Tetrakis[tris(2,2′-bi-1H-benzimidazole)-nickel(II)] bis(phosphate) sulfate

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The title compound, $[Ni(C_{14}H_{10}N_4)_3]_4(PO_4)_2(SO_4)$, consists of $[Ni(C_{14}H_{10}N_4)_3]^{2+}$ complex cations (.3. symmetry) and disordered anions ($\bar{4}$ symmetry) with occupancy factors of two-thirds for PO_4^{3-} and one-third for SO_4^{2-}. The Ni^{2+} centre is chelated by three bidentate 2,2′-bi-1H-benzimidazole molecules in a distorted octahedral coordination. N—H⋯O hydrogen bonds consolidate the building units into a framework structure.

Related literature

For the potential applications of metal–organic coordination compounds in gas absorption and separation, catalysis, non-linear optics, luminescence and magnetism, see: Kitagawa & Matsuda (2007); Maspoch *et al.* (2007).
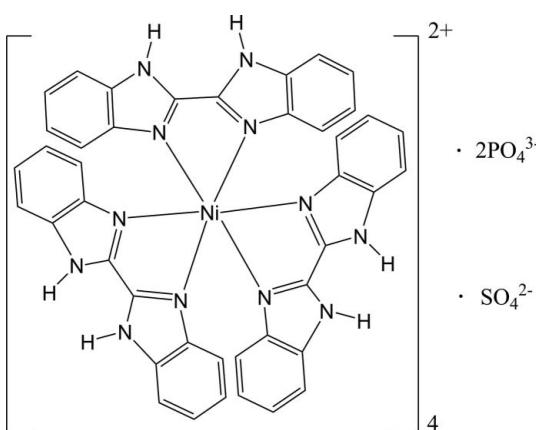
Experimental

Crystal data

$[Ni(C_{14}H_{10}N_4)_3]_4(PO_4)_2(SO_4)$	$Z = 4$
$M_r = 3331.96$	Mo $K\alpha$ radiation
Cubic, $I\bar{4}3d$	$\mu = 0.59$ mm^{-1}
$a = 24.964 (7)$ Å	$T = 296 (2)$ K
$V = 15558 (8)$ Å^3	$0.32 \times 0.27 \times 0.23$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	20222 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	2551 independent reflections
	1782 reflections with $I > 2\sigma(I)$
$T_{min} = 0.834$, $T_{max} = 0.876$	$R_{int} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
$wR(F^2) = 0.098$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
$S = 1.01$	Absolute structure: Flack (1983),
2551 reflections	1182 Friedel pairs
177 parameters	Flack parameter: $-0.02 (2)$
H-atom parameters constrained	

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4—H4B⋯O1^i	0.86	1.96	2.766 (4)	156
N2—H2B⋯O1^{ii}	0.86	1.82	2.675 (4)	170

Symmetry codes: (i) $x - \frac{1}{4}, -z + \frac{5}{4}, -y + \frac{3}{4}$; (ii) $x, y, z - 1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

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Maspoch, D., Ruiz-Molina, D. & Veciana, J. (2007). *Chem. Soc. Rev.* **36**, 770–818.

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supporting information

Tetrakis[tris(2,2′-bi-1*H*-benzimidazole)nickel(II)] bis(phosphate) sulfate

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S1. Comment

More attentions have been paid to metal-organic coordination compounds (MOCCs) because of their potential applications in gas absorption and separation, catalysis, nonlinear optics, luminescence and magnetism (Kitagawa & Matsuda 2007, Maspoch *et al.* 2007). In the field of coordination chemistry, the N,*N*-bidentate ligands, such as 2,2′-bi-pyridine, 1,10-phenanthroline and their derivatives act as versatile ligands owing to the stable coordination configuration in the bidentate N-donors chelating manner. Herein, we report the title compound (I).

