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Tris(2,2′-bi-1*H*-imidazole-$\kappa^2N^3,N^{3'}$)-nickel(II) dinitrate *N*,*N*-dimethylformamide monosolvate

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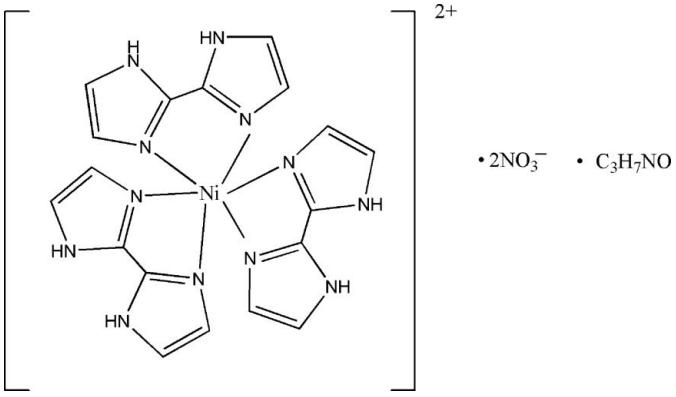
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.030 Å; disorder in solvent or counterion; R factor = 0.109; wR factor = 0.276; data-to-parameter ratio = 9.8.

The reaction of nickel salts and 4,4′-bipyridine with 2,2′-biimidazole (H_2biim) yielded the title complex, $[Ni(C_6H_6N_4)_3](NO_3)_2\cdot C_3H_7NO$. The Ni^{II} atom is chelated by three H_2biim ligands in a distorted octahedral coordination geometry. The two nitrate anions and one dimethylformamide (DMF) molecule are not coordinated. The compound has a three-dimensional structure, formed by extensive hydrogen bonding between $[Ni(H_2biim)_3]^{2+}$ cations and nitrate anions, each nitrate anion forming hydrogen bonds with an $R_1^2(4)$ motif. The DMF molecule is disordered over three sets of sites, with occupancy ratios of 0.341 (16):0.350 (17):0.309 (19).

Related literature

For related literature on the 2,2′-biimidazole ligand, see: Ding *et al.* (2005); Gruia *et al.* (2007); Martinez Lorente *et al.* (1995). For related structures, see: Dai *et al.* (2010); Jin *et al.* (2010); Yang *et al.* (2005).



Experimental

Crystal data

$[Ni(C_6H_6N_4)_3](NO_3)_2\cdot C_3H_7NO$
M_r = 658.27
Monoclinic, *Cc*
a = 12.2150 (11) Å
b = 20.864 (2) Å
c = 12.1080 (12) Å
β = 90.528 (1)°
V = 3085.6 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.69 mm^{-1}
T = 298 K
0.36 × 0.19 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.788, T_{max} = 0.921
7496 measured reflections
4289 independent reflections
1969 reflections with $I > 2\sigma(I)$
R_{int} = 0.131

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.109
$wR(F^2)$ = 0.276
S = 1.06
4289 reflections
437 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}
Absolute structure: Flack (1983), 2702 Friedel pairs
Flack parameter: 0.00 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O5^{i}	0.86	2.19	2.93 (2)	144
N2—H2···O4^{i}	0.86	2.30	2.98 (2)	136
N4—H4···O1^{ii}	0.86	1.91	2.77 (2)	176
N4—H4···O3^{ii}	0.86	2.45	3.04 (3)	127
N6—H6···O6	0.86	2.05	2.90 (3)	171
N6—H6···O4	0.86	2.43	3.09 (2)	133
N8—H8···O2^{iii}	0.86	2.09	2.82 (3)	141
N8—H8···O3^{iii}	0.86	2.36	2.98 (2)	130
N10—H10···O5^{iv}	0.86	2.17	2.98 (3)	156
N10—H10···O6^{iv}	0.86	2.45	3.16 (2)	140
N12—H12···O2^{v}	0.86	2.29	2.97 (2)	136

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZK2032).

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supporting information

Acta Cryst. (2011). E**67**, m1589–m1590 [doi:10.1107/S1600536811043030]

Tris(2,2′-bi-1*H*-imidazole-$\kappa^2N^3,N^{3'}$)nickel(II) dinitrate *N*,*N*-dimethylformamide monosolvate

Qi-Ming Qiu, Wei Yang, Zhong-Feng Li, Qiong-Hua Jin and Cun-Lin Zhang

S1. Comment

2,2′-Biimidazole is an excellent candidate for building a supramolecular structure involving directed hydrogen bonding interactions (Dai *et al.*, 2010; Ding *et al.*, 2005; Gruia *et al.*, 2007; Jin *et al.*, 2010; Yang *et al.*, 2005). This versatile molecule can act as a non-deprotonated, mono-deprotonated or bis-deprotonated ligand (Martinez Lorente *et al.*, 1995). Furthermore, the uncoordinated N—H groups in H_2biim can participate in various patterns of hydrogen bonds with other acceptors. This may provides useful information to understand the complicated process in biological systems (Gruia *et al.*, 2007; Ding *et al.*, 2005). Herein we report the compound $[Ni(H_2biim)_3(NO_3)_2].C_3H_7NO$.

The asymmetry unit of the title compound consists of one $[Ni(H_2biim)_3]^{2+}$ cation,two nitrate anions and one free *N*,*N*-dimethyl formamide molecule(Fig.1). The complex is monoclinic in *Cc* space group. In the title complex, the metal center allows the formation of a distorted octahedral geometry with six nitrogen atoms of three chelating H_2biim ligands. The compound contains three bidentate H_2biim ligands which provide six external N—H groups, which form hyfrogen bonds with the O atoms of NO_3^- anions to generate an extended hydrogen-bonded three-dimensional structure (Fig.2).

