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ISSN 2414-3146

Ethanol(nitrato)[tris(4-cyano-3-phenyl-1*H*-pyrazol-1-yl)hydroborato]nickel(II)

Elvin V. Salerno, Lava R. Kadel and David M. Eichhorn*

Department of Chemistry and Biochemistry, Wichita State University, 1845 Fairmount St., Wichita, KS 67260-0051, USA. *Correspondence e-mail: david.eichhorn@wichita.edu

Received 3 June 2021
Accepted 5 July 2021

Edited by R. J. Butcher, Howard University, USA

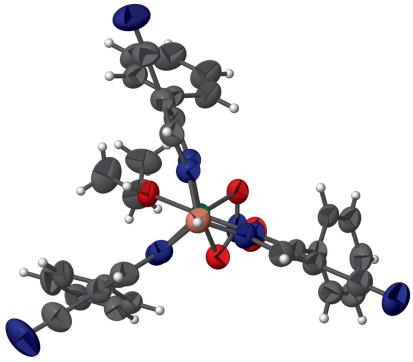
Keywords: crystal structure; nickel complex; scorpionate ligand.

CCDC reference: 2094536

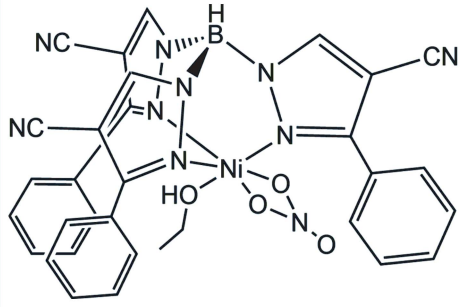
Structural data: full structural data are available from iucrdata.iucr.org

The synthesis and structure is reported of $Tp^{Ph,4CN}Ni(NO_3)(EtOH)$ or $[Ni(C_{30}H_{19}BN_9)(NO_3)(C_2H_6O)]$, the first half-sandwich complex of a cyano-scorpionate ligand. The pseudooctahedral coordination sphere of the Ni^{II} ion is comprised of a tridentate tris(4-cyano-3-phenylpyrazolyl)borate ligand, a bidentate nitrate ligand and a neutral ethanol ligand. The phenyl substituents on the $Tp^{Ph,4CN}$ ligand are relatively parallel to the planes of the ethanol and nitrate ligands. An intermolecular hydrogen-bonding interaction is evident between the ethanol OH group and the pyrazole CN substituent. The ethanol ligand was modeled with a 0.572 (13)/0.428 (13) disorder of the methyl C atom.

3D view



Chemical scheme



Structure description

Scorpionate, or trispyrazolylborate (Tp), ligands were shown early in their existence to readily form octahedral sandwich complexes (Tp_2M) with transition metals (Trofimenko, 1966; Trofimenko, 1967). Trofimenko and coworkers reported, in 1987, the synthesis of Tp^{Ph}, which they showed was resistant to formation of such complexes due to the bulk of the phenyl substituents (Trofimenko *et al.*, 1987). Eichhorn and Armstrong showed that this ligand could still form sandwich compounds with increased *M*—N bond lengths (Eichhorn & Armstrong, 1990). Eichhorn and coworkers later reported the cyano-scorpionates, including the $Tp^{Ph,4CN}$ ligand, for which to date only sandwich compounds have been reported, including those with two borotropic shifted $Tp^{Ph,4CN}$ ligands (Zhao *et al.*, 2007) and those with one $Tp^{Ph,4CN}$ and one $Bp^{Ph,4CN}$ (bispyrazolylborate) ligand (Kadel *et al.*, 2016). The title Ni^{II} compound (Fig. 1) is the first reported 'half-sandwich' complex of $Tp^{Ph,4CN}$. The Ni atom is coordinated by one $Tp^{Ph,4CN}$ ligand, occupying one face of the pseudo-octahedral coordination sphere, one bidentate nitrate ligand and one ethanol ligand. Selected bond distances and angles are given in Table 1. The Ni—N bond lengths [2.079 (2)–2.103 (2) Å; Table 1] are similar to those in $Tp^{Ph,4CN}Bp^{Ph,4CN}Ni$ (Kadel

Table 1
Selected geometric parameters (Å, °).