The title compound (I) consists of four $[Ni(C_{14}H_{10}N_4)_3]^{2+}$ complex cations, one $[SO_4]^{2-}$ and two $[PO_4]^{3-}$ anions. In the mlecular structure, the Ni^{2+} centre is coordinated by six N atoms from three bidentate 1H,1′*H*-2,2′-bi-1*H*-benzimidazole molecules (Fig.1). The 1H,1′*H*-2,2′-bi-1*H*-benzimidazole ligand was prepared *in situ* and coordinated to the Ni^{2+} cations in hydrothermal reaction. Additionally, the $[SO_4]^{2-}$ and $[PO_4]^{3-}$ anions statistically distribute in one position with 1/3 probability for S and 2/3 probability for P atoms. The environment of the Ni^{2+} caion is in a distorted octahedral geometry with the Ni—N distances ranging from 2.088 (3) to 2.122 (3) Å (Table 1).

In addition, the $[Ni(C_{14}H_{10}N_4)_3]^{2+}$ complex cations, $[SO_4]^{2-}$ and $[PO_4]^{3-}$ anions in the complexes are linked together *via* many N—H⋯O hydrogen bonds resulting in a three-dimensional structural frameworks (Fig.2 and Table 2).

S2. Experimental

All reagents were commercially available and of analytical grade. The mixture of $NiSO_4.6H_2O$, H_3PO_4, oxalic acid, and 1,2-diaminobenzene in the mole ratio of 1: 1.5: 6: 6 was dissolved in 25 ml H_2O, which was heated in a Teflon-lined steel autoclave inside a programmable electric furnace at 393 K for five days. After cooling the autoclave to room temperature, green block crystals of (I) were obtained.