In $[Ni(H_2biim)_3(NO_3)_2].C_3H_7NO$, the Ni—N bond lengths are in the range 2.005 (2)–2.106 (2) Å, which agree with those in the compound $[Ni(C_6H_6N_4)_3](C_8H_4O_4)$ ($C_8H_4O_4$ = phthalate dianions)(Yang *et al.*, 2005). The distorted N—Ni—N bite angles of H_2biim ligands [N3—Ni1—N1 = 81.1 (7)°, N5—Ni1—N7 = 81.6 (8)°, N9—Ni1—N11 = 80.2 (8)°] agree with the corresponding angles for $[Ni(H_2biim)_3]^{2+}$ complexes (Yang *et al.*, 2005). The hydrogen bonds are formed between the N—H donors of H_2biim and the oxygen atoms from NO_3^- (O4 and O5), with d(N2···O4) = 2.979 Å, d(N2···O5) = 2.930 Å, N2—H2···O4 =136.28° and N2—H2···O5 = 144.29°.

It is interesting that the solvated DMF did not come from the starting materials. This phenomena also appeared in other similar reactions of H_2biim with metal salts in the solvent CH_3OH and H_2O.

S2. Experimental

The title complex has been prepared by adding 4,4′-bipyridine (0.2 mmol) and H_2biim (0.4 mmol) into a stirred CH_3OH (5 mL) and H_2O (5 mL) containing $Ni(NO_3)_2.6H_2O$ (0.2 mmol). The mixture was refluxed for 30 min and then allowed to cool to ambient temperature. The filtrate was evaporated slowly at room temperature for several weeks to yield purple crystalline products.

S3. Refinement

Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2.

The final refinements were performed with isotropic thermal parameters. All hydrogen atoms were located in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded.

Data collection: *SMART* (Bruker, 2007); cell refinement: SAINTPlus (Bruker, 2007); 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*.

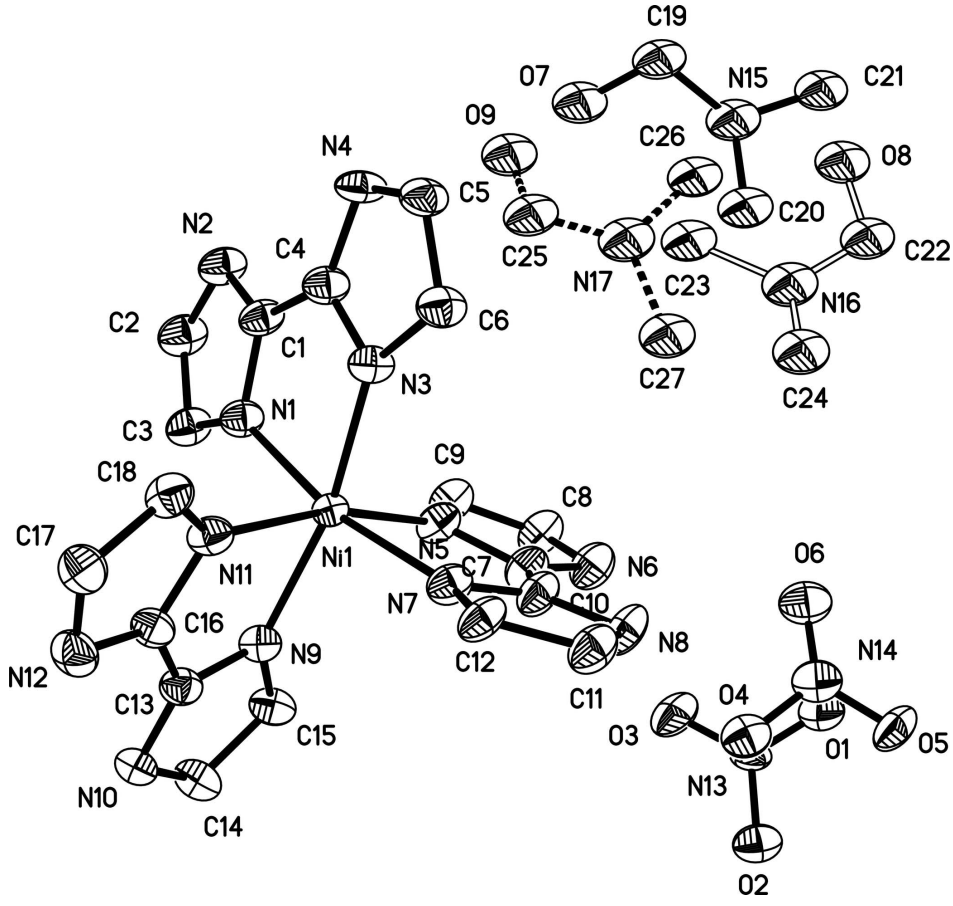

Figure 1

1. The molecular entities of the title compound, showing the atom-numbering scheme and with displacement ellipsoids drawn at the 50% probability level.

