{vii}	0.80 (2)	1.97 (2)	2.7658 (18)	173 (2)

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