S3. Refinement

H atoms were treated as riding, with C—H = 0.93 Å and N—H = 0.86 Å, and were refined as riding with $U_{iso}(H) = 1.2U_{eq}$(N and C).
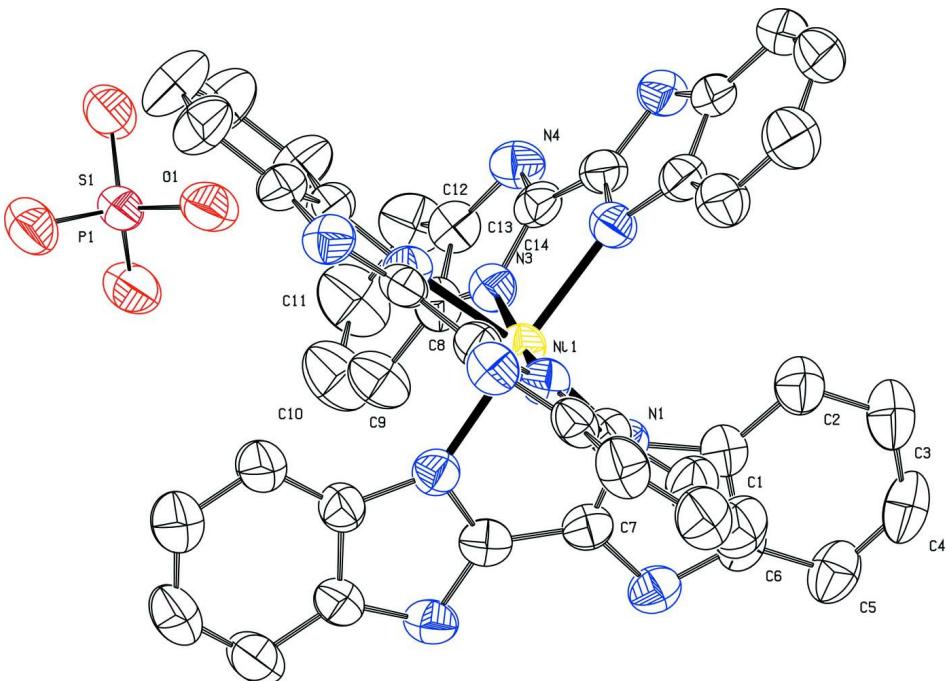
Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.
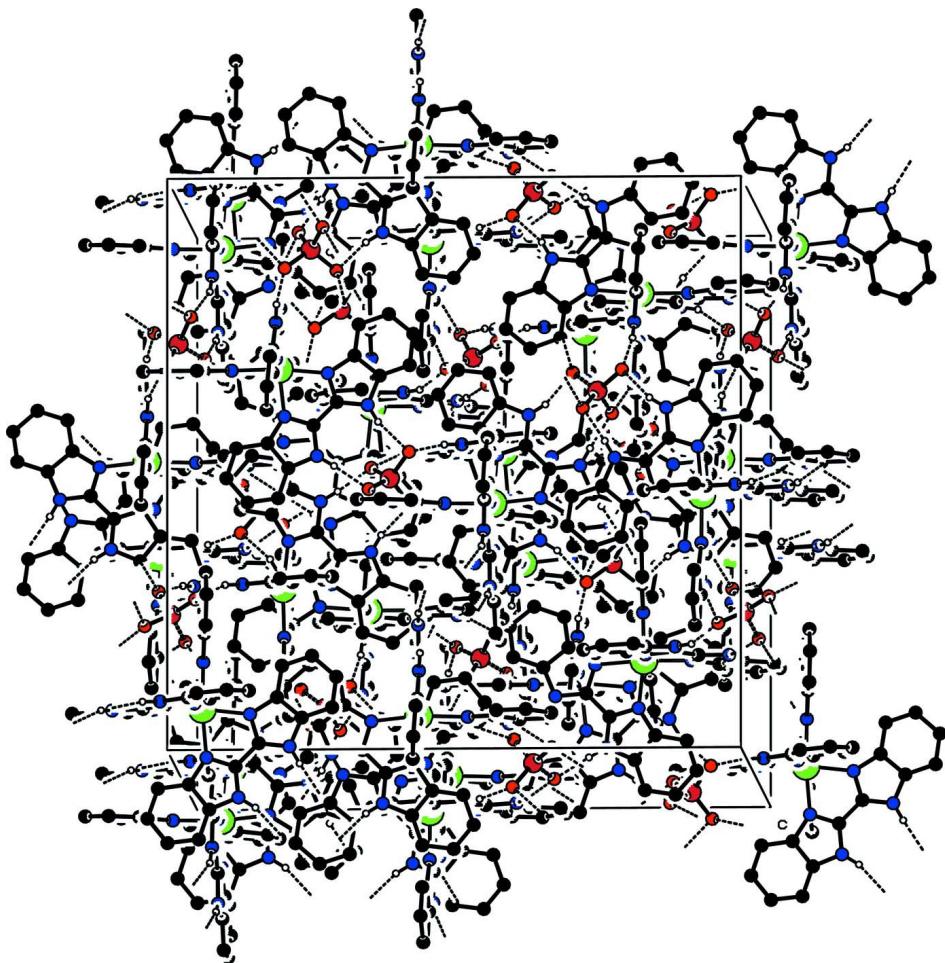
Figure 2

Three-dimensional structure of (I). Displacement ellipsoids are drawn at the 50% probability level. For clarity, H atoms not involved in hydrogen bonds are omitted.

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Crystal data
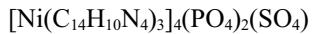
[Ni(C$_{14}$H$_{10}$N$_4$)$_3$]$_4$(PO$_4$)$_2$(SO$_4$)	$D_x = 1.423$ Mg m^{-3}
$M_r = 3331.96$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cubic, $I\bar{4}3d$	Cell parameters from 3375 reflections
Hall symbol: I -4bd 2c 3	$\theta = 2.3–19.2°$
$a = 24.964$ (7) Å	$\mu = 0.59$ mm^{-1}
$V = 15558$ (8) Å^3	$T = 296$ K
$Z = 4$	Block, green
$F(000) = 6872$	$0.32 \times 0.27 \times 0.23$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
Radiation source: fine-focus sealed tube	$T_{min} = 0.834$, $T_{max} = 0.876$
Graphite monochromator	20222 measured reflections
φ and ω scans	2551 independent reflections