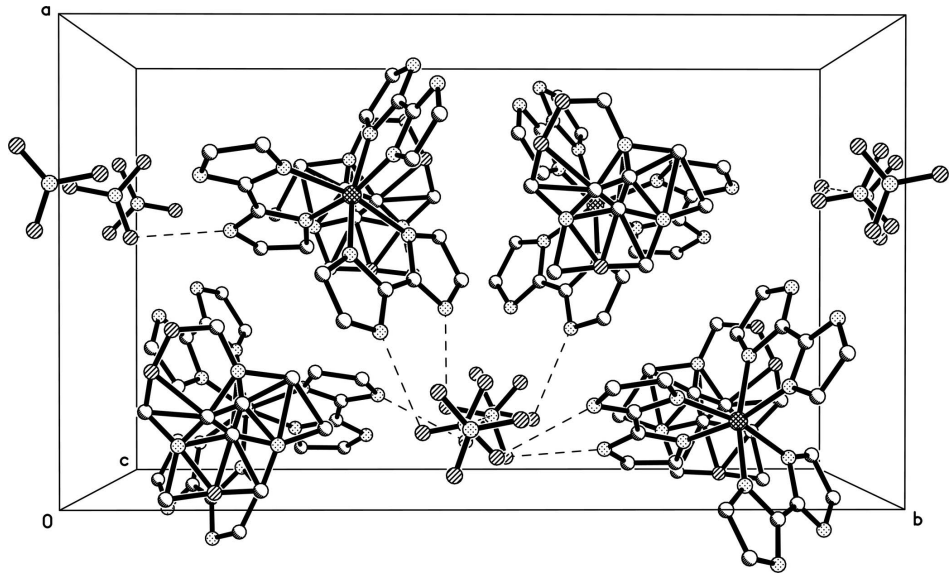

Figure 2

The three-dimensional structure of the title complex formed through intermolecular N—H···O hydrogen bonds.

Tris(2,2′-bi-1*H*-imidazole-$\kappa^2N^3,N^{3'}$)nickel(II) dinitrate *N*,*N*-dimethylformamide monosolvate

Crystal data

$[Ni(C_6H_6N_4)_3](NO_3)_2\cdot C_3H_7NO$
$M_r = 658.27$
Monoclinic, *Cc*
$a = 12.2150$ (11) Å
$b = 20.864$ (2) Å
$c = 12.1080$ (12) Å
$\beta = 90.528$ (1)°
$V = 3085.6$ (5) Å^3
$Z = 4$
$F(000) = 1360$
$D_x = 1.417$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1160 reflections
$\theta = 2.5$–17.3°
$\mu = 0.69$ mm^{-1}
$T = 298$ K
Block, purple
0.36 × 0.19 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{min} = 0.788$, $T_{max} = 0.921$
7496 measured reflections
4289 independent reflections
1969 reflections with $I > 2\sigma(I)$
$R_{int} = 0.131$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.6°$
$h = -14\rightarrow14$
$k = -23\rightarrow24$
$l = -14\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.109$
$wR(F^2) = 0.276$
$S = 1.06$
4289 reflections
437 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.117P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Absolute structure: Flack (1983), **1549 Friedel pairs**
Absolute structure parameter: 0.00 (6)

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	0.6556 (2)	0.33319 (8)	0.3945 (2)	0.0423 (5)	
N1	0.7111 (15)	0.2490 (8)	0.3170 (16)	0.065 (5)	
N2	0.6946 (14)	0.1433 (8)	0.3119 (16)	0.075 (5)	
H2	0.6816	0.1045	0.3317	0.090*	
N3	0.6035 (15)	0.2688 (8)	0.5051 (14)	0.062 (5)	
N4	0.5823 (19)	0.1662 (7)	0.5541 (19)	0.072 (6)	
H4	0.5800	0.1251	0.5481	0.086*	
N5	0.5220 (19)	0.3337 (7)	0.2926 (18)	0.068 (6)	
N6	0.3559 (17)	0.3726 (9)	0.2553 (18)	0.085 (6)	
H6	0.2946	0.3922	0.2640	0.102*	
N7	0.5692 (17)	0.4055 (8)	0.4700 (15)	0.067 (5)	
N8	0.4052 (15)	0.4534 (8)	0.4806 (16)	0.079 (6)	
H8	0.3384	0.4638	0.4666	0.095*	
N9	0.7373 (16)	0.3892 (8)	0.2801 (16)	0.065 (5)	
N10	0.8848 (15)	0.4446 (7)	0.2328 (16)	0.067 (5)	
H10	0.9503	0.4596	0.2342	0.081*	
N11	0.7983 (16)	0.3544 (8)	0.4856 (16)	0.064 (5)	
N12	0.9522 (14)	0.4110 (8)	0.4904 (17)	0.076 (5)	
H12	1.0047	0.4360	0.4712	0.091*	
N13	0.161 (2)	0.4854 (9)	0.0305 (15)	0.072 (5)	
N14	0.154 (2)	0.4795 (11)	0.2929 (17)	0.081 (6)	
N15	0.102 (8)	0.110 (4)	0.383 (5)	0.103 (14)	0.341 (16)
N16	0.103 (6)	0.237 (4)	0.409 (5)	0.103 (14)	0.350 (17)
N17	0.266 (9)	0.186 (4)	0.395 (7)	0.103 (14)	0.309 (19)
O1	0.0657 (16)	0.4662 (7)	0.0412 (16)	0.102 (5)	
O2	0.1804 (15)	0.5453 (8)	0.0304 (14)	0.093 (5)	
O3	0.2365 (15)	0.4472 (8)	0.0272 (12)	0.098 (5)	
O4	0.2461 (15)	0.5046 (7)	0.2861 (11)	0.081 (4)	
O5	0.0835 (15)	0.5192 (7)	0.2951 (14)	0.091 (5)	
O6	0.1376 (15)	0.4256 (8)	0.2796 (14)	0.097 (5)	
O7	0.266 (6)	0.077 (3)	0.364 (4)	0.104 (11)	0.341 (16)
O8	−0.002 (5)	0.155 (3)	0.400 (4)	0.104 (11)	0.350 (17)