Ni1—O4	2.071 (2)	Ni1—N2	2.079 (2)
Ni1—N5	2.087 (2)	Ni1—O1	2.104 (2)
Ni1—N8	2.103 (2)	Ni1—O2	2.0812 (19)
N5—Ni1—O1	106.86 (8)	O2—Ni1—O1	61.98 (8)
N2—Ni1—O2	100.89 (8)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···N9^{i}	0.83 (3)	2.17 (3)	2.999 (4)	178 (3)

Symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

et al., 2016) and shorter than those in the related full sandwich compound $Tp^{Ph,Me}{}_2Ni$ (Deb *et al.*, 2012), in which the steric interactions between the phenyl substituents on the two ligands require the ligands to pull away from the metal. The coordination sphere bond angles are as expected for an octahedral complex involving a bidentate nitrate ligand, with only the in-plane angles involving the nitrate [O—Ni—O = 61.98 (8), N—Ni—O = 100.89 (8) and 106.86 (8)°] deviating significantly from ideal octahedral values. The phenyl rings are rotated such that they are relatively parallel to the other ligands, with dihedral angles between the C—C—O plane of the ethanol ligand and the two phenyl rings surrounding it of 17.278 (7) and 339.433 (16)°, and between the plane of the nitrate ligand and the adjacent phenyl ring of 19.578 (7)°. This results in dihedral angles between the phenyl rings and the pyrazole rings to which they are attached of 51.981 (11) and 52.528 (11)° for the groups surrounding the ethanol ligand and 62.302 (13)° for that adjacent to the nitrate, which are normal for a phenylpyrazole moiety and allow for minimization of the interaction between the *ortho*-H on the phenyl ring and the 4-substituent (or H) on the pyrazole. Full sandwich compounds, because of the need to alleviate inter-ligand interactions, are forced to have smaller Ph/pz angles, as evidenced by those in $Tp^{Ph,Me}{}_2Ni$ (12–30°) (Deb *et al.*, 2012), $Tp^{Ph}{}_2M$ (*M* = Fe, Mn, Cd; 9–31°; Eichhorn & Armstrong, 1990; Reger *et al.*, 1995), and $Tp^{Ph,4CN}{}_2M$ (*M* = Fe, Co, Mn; 42–53°; Zhao *et al.*, 2007). An intermolecular hydrogen-bonding interaction exists between the ethanol ligand and the CN substituent on one Tp pyrazole ring (Table 2).

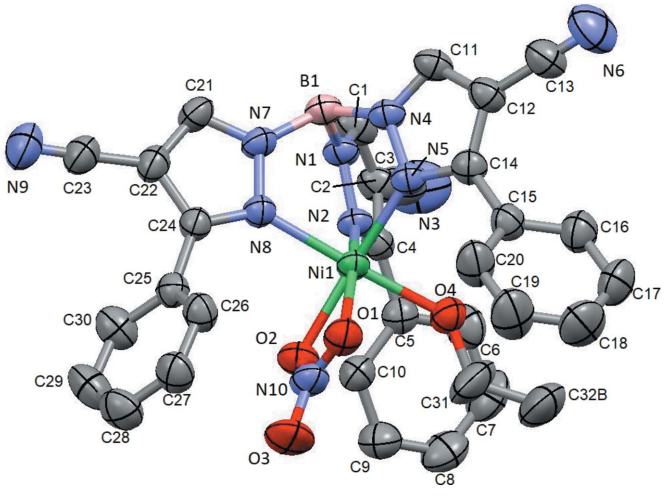


Figure 1
The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. Only the major component of the Me atom is shown.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ni(C_{30}H_{19}BN_9)(NO_3)(C_2H_6O)]$
M_r	683.14
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	150
a, *b*, *c* (Å)	16.627 (6), 18.030 (7), 21.293 (8)
V (Å^3)	6383 (4)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.66
Crystal size (mm)	0.59 × 0.52 × 0.32
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.673, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	118458, 7103, 4543
R_{int}	0.065
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.146, 1.03
No. of reflections	7103
No. of parameters	448
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SIR2004* (Burla *et al.*, 2007), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