1782 reflections with $I > 2\sigma(I)$		$h = -30 \rightarrow 11$
$R_{int} = 0.066$		$k = -30 \rightarrow 29$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$		$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
2551 reflections	$(\Delta/\sigma)_{max} = 0.001$
177 parameters	$\Delta\rho_{max} = 0.61$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1182 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: −0.02 (2)

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}	Occ. (<1)
Ni1	0.564621 (16)	0.435379 (16)	−0.064621 (16)	0.0428 (2)	
P1	0.7500	0.6250	1.0000	0.0427 (4)	0.67
S1	0.7500	0.6250	1.0000	0.0427 (4)	0.33
N1	0.64773 (10)	0.44469 (11)	−0.06574 (11)	0.0443 (6)	
N2	0.71668 (10)	0.50117 (12)	−0.06248 (11)	0.0498 (7)	
H2B	0.7340	0.5309	−0.0604	0.060*	
N3	0.56297 (10)	0.42828 (11)	0.02009 (10)	0.0444 (6)	
N4	0.55652 (11)	0.37290 (12)	0.08942 (11)	0.0502 (7)	
H4B	0.5538	0.3435	0.1072	0.060*	
C1	0.69498 (13)	0.41559 (13)	−0.06917 (13)	0.0462 (8)	
C2	0.70405 (15)	0.36114 (16)	−0.07434 (15)	0.0594 (9)	
H2	0.6758	0.3370	−0.0763	0.071*	
C3	0.75637 (17)	0.34409 (18)	−0.07642 (16)	0.0744 (13)	
H3	0.7638	0.3077	−0.0797	0.089*	
C4	0.79858 (16)	0.3808 (2)	−0.07359 (16)	0.0707 (12)	
H4	0.8335	0.3679	−0.0750	0.085*	
C5	0.79104 (13)	0.43383 (18)	−0.06895 (15)	0.0627 (10)	
H5	0.8197	0.4576	−0.0670	0.075*	
C6	0.73810 (12)	0.45147 (14)	−0.06724 (14)	0.0473 (8)	
C7	0.66286 (13)	0.49523 (14)	−0.06164 (13)	0.0443 (8)	