O9	0.358 (5)	0.104 (3)	0.352 (5)	0.104 (11)	0.309 (19)
C1	0.6771 (18)	0.1972 (8)	0.3734 (19)	0.066 (6)	
C2	0.737 (3)	0.1628 (11)	0.212 (3)	0.089 (9)	
H2B	0.7517	0.1368	0.1521	0.107*	
C3	0.7530 (18)	0.2277 (10)	0.219 (2)	0.071 (6)	
H3	0.7867	0.2530	0.1663	0.086*	
C4	0.6245 (18)	0.2077 (10)	0.4790 (18)	0.068 (6)	
C5	0.5439 (16)	0.2016 (10)	0.6411 (19)	0.074 (6)	
H5	0.5196	0.1846	0.7075	0.089*	
C6	0.5468 (17)	0.2652 (10)	0.6160 (18)	0.074 (6)	
H6A	0.5199	0.2991	0.6577	0.089*	
C7	0.446 (2)	0.3781 (10)	0.321 (2)	0.075 (7)	
C8	0.380 (2)	0.3300 (10)	0.173 (2)	0.088 (7)	
H8A	0.3379	0.3212	0.1104	0.106*	
C9	0.479 (2)	0.3029 (11)	0.2000 (19)	0.083 (7)	
H9	0.5120	0.2692	0.1626	0.099*	
C10	0.469 (2)	0.4126 (10)	0.422 (2)	0.073 (7)	
C11	0.469 (2)	0.4745 (10)	0.567 (2)	0.080 (7)	
H11	0.4484	0.5041	0.6199	0.096*	
C12	0.5682 (19)	0.4447 (9)	0.5607 (19)	0.071 (6)	
H12A	0.6259	0.4501	0.6105	0.085*	
C13	0.833 (2)	0.4131 (9)	0.317 (2)	0.064 (6)	
C14	0.8125 (19)	0.4477 (10)	0.147 (2)	0.082 (6)	
H14	0.8234	0.4689	0.0801	0.099*	
C15	0.7209 (19)	0.4138 (9)	0.1757 (19)	0.073 (6)	
H15	0.6584	0.4085	0.1324	0.088*	
C16	0.8647 (18)	0.3931 (10)	0.427 (2)	0.062 (6)	
C17	0.9403 (19)	0.3817 (11)	0.591 (2)	0.077 (7)	
H17	0.9886	0.3849	0.6504	0.092*	
C18	0.8452 (18)	0.3468 (9)	0.5885 (19)	0.071 (6)	
H18	0.8174	0.3224	0.6461	0.086*	
C19	0.176 (8)	0.065 (3)	0.405 (7)	0.097 (15)	0.341 (16)
H19	0.1619	0.0286	0.4466	0.117*	0.341 (16)
C20	0.126 (11)	0.178 (6)	0.403 (10)	0.10 (2)	0.341 (16)
H20A	0.1347	0.1849	0.4811	0.143*	0.341 (16)
H20B	0.0657	0.2034	0.3760	0.143*	0.341 (16)
H20C	0.1914	0.1899	0.3657	0.143*	0.341 (16)
C21	−0.015 (7)	0.094 (4)	0.373 (6)	0.100 (14)	0.341 (16)
H21A	−0.0309	0.0804	0.2988	0.150*	0.341 (16)
H21B	−0.0573	0.1315	0.3897	0.150*	0.341 (16)
H21C	−0.0325	0.0604	0.4236	0.150*	0.341 (16)
C22	0.001 (7)	0.214 (4)	0.413 (6)	0.097 (15)	0.350 (17)
H22	−0.0604	0.2396	0.4246	0.117*	0.350 (17)
C23	0.195 (11)	0.192 (7)	0.390 (9)	0.10 (2)	0.350 (17)
H23A	0.1675	0.1534	0.3550	0.143*	0.350 (17)
H23B	0.2286	0.1809	0.4591	0.143*	0.350 (17)
H23C	0.2477	0.2116	0.3427	0.143*	0.350 (17)
C24	0.135 (6)	0.296 (3)	0.467 (6)	0.100 (14)	0.350 (17)