The title compound was synthesized by adding a solution of 0.200 g (0.36 mmol) of potassium tris(4-cyano-3-phenylpyrazolyl)hydroborate ($KTp^{Ph,4CN}$; Zhao *et al.*, 2007) in 10 ml of acetone dropwise to a solution of $Ni(NO_3)_2{\cdot}6H_2O$ (0.100 g, 0.36 mmol) in 5 ml of ethanol. After stirring for 5 minutes, the navy blue solution was filtered and the blue precipitate was washed with ethanol. X-ray quality crystals were grown by slow diffusion of ethanol into an acetonitrile solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The ethanol ligand was modeled with a 0.572 (13)/0.428 (13) disorder of the methyl C atom.

Funding information

This project was supported in part by the Ronald E. McNair Post-baccalaureate Achievement Program on the campus of Wichita State University through the US Department of Education and by an Institutional Development Award (IDeA) from the National Institute of General Medical Sciences of the National Institutes of Health under grant No. P20 GM103418. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute of General Medical Sciences or the National Institutes of Health.

References

Bruker (2013). *APEX2*, *SAINT* and *SADABS*. Bruker AXS, Inc., Madison, Wisconsin, USA.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D. & Spagna, R. (2007). *J. Appl. Cryst.* **40**, 609–613.

Deb, T., Rohde, G. T., Young, V. G. & Jensen, M. P. (2012). *Inorg. Chem.* **51**, 7257–7270.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Eichhorn, D. M. & Armstrong, W. H. (1990). *Inorg. Chem.* **29**, 3607–3612.

Kadel, L. R., Bullinger, J. R., Baum, R. R., Moore, C. E., Tierney, D. L. & Eichhorn, D. M. (2016). *Eur. J. Inorg. Chem.* pp. 2543–2551.

Reger, D. L., Myers, S. M., Mason, S. S., Darensbourg, D. J., Holtcamp, M. W., Reibenspies, J. H., Lipton, A. S. & Ellis, P. D. (1995). *J. Am. Chem. Soc.* **117**, 10998–11005.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Trofimenko, S. (1966). *J. Am. Chem. Soc.* **88**, 1842–1844.

Trofimenko, S. (1967). *J. Am. Chem. Soc.* **89**, 3170–3177.

Trofimenko, S., Calabrese, J. C. & Thompson, J. S. (1987). *Inorg. Chem.* **26**, 1507–1514.

Zhao, N., Van Stipdonk, M. J., Bauer, C., Campana, C. & Eichhorn, D. M. (2007). *Inorg. Chem.* **46**, 8662–8667.

full crystallographic data

IUCrData (2021). **6**, x210690 [https://doi.org/10.1107/S2414314621006908]

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Ethanol(nitrato)[tris(4-cyano-3-phenyl-1*H*-pyrazol-1-yl)hydroborato]nickel(II)