C8	0.56226 (15)	0.45873 (13)	0.06673 (14)	0.0487 (9)
C9	0.56566 (17)	0.51278 (15)	0.07424 (15)	0.0645 (11)
H9	0.5681	0.5363	0.0455	0.077*
C10	0.5653 (2)	0.53090 (18)	0.12671 (19)	0.0848 (13)
H10	0.5672	0.5675	0.1333	0.102*
C11	0.5623 (2)	0.49628 (19)	0.16920 (17)	0.0863 (14)
H11	0.5627	0.5102	0.2037	0.104*
C12	0.55859 (18)	0.44183 (18)	0.16272 (14)	0.0698 (11)
H12	0.5562	0.4186	0.1917	0.084*
C13	0.55865 (13)	0.42369 (14)	0.11042 (13)	0.0489 (8)
C14	0.55946 (13)	0.37792 (14)	0.03571 (13)	0.0443 (8)
O1	0.77314 (11)	0.59036 (9)	0.95604 (10)	0.0629 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0428 (2)	0.0428 (2)	0.0428 (2)	−0.00140 (19)	−0.00140 (19)	0.00140 (19)
P1	0.0469 (6)	0.0341 (9)	0.0469 (6)	0.000	0.000	0.000
S1	0.0469 (6)	0.0341 (9)	0.0469 (6)	0.000	0.000	0.000
N1	0.0386 (14)	0.0485 (17)	0.0458 (16)	0.0000 (13)	−0.0006 (13)	0.0019 (15)
N2	0.0447 (17)	0.0543 (18)	0.0503 (17)	−0.0083 (14)	−0.0009 (14)	−0.0019 (15)
N3	0.0432 (16)	0.0445 (16)	0.0456 (15)	0.0006 (15)	−0.0046 (13)	−0.0007 (13)
N4	0.0552 (19)	0.0518 (18)	0.0436 (17)	−0.0046 (14)	−0.0034 (14)	0.0093 (14)
C1	0.049 (2)	0.0486 (19)	0.0411 (18)	0.0030 (16)	−0.0031 (17)	−0.0036 (15)
C2	0.054 (2)	0.060 (2)	0.065 (2)	0.0073 (18)	−0.0023 (19)	−0.0042 (19)
C3	0.064 (3)	0.076 (3)	0.084 (3)	0.024 (2)	−0.003 (2)	−0.009 (2)
C4	0.045 (2)	0.097 (4)	0.070 (3)	0.021 (2)	−0.002 (2)	−0.014 (2)
C5	0.0439 (19)	0.083 (3)	0.061 (3)	0.000 (2)	−0.0050 (18)	−0.016 (3)
C6	0.0417 (19)	0.064 (2)	0.0366 (18)	0.0018 (16)	−0.0048 (16)	−0.0077 (17)
C7	0.044 (2)	0.048 (2)	0.0410 (19)	−0.0065 (15)	−0.0027 (15)	−0.0012 (16)
C8	0.049 (2)	0.052 (2)	0.0449 (19)	0.0051 (16)	−0.0042 (18)	−0.0057 (16)
C9	0.092 (3)	0.050 (2)	0.051 (2)	−0.002 (2)	−0.009 (2)	−0.0036 (17)
C10	0.124 (4)	0.065 (3)	0.066 (3)	0.006 (3)	−0.010 (3)	−0.013 (2)
C11	0.133 (4)	0.077 (3)	0.049 (3)	0.001 (3)	−0.013 (3)	−0.017 (2)
C12	0.093 (3)	0.074 (3)	0.042 (2)	−0.006 (3)	−0.005 (2)	0.001 (2)
C13	0.050 (2)	0.055 (2)	0.0423 (19)	−0.0009 (18)	−0.0050 (16)	−0.0006 (16)
C14	0.0315 (18)	0.053 (2)	0.049 (2)	−0.0032 (16)	−0.0021 (15)	0.0045 (17)
O1	0.0818 (18)	0.0455 (15)	0.0616 (17)	−0.0077 (13)	0.0150 (14)	−0.0033 (12)

Geometric parameters (Å, º)

Ni1—N1	2.088 (3)	C1—C6	1.401 (5)
Ni1—N1^i	2.088 (3)	C2—C3	1.375 (5)
Ni1—N1^{ii}	2.088 (3)	C2—H2	0.9300
Ni1—N3^{ii}	2.122 (3)	C3—C4	1.398 (6)
Ni1—N3	2.122 (3)	C3—H3	0.9300
Ni1—N3^i	2.122 (3)	C4—C5	1.342 (6)
P1—O1^{iii}	1.512 (3)	C4—H4	0.9300