H24A	0.0830	0.3288	0.4518	0.150*	0.350 (17)
H24B	0.2063	0.3088	0.4425	0.150*	0.350 (17)
H24C	0.1380	0.2875	0.5452	0.150*	0.350 (17)
C25	0.364 (9)	0.159 (5)	0.392 (7)	0.097 (15)	0.309 (19)
H25	0.4286	0.1781	0.4163	0.117*	0.309 (19)
C26	0.166 (12)	0.147 (6)	0.386 (12)	0.10 (2)	0.309 (19)
H26A	0.1795	0.1111	0.3375	0.143*	0.309 (19)
H26B	0.1077	0.1725	0.3559	0.143*	0.309 (19)
H26C	0.1463	0.1313	0.4574	0.143*	0.309 (19)
C27	0.251 (8)	0.256 (4)	0.397 (6)	0.100 (14)	0.309 (19)
H27A	0.2538	0.2709	0.4717	0.150*	0.309 (19)
H27B	0.1813	0.2663	0.3645	0.150*	0.309 (19)
H27C	0.3081	0.2760	0.3552	0.150*	0.309 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0549 (11)	0.0431 (10)	0.0289 (10)	0.0010 (13)	−0.0019 (7)	−0.0009 (13)
N1	0.083 (13)	0.054 (10)	0.059 (13)	−0.001 (9)	0.002 (9)	−0.003 (10)
N2	0.113 (15)	0.051 (9)	0.061 (12)	0.011 (8)	0.017 (10)	−0.010 (9)
N3	0.084 (12)	0.052 (10)	0.051 (12)	−0.004 (8)	0.005 (9)	−0.002 (8)
N4	0.108 (18)	0.052 (11)	0.055 (14)	−0.008 (10)	0.012 (12)	0.015 (10)
N5	0.084 (13)	0.059 (10)	0.061 (13)	0.010 (10)	−0.014 (10)	−0.009 (9)
N6	0.096 (15)	0.088 (14)	0.072 (15)	0.023 (12)	−0.014 (13)	−0.004 (11)
N7	0.084 (15)	0.058 (10)	0.058 (13)	0.007 (9)	0.001 (10)	−0.002 (9)
N8	0.094 (14)	0.077 (11)	0.067 (14)	0.039 (10)	0.001 (11)	−0.012 (10)
N9	0.073 (13)	0.056 (10)	0.066 (14)	−0.003 (8)	−0.001 (10)	0.004 (9)
N10	0.069 (13)	0.062 (10)	0.071 (14)	−0.014 (9)	0.005 (10)	0.006 (10)
N11	0.076 (14)	0.053 (9)	0.061 (13)	−0.004 (9)	−0.014 (11)	0.000 (9)
N12	0.070 (12)	0.075 (12)	0.084 (15)	−0.018 (9)	−0.011 (10)	−0.008 (11)
N13	0.096 (17)	0.057 (12)	0.064 (13)	−0.004 (12)	0.018 (11)	0.023 (9)
N14	0.101 (18)	0.073 (15)	0.071 (15)	−0.011 (15)	−0.015 (12)	−0.006 (12)
N15	0.14 (4)	0.11 (3)	0.05 (2)	0.01 (3)	−0.01 (3)	0.03 (2)
N16	0.14 (4)	0.11 (3)	0.05 (2)	0.01 (3)	−0.01 (3)	0.03 (2)
N17	0.14 (4)	0.11 (3)	0.05 (2)	0.01 (3)	−0.01 (3)	0.03 (2)
O1	0.114 (15)	0.084 (11)	0.107 (15)	0.007 (10)	0.011 (11)	0.028 (10)
O2	0.121 (14)	0.074 (10)	0.085 (12)	−0.001 (9)	−0.003 (10)	0.013 (9)
O3	0.131 (14)	0.097 (11)	0.065 (11)	0.043 (11)	−0.005 (9)	0.027 (8)
O4	0.107 (13)	0.083 (10)	0.054 (10)	0.006 (10)	−0.009 (9)	0.011 (8)
O5	0.111 (13)	0.066 (9)	0.094 (14)	0.036 (9)	0.010 (10)	−0.012 (8)
O6	0.124 (14)	0.088 (11)	0.080 (13)	−0.002 (11)	−0.006 (10)	0.015 (10)
O7	0.14 (4)	0.11 (3)	0.056 (18)	0.00 (2)	−0.01 (2)	0.032 (18)
O8	0.14 (4)	0.11 (3)	0.056 (18)	0.00 (2)	−0.01 (2)	0.032 (18)
O9	0.14 (4)	0.11 (3)	0.056 (18)	0.00 (2)	−0.01 (2)	0.032 (18)
C1	0.092 (19)	0.050 (10)	0.057 (18)	0.008 (11)	0.004 (13)	−0.002 (11)
C2	0.12 (3)	0.072 (18)	0.07 (2)	0.011 (13)	0.013 (17)	−0.006 (14)
C3	0.100 (17)	0.058 (14)	0.056 (16)	0.010 (11)	0.008 (12)	−0.006 (11)
C4	0.089 (16)	0.061 (14)	0.054 (16)	−0.002 (11)	0.002 (12)	0.004 (12)

C5	0.101 (17)	0.061 (13)	0.060 (15)	0.004 (11)	0.030 (12)	0.008 (11)
C6	0.101 (17)	0.063 (13)	0.058 (15)	0.001 (11)	0.019 (12)	0.000 (10)
C7	0.084 (19)	0.069 (14)	0.071 (18)	0.011 (13)	−0.008 (14)	−0.014 (12)
C8	0.101 (19)	0.083 (15)	0.081 (17)	0.022 (15)	−0.014 (14)	−0.007 (15)
C9	0.096 (18)	0.078 (15)	0.074 (18)	0.017 (13)	−0.009 (14)	−0.005 (13)
C10	0.086 (18)	0.067 (13)	0.066 (17)	0.026 (12)	0.008 (13)	−0.006 (12)
C11	0.10 (2)	0.072 (14)	0.066 (17)	0.024 (13)	0.008 (14)	−0.010 (12)
C12	0.098 (17)	0.056 (12)	0.059 (15)	0.027 (12)	0.004 (12)	−0.010 (11)
C13	0.073 (16)	0.053 (11)	0.066 (17)	−0.004 (11)	0.004 (13)	−0.004 (11)
C14	0.088 (17)	0.082 (15)	0.077 (18)	−0.022 (13)	0.007 (14)	0.004 (13)
C15	0.090 (16)	0.064 (13)	0.066 (16)	−0.015 (11)	0.001 (12)	0.000 (11)
C16	0.067 (15)	0.056 (13)	0.064 (16)	−0.012 (10)	−0.002 (12)	−0.006 (11)
C17	0.073 (16)	0.075 (14)	0.083 (19)	−0.012 (12)	−0.018 (13)	−0.011 (14)
C18	0.078 (16)	0.063 (12)	0.073 (16)	0.001 (11)	−0.017 (12)	−0.002 (11)
C19	0.14 (5)	0.10 (3)	0.05 (3)	0.01 (3)	−0.01 (3)	0.03 (3)
C20	0.14 (7)	0.11 (6)	0.04 (3)	0.01 (5)	−0.02 (4)	0.04 (4)
C21	0.14 (4)	0.11 (3)	0.05 (3)	0.01 (3)	−0.01 (2)	0.03 (3)
C22	0.14 (5)	0.10 (3)	0.05 (3)	0.01 (3)	−0.01 (3)	0.03 (3)
C23	0.14 (7)	0.11 (6)	0.04 (3)	0.01 (5)	−0.02 (4)	0.04 (4)
C24	0.14 (4)	0.11 (3)	0.05 (3)	0.01 (3)	−0.01 (2)	0.03 (3)
C25	0.14 (5)	0.10 (3)	0.05 (3)	0.01 (3)	−0.01 (3)	0.03 (3)
C26	0.14 (7)	0.11 (6)	0.04 (3)	0.01 (5)	−0.02 (4)	0.04 (4)
C27	0.14 (4)	0.11 (3)	0.05 (3)	0.01 (3)	−0.01 (2)	0.03 (3)