Crystal data

$[Ni(C_{30}H_{19}BN_9)(NO_3)(C_2H_6O)]$
M_r = 683.14
Orthorhombic, *Pbca*
a = 16.627 (6) Å
b = 18.030 (7) Å
c = 21.293 (8) Å
V = 6383 (4) Å^3
Z = 8
F(000) = 2816
D_x = 1.422 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 9305 reflections
θ = 3.0–22.8°
μ = 0.66 mm^{-1}
T = 150 K
Block, light blue
0.59 × 0.52 × 0.32 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube
Graphite monochromator
Detector resolution: 5.6 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (SADABS; Bruker, 2013)
T_{min} = 0.673, T_{max} = 0.746
118458 measured reflections
7103 independent reflections
4543 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 27.5°, θ_{min} = 3.7°
h = −21→20
k = −23→23
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.146
S = 1.03
7103 reflections
448 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 1.0693P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.46783 (2)	0.32105 (2)	0.75782 (2)	0.04004 (13)	
O4	0.45090 (12)	0.34845 (12)	0.85134 (10)	0.0554 (5)	
N4	0.59048 (13)	0.20364 (12)	0.75765 (10)	0.0459 (5)	
N7	0.51417 (12)	0.21874 (12)	0.65688 (10)	0.0479 (5)	
N5	0.57845 (12)	0.27386 (11)	0.78134 (10)	0.0455 (5)	
N1	0.44970 (14)	0.15850 (13)	0.75030 (10)	0.0456 (5)	
N8	0.49015 (12)	0.29152 (11)	0.66387 (10)	0.0444 (5)	
N2	0.41089 (12)	0.22004 (11)	0.77343 (10)	0.0435 (5)	
O3	0.38604 (17)	0.50607 (12)	0.71996 (12)	0.0887 (7)	
N10	0.41371 (17)	0.44527 (13)	0.73128 (11)	0.0577 (6)	
C22	0.49747 (15)	0.26308 (16)	0.56234 (13)	0.0511 (7)	
C12	0.68610 (15)	0.22229 (14)	0.82726 (13)	0.0504 (7)	
C21	0.51872 (15)	0.20149 (17)	0.59654 (14)	0.0525 (7)	
H21	0.5340	0.1547	0.5798	0.063*	
C5	0.29602 (14)	0.24381 (15)	0.84526 (13)	0.0482 (6)	
C24	0.48020 (14)	0.31881 (14)	0.60640 (13)	0.0432 (6)	
C2	0.35174 (15)	0.11721 (15)	0.80951 (14)	0.0537 (7)	
C14	0.63667 (14)	0.28587 (14)	0.82355 (12)	0.0458 (6)	
C4	0.35099 (14)	0.19523 (14)	0.80997 (12)	0.0457 (6)	
C11	0.65437 (15)	0.17294 (14)	0.78480 (14)	0.0496 (7)	
H11	0.6747	0.1248	0.7762	0.060*	
N9	0.49338 (19)	0.27259 (18)	0.44209 (14)	0.0826 (8)	
C10	0.25357 (16)	0.30045 (15)	0.81617 (13)	0.0518 (6)	
H10	0.2592	0.3082	0.7723	0.062*	
C1	0.41527 (16)	0.09678 (15)	0.77214 (15)	0.0569 (7)	
H1	0.4318	0.0474	0.7634	0.068*	
C23	0.49527 (19)	0.26954 (18)	0.49556 (16)	0.0611 (8)	
C25	0.45741 (14)	0.39623 (15)	0.59128 (12)	0.0465 (6)	
C15	0.64625 (15)	0.35621 (15)	0.85781 (13)	0.0502 (7)	
C13	0.75612 (18)	0.21118 (17)	0.86449 (15)	0.0632 (8)	
C27	0.48543 (19)	0.52701 (18)	0.58728 (15)	0.0641 (8)	
H27	0.5191	0.5676	0.5981	0.077*	
C28	0.4170 (2)	0.53909 (19)	0.55438 (16)	0.0732 (9)	
H28	0.4024	0.5882	0.5428	0.088*	
C26	0.50660 (17)	0.45578 (16)	0.60520 (13)	0.0541 (7)	
H26	0.5555	0.4478	0.6273	0.065*	
N6	0.81161 (18)	0.20048 (19)	0.89414 (16)	0.0960 (10)	
C3	0.29669 (19)	0.07076 (17)	0.84334 (19)	0.0744 (9)	
C20	0.6497 (2)	0.42321 (17)	0.82685 (16)	0.0735 (9)	
H20	0.6444	0.4242	0.7824	0.088*	
C6	0.28563 (18)	0.23255 (19)	0.90931 (15)	0.0690 (9)	
H6	0.3125	0.1929	0.9299	0.083*	
C16	0.65492 (18)	0.35574 (19)	0.92228 (15)	0.0637 (8)	
H16	0.6536	0.3100	0.9443	0.076*	
N3	0.2532 (2)	0.03462 (18)	0.87100 (18)	0.1132 (12)	