P1—O1^{iv}	1.512 (3)	C5—C6	1.394 (4)
P1—O1	1.512 (3)	C5—H5	0.9300
P1—O1^{v}	1.512 (3)	C7—C14^{ii}	1.435 (5)
N1—C7	1.321 (4)	C8—C9	1.365 (5)
N1—C1	1.388 (4)	C8—C13	1.401 (5)
N2—C7	1.352 (4)	C9—C10	1.386 (6)
N2—C6	1.356 (4)	C9—H9	0.9300
N2—H2B	0.8600	C10—C11	1.370 (6)
N3—C14	1.319 (4)	C10—H10	0.9300
N3—C8	1.391 (4)	C11—C12	1.372 (6)
N4—C14	1.349 (4)	C11—H11	0.9300
N4—C13	1.373 (4)	C12—C13	1.382 (5)
N4—H4B	0.8600	C12—H12	0.9300
C1—C2	1.384 (5)	C14—C7^{i}	1.435 (5)
N1—Ni1—N1^{i}	95.67 (10)	C1—C2—H2	121.2
N1—Ni1—N1^{ii}	95.67 (10)	C2—C3—C4	120.7 (4)
N1^{i}—Ni1—N1^{ii}	95.67 (10)	C2—C3—H3	119.6
N1—Ni1—N3^{ii}	78.84 (10)	C4—C3—H3	119.6
N1^{i}—Ni1—N3^{ii}	170.67 (9)	C5—C4—C3	123.0 (4)
N1^{ii}—Ni1—N3^{ii}	92.40 (9)	C5—C4—H4	118.5
N1—Ni1—N3	92.40 (9)	C3—C4—H4	118.5
N1^{i}—Ni1—N3	78.84 (10)	C4—C5—C6	116.6 (4)
N1^{ii}—Ni1—N3	170.67 (9)	C4—C5—H5	121.7
N3^{ii}—Ni1—N3	93.75 (9)	C6—C5—H5	121.7
N1—Ni1—N3^{i}	170.67 (9)	N2—C6—C5	131.7 (3)
N1^{i}—Ni1—N3^{i}	92.40 (9)	N2—C6—C1	106.6 (3)
N1^{ii}—Ni1—N3^{i}	78.84 (10)	C5—C6—C1	121.7 (3)
N3^{ii}—Ni1—N3^{i}	93.75 (9)	N1—C7—N2	112.8 (3)
N3—Ni1—N3^{i}	93.75 (9)	N1—C7—C14^{ii}	118.2 (3)
O1^{iii}—P1—O1^{iv}	110.22 (17)	N2—C7—C14^{ii}	128.9 (3)
O1^{iii}—P1—O1	109.10 (9)	C9—C8—N3	130.9 (3)
O1^{iv}—P1—O1	109.10 (9)	C9—C8—C13	121.0 (3)
O1^{iii}—P1—O1^{v}	109.10 (9)	N3—C8—C13	108.1 (3)
O1^{iv}—P1—O1^{v}	109.10 (9)	C8—C9—C10	116.9 (4)
O1—P1—O1^{v}	110.22 (17)	C8—C9—H9	121.6
C7—N1—C1	105.2 (3)	C10—C9—H9	121.6
C7—N1—Ni1	112.9 (2)	C11—C10—C9	121.7 (4)
C1—N1—Ni1	141.9 (2)	C11—C10—H10	119.1
C7—N2—C6	107.0 (3)	C9—C10—H10	119.1
C7—N2—H2B	126.5	C10—C11—C12	122.5 (4)
C6—N2—H2B	126.5	C10—C11—H11	118.7
C14—N3—C8	105.8 (3)	C12—C11—H11	118.7
C14—N3—Ni1	112.0 (2)	C11—C12—C13	115.8 (4)
C8—N3—Ni1	142.1 (2)	C11—C12—H12	122.1
C14—N4—C13	107.0 (3)	C13—C12—H12	122.1
C14—N4—H4B	126.5	N4—C13—C12	131.5 (3)
C13—N4—H4B	126.5	N4—C13—C8	106.4 (3)