Geometric parameters (Å, º)

Ni1—N3	2.005 (18)	N17—C25	1.32 (11)
Ni1—N5	2.04 (2)	N17—C27	1.47 (11)
Ni1—N7	2.060 (19)	N17—C26	1.48 (16)
Ni1—N9	2.075 (19)	O7—C19	1.24 (10)
Ni1—N11	2.101 (18)	O8—C22	1.25 (8)
Ni1—N1	2.106 (18)	O9—C25	1.24 (9)
N1—C1	1.35 (2)	C1—C4	1.45 (3)
N1—C3	1.37 (3)	C2—C3	1.37 (3)
N2—C1	1.37 (2)	C2—H2B	0.9300
N2—C2	1.38 (4)	C3—H3	0.9300
N2—H2	0.8600	C5—C6	1.36 (3)
N3—C4	1.34 (2)	C5—H5	0.9300
N3—C6	1.52 (3)	C6—H6A	0.9300
N4—C4	1.36 (3)	C7—C10	1.44 (3)
N4—C5	1.37 (3)	C8—C9	1.37 (3)
N4—H4	0.8600	C8—H8A	0.9300
N5—C7	1.35 (3)	C9—H9	0.9300
N5—C9	1.39 (3)	C11—C12	1.36 (3)
N6—C7	1.36 (3)	C11—H11	0.9300
N6—C8	1.37 (3)	C12—H12A	0.9300
N6—H6	0.8600	C13—C16	1.45 (3)
N7—C10	1.36 (3)	C14—C15	1.37 (3)

N7—C12	1.37 (3)	C14—H14	0.9300
N8—C10	1.36 (3)	C15—H15	0.9300
N8—C11	1.37 (3)	C17—C18	1.37 (3)
N8—H8	0.8600	C17—H17	0.9300
N9—C13	1.35 (3)	C18—H18	0.9300
N9—C15	1.38 (3)	C19—H19	0.9300
N10—C14	1.36 (3)	C20—H20A	0.9600
N10—C13	1.37 (3)	C20—H20B	0.9600
N10—H10	0.8600	C20—H20C	0.9600
N11—C16	1.35 (3)	C21—H21A	0.9600
N11—C18	1.38 (3)	C21—H21B	0.9600
N12—C16	1.36 (2)	C21—H21C	0.9600
N12—C17	1.37 (3)	C22—H22	0.9300
N12—H12	0.8600	C23—H23A	0.9600
N13—O3	1.22 (2)	C23—H23B	0.9600
N13—O1	1.23 (2)	C23—H23C	0.9600
N13—O2	1.27 (2)	C24—H24A	0.9600
N14—O6	1.15 (2)	C24—H24B	0.9600
N14—O5	1.20 (2)	C24—H24C	0.9600
N14—O4	1.24 (3)	C25—H25	0.9300
N15—C19	1.32 (8)	C26—H26A	0.9600
N15—C21	1.47 (11)	C26—H26B	0.9600
N15—C20	1.48 (12)	C26—H26C	0.9600
N16—C22	1.33 (9)	C27—H27A	0.9600
N16—C24	1.47 (9)	C27—H27B	0.9600
N16—C23	1.48 (13)	C27—H27C	0.9600

N3—Ni1—N5	98.6 (8)	N2—C2—H2B	126.5
N3—Ni1—N7	91.5 (8)	N1—C3—C2	109 (3)
N5—Ni1—N7	81.6 (8)	N1—C3—H3	125.7
N3—Ni1—N9	168.8 (8)	C2—C3—H3	125.7
N5—Ni1—N9	88.9 (8)	N3—C4—N4	112 (2)
N7—Ni1—N9	97.8 (6)	N3—C4—C1	116.0 (19)
N3—Ni1—N11	93.3 (7)	N4—C4—C1	132 (2)
N5—Ni1—N11	166.6 (7)	C6—C5—N4	110 (2)
N7—Ni1—N11	92.2 (8)	C6—C5—H5	125.0
N9—Ni1—N11	80.2 (8)	N4—C5—H5	125.0
N3—Ni1—N1	81.1 (7)	C5—C6—N3	105.0 (18)
N5—Ni1—N1	89.7 (7)	C5—C6—H6A	127.5
N7—Ni1—N1	167.6 (8)	N3—C6—H6A	127.5
N9—Ni1—N1	90.8 (7)	N5—C7—N6	110 (2)
N11—Ni1—N1	98.1 (7)	N5—C7—C10	115 (2)
C1—N1—C3	107.2 (17)	N6—C7—C10	133 (3)
C1—N1—Ni1	110.0 (15)	C9—C8—N6	107 (2)
C3—N1—Ni1	141.4 (15)	C9—C8—H8A	126.6
C1—N2—C2	107.2 (17)	N6—C8—H8A	126.6
C1—N2—H2	126.4	C8—C9—N5	109 (2)
C2—N2—H2	126.4	C8—C9—H9	125.4