C9	0.20337 (18)	0.34536 (18)	0.85066 (17)	0.0676 (8)	
H9	0.1743	0.3838	0.8302	0.081*	
C30	0.38781 (16)	0.40902 (18)	0.55660 (15)	0.0653 (8)	
H30	0.3535	0.3689	0.5459	0.078*	
C7	0.2353 (2)	0.2801 (2)	0.94312 (17)	0.0846 (10)	
H7	0.2294	0.2737	0.9872	0.102*	
C8	0.1946 (2)	0.3357 (2)	0.91353 (18)	0.0764 (10)	
H8	0.1603	0.3675	0.9368	0.092*	
C19	0.6607 (2)	0.4889 (2)	0.85900 (19)	0.0934 (12)	
H19	0.6635	0.5346	0.8369	0.112*	
C18	0.6677 (2)	0.4876 (2)	0.9229 (2)	0.0931 (12)	
H18	0.6740	0.5327	0.9453	0.112*	
C29	0.36861 (19)	0.4806 (2)	0.53762 (17)	0.0801 (10)	
H29	0.3219	0.4891	0.5130	0.096*	
C17	0.6655 (2)	0.4213 (2)	0.95511 (17)	0.0780 (10)	
H17	0.6712	0.4207	0.9995	0.094*	
B1	0.52890 (17)	0.16769 (17)	0.71325 (17)	0.0480 (7)	
H1A	0.5488	0.1183	0.6987	0.058*	
O1	0.48821 (13)	0.43502 (10)	0.74386 (9)	0.0553 (5)	
O2	0.37070 (11)	0.38682 (11)	0.73135 (9)	0.0562 (5)	
C31	0.4158 (2)	0.4038 (2)	0.88379 (19)	0.0963 (13)	
H31A	0.3580	0.4010	0.8729	0.116*	0.572 (13)
H31B	0.4361	0.4501	0.8643	0.116*	0.572 (13)
H31C	0.3840	0.3799	0.9174	0.116*	0.428 (13)
H31D	0.3766	0.4271	0.8549	0.116*	0.428 (13)
C32A	0.4179 (7)	0.4169 (5)	0.9490 (4)	0.101 (4)	0.572 (13)
H32A	0.3834	0.3808	0.9704	0.152*	0.572 (13)
H32B	0.3986	0.4672	0.9577	0.152*	0.572 (13)
H32C	0.4733	0.4118	0.9642	0.152*	0.572 (13)
C32B	0.4565 (6)	0.4602 (7)	0.9114 (7)	0.099 (5)	0.428 (13)
H32D	0.4744	0.4448	0.9533	0.149*	0.428 (13)
H32E	0.4211	0.5035	0.9152	0.149*	0.428 (13)
H32F	0.5033	0.4732	0.8857	0.149*	0.428 (13)
H4	0.4630 (15)	0.3142 (16)	0.8759 (14)	0.050*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0524 (2)	0.0270 (2)	0.0407 (2)	0.00113 (13)	−0.00158 (13)	−0.00124 (14)
O4	0.0763 (12)	0.0436 (12)	0.0462 (12)	0.0038 (10)	0.0028 (10)	−0.0018 (10)
N4	0.0548 (11)	0.0306 (12)	0.0522 (14)	0.0034 (10)	−0.0021 (10)	−0.0030 (10)
N7	0.0626 (12)	0.0351 (12)	0.0458 (14)	0.0041 (10)	0.0011 (10)	−0.0070 (11)
N5	0.0535 (11)	0.0338 (13)	0.0492 (13)	0.0022 (9)	−0.0025 (10)	−0.0026 (10)
N1	0.0547 (11)	0.0284 (12)	0.0538 (15)	0.0047 (10)	−0.0050 (9)	−0.0038 (10)
N8	0.0580 (11)	0.0345 (12)	0.0407 (13)	0.0032 (10)	−0.0022 (10)	−0.0013 (10)
N2	0.0531 (11)	0.0294 (12)	0.0480 (13)	0.0044 (9)	−0.0024 (10)	−0.0051 (10)
O3	0.135 (2)	0.0379 (13)	0.0930 (17)	0.0297 (13)	−0.0026 (15)	0.0070 (12)
N10	0.0906 (18)	0.0320 (14)	0.0506 (15)	0.0094 (13)	0.0056 (12)	0.0011 (11)