C2—C1—N1	131.2 (3)	C12—C13—C8	122.1 (3)
C2—C1—C6	120.4 (3)	N3—C14—N4	112.7 (3)
N1—C1—C6	108.4 (3)	N3—C14—C7[i]	117.7 (3)
C3—C2—C1	117.6 (4)	N4—C14—C7[i]	129.5 (3)
C3—C2—H2	121.2		
N1[i]—Ni1—N1—C7	−168.5 (2)	C2—C1—C6—N2	179.6 (3)
N1[ii]—Ni1—N1—C7	95.2 (3)	N1—C1—C6—N2	0.3 (4)
N3[ii]—Ni1—N1—C7	3.9 (2)	C2—C1—C6—C5	−1.8 (5)
N3—Ni1—N1—C7	−89.5 (3)	N1—C1—C6—C5	178.9 (3)
N3[i]—Ni1—N1—C7	41.7 (7)	C1—N1—C7—N2	0.4 (4)
N1[i]—Ni1—N1—C1	11.1 (4)	Ni1—N1—C7—N2	−179.9 (2)
N1[ii]—Ni1—N1—C1	−85.2 (3)	C1—N1—C7—C14[ii]	177.6 (3)
N3[ii]—Ni1—N1—C1	−176.5 (4)	Ni1—N1—C7—C14[ii]	−2.6 (4)
N3—Ni1—N1—C1	90.1 (4)	C6—N2—C7—N1	−0.2 (4)
N3[i]—Ni1—N1—C1	−138.6 (6)	C6—N2—C7—C14[ii]	−177.1 (3)
N1—Ni1—N3—C14	−100.0 (2)	C14—N3—C8—C9	178.8 (4)
N1[i]—Ni1—N3—C14	−4.7 (2)	Ni1—N3—C8—C9	−4.5 (7)
N1[ii]—Ni1—N3—C14	49.9 (7)	C14—N3—C8—C13	0.5 (4)
N3[ii]—Ni1—N3—C14	−178.9 (2)	Ni1—N3—C8—C13	177.2 (3)
N3[i]—Ni1—N3—C14	87.1 (3)	N3—C8—C9—C10	−178.2 (4)
N1—Ni1—N3—C8	83.5 (4)	C13—C8—C9—C10	0.0 (6)
N1[i]—Ni1—N3—C8	178.8 (4)	C8—C9—C10—C11	0.7 (7)
N1[ii]—Ni1—N3—C8	−126.7 (6)	C9—C10—C11—C12	−1.0 (8)
N3[ii]—Ni1—N3—C8	4.5 (4)	C10—C11—C12—C13	0.6 (8)
N3[i]—Ni1—N3—C8	−89.5 (3)	C14—N4—C13—C12	−178.1 (4)
C7—N1—C1—C2	−179.6 (4)	C14—N4—C13—C8	0.8 (4)
Ni1—N1—C1—C2	0.7 (7)	C11—C12—C13—N4	178.7 (4)
C7—N1—C1—C6	−0.4 (4)	C11—C12—C13—C8	0.0 (6)
Ni1—N1—C1—C6	180.0 (3)	C9—C8—C13—N4	−179.3 (3)
N1—C1—C2—C3	−179.6 (3)	N3—C8—C13—N4	−0.8 (4)
C6—C1—C2—C3	1.2 (5)	C9—C8—C13—C12	−0.3 (6)
C1—C2—C3—C4	−0.3 (6)	N3—C8—C13—C12	178.2 (4)
C2—C3—C4—C5	−0.2 (6)	C8—N3—C14—N4	0.0 (4)
C3—C4—C5—C6	−0.3 (6)	Ni1—N3—C14—N4	−177.9 (2)
C7—N2—C6—C5	−178.5 (4)	C8—N3—C14—C7[i]	−177.4 (3)
C7—N2—C6—C1	0.0 (4)	Ni1—N3—C14—C7[i]	4.8 (3)
C4—C5—C6—N2	179.5 (4)	C13—N4—C14—N3	−0.5 (4)
C4—C5—C6—C1	1.3 (6)	C13—N4—C14—C7[i]	176.5 (3)

Symmetry codes: (i) −z+1/2, −x+1, y−1/2; (ii) −y+1, z+1/2, −x+1/2; (iii) −z+7/4, −y+5/4, x+1/4; (iv) z−1/4, −y+5/4, −x+7/4; (v) −x+3/2, y, −z+2.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···O1[vi]	0.86	1.96	2.766 (4)	156
N2—H2B···O1[vii]	0.86	1.82	2.675 (4)	170

Symmetry codes: (vi) x−1/4, −z+5/4, −y+3/4; (vii) x, y, z−1.