C4—N3—C6	104.5 (18)	N5—C9—H9	125.4
C4—N3—Ni1	114.7 (15)	N7—C10—N8	111 (2)
C6—N3—Ni1	140.7 (13)	N7—C10—C7	118 (2)
C4—N4—C5	107.7 (16)	N8—C10—C7	130 (2)
C4—N4—H4	126.1	C12—C11—N8	108 (2)
C5—N4—H4	126.1	C12—C11—H11	125.8
C7—N5—C9	105 (2)	N8—C11—H11	125.8
C7—N5—Ni1	113.4 (16)	C11—C12—N7	109 (2)
C9—N5—Ni1	141.2 (17)	C11—C12—H12A	125.4
C7—N6—C8	107 (2)	N7—C12—H12A	125.4
C7—N6—H6	126.3	N9—C13—N10	110 (2)
C8—N6—H6	126.3	N9—C13—C16	115 (2)
C10—N7—C12	105.4 (19)	N10—C13—C16	135 (2)
C10—N7—Ni1	110.6 (15)	N10—C14—C15	108 (2)
C12—N7—Ni1	143.3 (16)	N10—C14—H14	126.2
C10—N8—C11	106 (2)	C15—C14—H14	126.2
C10—N8—H8	127.1	C14—C15—N9	108 (2)
C11—N8—H8	127.1	C14—C15—H15	125.8
C13—N9—C15	106.4 (19)	N9—C15—H15	125.8
C13—N9—Ni1	114.3 (16)	N11—C16—N12	110 (2)
C15—N9—Ni1	139.1 (16)	N11—C16—C13	120 (2)
C14—N10—C13	107.1 (19)	N12—C16—C13	130 (2)
C14—N10—H10	126.5	N12—C17—C18	108 (2)
C13—N10—H10	126.5	N12—C17—H17	125.8
C16—N11—C18	107.3 (19)	C18—C17—H17	125.8
C16—N11—Ni1	110.4 (15)	C17—C18—N11	108 (2)
C18—N11—Ni1	142.0 (17)	C17—C18—H18	126.2
C16—N12—C17	107 (2)	N11—C18—H18	126.2
C16—N12—H12	126.6	O7—C19—N15	113 (8)
C17—N12—H12	126.6	O7—C19—H19	123.6
O3—N13—O1	120.2 (19)	N15—C19—H19	123.6
O3—N13—O2	120 (2)	O8—C22—N16	112 (8)
O1—N13—O2	120 (2)	O8—C22—H22	124.0
O6—N14—O5	124 (3)	N16—C22—H22	124.0
O6—N14—O4	124 (3)	N16—C23—H23A	109.5
O5—N14—O4	111 (2)	N16—C23—H23B	109.5
C19—N15—C21	122 (8)	H23A—C23—H23B	109.5
C19—N15—C20	121 (9)	N16—C23—H23C	109.5
C21—N15—C20	114 (8)	H23A—C23—H23C	109.5
C22—N16—C24	122 (8)	H23B—C23—H23C	109.5
C22—N16—C23	120 (9)	N16—C24—H24A	109.5
C24—N16—C23	114 (8)	N16—C24—H24B	109.5
C25—N17—C27	123 (10)	H24A—C24—H24B	109.5
C25—N17—C26	120 (10)	N16—C24—H24C	109.5
C27—N17—C26	116 (10)	H24A—C24—H24C	109.5
N1—C1—N2	109.6 (18)	H24B—C24—H24C	109.5
N1—C1—C4	117.7 (18)	O9—C25—N17	111 (10)
N2—C1—C4	132.5 (18)	O9—C25—H25	124.5