C22	0.0545 (14)	0.0569 (19)	0.0418 (16)	−0.0010 (13)	−0.0016 (12)	−0.0085 (14)
C12	0.0508 (13)	0.0425 (16)	0.0579 (18)	0.0007 (12)	−0.0047 (12)	0.0049 (14)
C21	0.0626 (15)	0.0471 (17)	0.0478 (18)	0.0010 (13)	0.0021 (12)	−0.0143 (14)
C5	0.0495 (13)	0.0447 (16)	0.0505 (17)	−0.0061 (11)	−0.0008 (12)	0.0010 (13)
C24	0.0470 (12)	0.0440 (16)	0.0385 (15)	−0.0008 (10)	−0.0007 (10)	−0.0017 (12)
C2	0.0584 (15)	0.0334 (15)	0.069 (2)	−0.0043 (12)	−0.0035 (13)	0.0065 (14)
C14	0.0519 (13)	0.0370 (15)	0.0484 (16)	−0.0045 (11)	−0.0010 (12)	0.0020 (13)
C4	0.0496 (13)	0.0393 (16)	0.0482 (16)	−0.0003 (11)	−0.0083 (12)	0.0026 (12)
C11	0.0512 (13)	0.0364 (15)	0.0614 (18)	0.0037 (11)	−0.0010 (13)	0.0042 (13)
N9	0.108 (2)	0.090 (2)	0.0493 (18)	0.0042 (17)	−0.0003 (16)	−0.0112 (16)
C10	0.0562 (14)	0.0512 (17)	0.0481 (16)	0.0014 (13)	−0.0005 (12)	−0.0046 (13)
C1	0.0584 (15)	0.0320 (16)	0.080 (2)	−0.0033 (12)	−0.0101 (14)	0.0009 (14)
C23	0.0725 (18)	0.061 (2)	0.050 (2)	0.0016 (15)	0.0000 (15)	−0.0106 (16)
C25	0.0539 (13)	0.0471 (17)	0.0384 (15)	0.0024 (12)	0.0038 (11)	0.0017 (12)
C15	0.0536 (13)	0.0453 (17)	0.0516 (18)	−0.0026 (12)	−0.0090 (12)	−0.0001 (14)
C13	0.0588 (15)	0.0551 (19)	0.076 (2)	0.0036 (14)	−0.0108 (15)	0.0059 (16)
C27	0.085 (2)	0.0492 (19)	0.057 (2)	−0.0017 (15)	−0.0079 (16)	0.0061 (15)
C28	0.089 (2)	0.057 (2)	0.073 (2)	0.0104 (18)	0.0012 (18)	0.0193 (17)
C26	0.0648 (15)	0.0495 (18)	0.0481 (17)	−0.0026 (13)	−0.0068 (13)	0.0064 (14)
N6	0.0773 (18)	0.094 (2)	0.116 (3)	0.0064 (17)	−0.0359 (18)	0.004 (2)
C3	0.0740 (19)	0.0429 (19)	0.106 (3)	−0.0052 (15)	0.0088 (19)	0.0059 (19)
C20	0.105 (2)	0.049 (2)	0.066 (2)	−0.0111 (17)	−0.0229 (18)	0.0021 (17)
C6	0.0778 (19)	0.069 (2)	0.060 (2)	−0.0040 (16)	0.0055 (16)	0.0170 (17)
C16	0.0732 (18)	0.062 (2)	0.056 (2)	−0.0017 (15)	−0.0090 (15)	−0.0040 (16)
N3	0.112 (2)	0.068 (2)	0.160 (4)	−0.0303 (19)	0.036 (2)	0.015 (2)
C9	0.0640 (17)	0.066 (2)	0.072 (2)	0.0116 (15)	0.0034 (16)	−0.0066 (18)
C30	0.0590 (16)	0.063 (2)	0.074 (2)	−0.0024 (14)	−0.0077 (15)	0.0116 (17)
C7	0.092 (2)	0.105 (3)	0.056 (2)	−0.014 (2)	0.0274 (19)	−0.004 (2)
C8	0.0664 (18)	0.084 (3)	0.078 (3)	0.0008 (17)	0.0190 (18)	−0.015 (2)
C19	0.137 (3)	0.053 (2)	0.090 (3)	−0.014 (2)	−0.037 (2)	−0.006 (2)
C18	0.121 (3)	0.062 (3)	0.097 (3)	−0.004 (2)	−0.026 (2)	−0.029 (2)
C29	0.0684 (18)	0.087 (3)	0.086 (3)	0.0123 (18)	−0.0122 (17)	0.031 (2)
C17	0.094 (2)	0.082 (3)	0.059 (2)	−0.0029 (19)	−0.0154 (17)	−0.021 (2)
B1	0.0575 (16)	0.0351 (18)	0.051 (2)	0.0062 (13)	−0.0023 (14)	−0.0067 (15)
O1	0.0778 (13)	0.0328 (11)	0.0553 (13)	−0.0067 (10)	−0.0019 (9)	0.0011 (9)
O2	0.0644 (11)	0.0387 (11)	0.0657 (13)	0.0056 (9)	−0.0004 (9)	0.0015 (9)
C31	0.107 (3)	0.105 (3)	0.077 (3)	0.005 (2)	0.006 (2)	−0.048 (2)
C32A	0.158 (8)	0.076 (6)	0.071 (5)	0.015 (6)	0.006 (5)	−0.030 (4)
C32B	0.085 (6)	0.081 (8)	0.131 (12)	−0.003 (5)	−0.013 (6)	−0.045 (8)

Geometric parameters (Å, º)

Ni1—O4	2.071 (2)	C25—C30	1.392 (4)
Ni1—N5	2.087 (2)	C15—C20	1.377 (4)
Ni1—N8	2.103 (2)	C15—C16	1.380 (4)
Ni1—N2	2.079 (2)	C13—N6	1.134 (4)
Ni1—O1	2.104 (2)	C27—H27	0.9500
Ni1—O2	2.0812 (19)	C27—C28	1.354 (4)

O4—C31	1.347 (4)	C27—C26	1.385 (4)
O4—H4	0.83 (3)	C28—H28	0.9500
N4—N5	1.378 (3)	C28—C29	1.374 (5)
N4—C11	1.330 (3)	C26—H26	0.9500
N4—B1	1.537 (4)	C3—N3	1.137 (4)
N7—N8	1.380 (3)	C20—H20	0.9500
N7—C21	1.324 (3)	C20—C19	1.380 (4)
N7—B1	1.532 (4)	C6—H6	0.9500
N5—C14	1.339 (3)	C6—C7	1.398 (5)
N1—N2	1.375 (3)	C16—H16	0.9500
N1—C1	1.335 (4)	C16—C17	1.385 (4)
N1—B1	1.544 (4)	C9—H9	0.9500
N8—C24	1.329 (3)	C9—C8	1.358 (5)
N2—C4	1.341 (3)	C30—H30	0.9500
O3—N10	1.213 (3)	C30—C29	1.389 (4)
N10—O1	1.281 (3)	C7—H7	0.9500
N10—O2	1.274 (3)	C7—C8	1.362 (5)
C22—C21	1.374 (4)	C8—H8	0.9500
C22—C24	1.404 (4)	C19—H19	0.9500
C22—C23	1.427 (4)	C19—C18	1.365 (5)
C12—C14	1.413 (3)	C18—H18	0.9500
C12—C11	1.374 (4)	C18—C17	1.378 (5)
C12—C13	1.423 (4)	C29—H29	0.9500
C21—H21	0.9500	C17—H17	0.9500
C5—C4	1.472 (4)	B1—H1A	1.0000
C5—C10	1.387 (4)	C31—H31A	0.9900
C5—C6	1.390 (4)	C31—H31B	0.9900
C24—C25	1.482 (4)	C31—H31C	0.9900
C2—C4	1.407 (4)	C31—H31D	0.9900
C2—C1	1.373 (4)	C31—C32A	1.409 (8)
C2—C3	1.435 (4)	C31—C32B	1.355 (10)
C14—C15	1.472 (4)	C32A—H32A	0.9800
C11—H11	0.9500	C32A—H32B	0.9800
N9—C23	1.140 (4)	C32A—H32C	0.9800
C10—H10	0.9500	C32B—H32D	0.9800
C10—C9	1.376 (4)	C32B—H32E	0.9800
C1—H1	0.9500	C32B—H32F	0.9800
C25—C26	1.382 (4)		