C3—C2—N2	107 (3)	N17—C25—H25	124.5
C3—C2—H2B	126.5		
N3—Ni1—N1—C1	4.9 (14)	N2—C2—C3—N1	−6 (3)
N5—Ni1—N1—C1	−93.9 (15)	C6—N3—C4—N4	4 (2)
N7—Ni1—N1—C1	−49 (4)	Ni1—N3—C4—N4	−176.8 (15)
N9—Ni1—N1—C1	177.2 (14)	C6—N3—C4—C1	178.6 (17)
N11—Ni1—N1—C1	97.0 (14)	Ni1—N3—C4—C1	−3 (2)
N3—Ni1—N1—C3	169 (2)	C5—N4—C4—N3	−8 (3)
N5—Ni1—N1—C3	70 (2)	C5—N4—C4—C1	179 (2)
N7—Ni1—N1—C3	115 (4)	N1—C1—C4—N3	7 (3)
N9—Ni1—N1—C3	−19 (2)	N2—C1—C4—N3	−168 (2)
N11—Ni1—N1—C3	−99 (2)	N1—C1—C4—N4	−180 (2)
N5—Ni1—N3—C4	87.1 (16)	N2—C1—C4—N4	5 (4)
N7—Ni1—N3—C4	168.8 (15)	C4—N4—C5—C6	9 (3)
N9—Ni1—N3—C4	−45 (5)	N4—C5—C6—N3	−6 (2)
N11—Ni1—N3—C4	−98.9 (15)	C4—N3—C6—C5	1 (2)
N1—Ni1—N3—C4	−1.2 (15)	Ni1—N3—C6—C5	−177.4 (17)
N5—Ni1—N3—C6	−95 (2)	C9—N5—C7—N6	5 (3)
N7—Ni1—N3—C6	−13 (2)	Ni1—N5—C7—N6	−175.1 (16)
N9—Ni1—N3—C6	134 (4)	C9—N5—C7—C10	175 (2)
N11—Ni1—N3—C6	79 (2)	Ni1—N5—C7—C10	−5 (3)
N1—Ni1—N3—C6	177 (2)	C8—N6—C7—N5	−9 (3)
N3—Ni1—N5—C7	90.6 (18)	C8—N6—C7—C10	−176 (3)
N7—Ni1—N5—C7	0.3 (18)	C7—N6—C8—C9	9 (3)
N9—Ni1—N5—C7	−97.8 (18)	N6—C8—C9—N5	−7 (3)
N11—Ni1—N5—C7	−63 (6)	C7—N5—C9—C8	1 (3)
N1—Ni1—N5—C7	171.5 (19)	Ni1—N5—C9—C8	−179 (2)
N3—Ni1—N5—C9	−89 (3)	C12—N7—C10—N8	−2 (2)
N7—Ni1—N5—C9	−179 (3)	Ni1—N7—C10—N8	171.0 (15)
N9—Ni1—N5—C9	83 (3)	C12—N7—C10—C7	178 (2)
N11—Ni1—N5—C9	118 (4)	Ni1—N7—C10—C7	−9 (3)
N1—Ni1—N5—C9	−8 (3)	C11—N8—C10—N7	2 (3)
N3—Ni1—N7—C10	−93.7 (15)	C11—N8—C10—C7	−177 (2)
N5—Ni1—N7—C10	4.8 (15)	N5—C7—C10—N7	10 (3)
N9—Ni1—N7—C10	92.5 (16)	N6—C7—C10—N7	177 (2)
N11—Ni1—N7—C10	172.9 (16)	N5—C7—C10—N8	−170 (2)
N1—Ni1—N7—C10	−41 (4)	N6—C7—C10—N8	−3 (5)
N3—Ni1—N7—C12	74 (3)	C10—N8—C11—C12	−2 (3)
N5—Ni1—N7—C12	173 (3)	N8—C11—C12—N7	1 (3)
N9—Ni1—N7—C12	−100 (2)	C10—N7—C12—C11	0 (2)
N11—Ni1—N7—C12	−19 (3)	Ni1—N7—C12—C11	−168 (2)
N1—Ni1—N7—C12	127 (4)	C15—N9—C13—N10	−8 (2)
N3—Ni1—N9—C13	−58 (4)	Ni1—N9—C13—N10	175.0 (13)
N5—Ni1—N9—C13	169.8 (15)	C15—N9—C13—C16	179.3 (18)
N7—Ni1—N9—C13	88.5 (16)	Ni1—N9—C13—C16	3 (2)
N11—Ni1—N9—C13	−2.4 (14)	C14—N10—C13—N9	8 (2)
N1—Ni1—N9—C13	−100.5 (14)	C14—N10—C13—C16	178 (2)

N3—Ni1—N9—C15	127 (4)	C13—N10—C14—C15	−4 (2)
N5—Ni1—N9—C15	−5 (2)	N10—C14—C15—N9	−1 (2)
N7—Ni1—N9—C15	−87 (2)	C13—N9—C15—C14	6 (2)
N11—Ni1—N9—C15	−177 (2)	Ni1—N9—C15—C14	−179.2 (16)
N1—Ni1—N9—C15	84 (2)	C18—N11—C16—N12	−1 (2)
N3—Ni1—N11—C16	172.5 (15)	Ni1—N11—C16—N12	174.7 (13)
N5—Ni1—N11—C16	−34 (6)	C18—N11—C16—C13	−176.3 (19)
N7—Ni1—N11—C16	−95.9 (15)	Ni1—N11—C16—C13	−1 (2)
N9—Ni1—N11—C16	1.7 (14)	C17—N12—C16—N11	1 (2)
N1—Ni1—N11—C16	91.0 (15)	C17—N12—C16—C13	176 (2)
N3—Ni1—N11—C18	−15 (2)	N9—C13—C16—N11	−1 (3)
N5—Ni1—N11—C18	139 (4)	N10—C13—C16—N11	−171 (2)
N7—Ni1—N11—C18	77 (2)	N9—C13—C16—N12	−176 (2)
N9—Ni1—N11—C18	175 (2)	N10—C13—C16—N12	15 (4)
N1—Ni1—N11—C18	−96 (2)	C16—N12—C17—C18	−1 (2)
C3—N1—C1—N2	−1 (2)	N12—C17—C18—N11	0 (3)
Ni1—N1—C1—N2	168.2 (14)	C16—N11—C18—C17	0 (2)
C3—N1—C1—C4	−177.3 (19)	Ni1—N11—C18—C17	−172.9 (18)
Ni1—N1—C1—C4	−8 (2)	C21—N15—C19—O7	150 (7)
C2—N2—C1—N1	−2 (3)	C20—N15—C19—O7	−51 (11)
C2—N2—C1—C4	173 (3)	C24—N16—C22—O8	−153 (6)
C1—N2—C2—C3	5 (3)	C23—N16—C22—O8	0 (10)
C1—N1—C3—C2	5 (3)	C27—N17—C25—O9	−156 (8)
Ni1—N1—C3—C2	−160 (2)	C26—N17—C25—O9	18 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O5^{i}	0.86	2.19	2.93 (2)	144
N2—H2···O4^{i}	0.86	2.30	2.98 (2)	136
N4—H4···O1^{ii}	0.86	1.91	2.77 (2)	176
N4—H4···O3^{ii}	0.86	2.45	3.04 (3)	127
N6—H6···O6	0.86	2.05	2.90 (3)	171
N6—H6···O4	0.86	2.43	3.09 (2)	133
N8—H8···O2^{iii}	0.86	2.09	2.82 (3)	141
N8—H8···O3^{iii}	0.86	2.36	2.98 (2)	130
N10—H10···O5^{iv}	0.86	2.17	2.98 (3)	156
N10—H10···O6^{iv}	0.86	2.45	3.16 (2)	140
N12—H12···O2^{v}	0.86	2.29	2.97 (2)	136

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