O4—Ni1—N5	89.22 (9)	C16—C15—C14	119.9 (3)
O4—Ni1—N8	177.46 (8)	N6—C13—C12	178.3 (3)
O4—Ni1—N2	89.62 (8)	C28—C27—H27	119.8
O4—Ni1—O1	85.68 (8)	C28—C27—C26	120.3 (3)
O4—Ni1—O2	91.09 (8)	C26—C27—H27	119.8
N5—Ni1—N8	88.25 (8)	C27—C28—H28	119.9
N5—Ni1—O1	106.86 (8)	C27—C28—C29	120.2 (3)
N8—Ni1—O1	94.85 (8)	C29—C28—H28	119.9
N2—Ni1—N5	90.33 (8)	C25—C26—C27	120.7 (3)

N2—Ni1—N8	90.61 (8)	C25—C26—H26	119.6
N2—Ni1—O1	162.07 (8)	C27—C26—H26	119.6
N2—Ni1—O2	100.89 (8)	N3—C3—C2	178.9 (4)
O2—Ni1—N5	168.77 (8)	C15—C20—H20	119.3
O2—Ni1—N8	91.36 (8)	C15—C20—C19	121.4 (3)
O2—Ni1—O1	61.98 (8)	C19—C20—H20	119.3
Ni1—O4—H4	113 (2)	C5—C6—H6	120.3
C31—O4—Ni1	136.8 (2)	C5—C6—C7	119.3 (3)
C31—O4—H4	109 (2)	C7—C6—H6	120.3
N5—N4—B1	121.1 (2)	C15—C16—H16	119.7
C11—N4—N5	109.8 (2)	C15—C16—C17	120.7 (3)
C11—N4—B1	128.6 (2)	C17—C16—H16	119.7
N8—N7—B1	122.2 (2)	C10—C9—H9	119.5
C21—N7—N8	110.2 (2)	C8—C9—C10	121.0 (3)
C21—N7—B1	127.6 (2)	C8—C9—H9	119.5
N4—N5—Ni1	114.50 (15)	C25—C30—H30	120.0
C14—N5—Ni1	137.08 (18)	C29—C30—C25	120.0 (3)
C14—N5—N4	106.83 (19)	C29—C30—H30	120.0
N2—N1—B1	119.8 (2)	C6—C7—H7	119.7
C1—N1—N2	110.3 (2)	C8—C7—C6	120.7 (3)
C1—N1—B1	129.3 (2)	C8—C7—H7	119.7
N7—N8—Ni1	113.23 (16)	C9—C8—C7	119.8 (3)
C24—N8—Ni1	139.46 (18)	C9—C8—H8	120.1
C24—N8—N7	106.8 (2)	C7—C8—H8	120.1
N1—N2—Ni1	115.84 (17)	C20—C19—H19	120.3
C4—N2—Ni1	136.33 (17)	C18—C19—C20	119.4 (4)
C4—N2—N1	106.7 (2)	C18—C19—H19	120.3
O3—N10—O1	122.6 (3)	C19—C18—H18	119.7
O3—N10—O2	122.3 (3)	C19—C18—C17	120.6 (3)
O2—N10—O1	115.0 (2)	C17—C18—H18	119.7
C21—C22—C24	106.1 (2)	C28—C29—C30	120.2 (3)
C21—C22—C23	126.9 (3)	C28—C29—H29	119.9
C24—C22—C23	127.0 (3)	C30—C29—H29	119.9
C14—C12—C13	128.4 (3)	C16—C17—H17	120.3
C11—C12—C14	105.4 (2)	C18—C17—C16	119.5 (3)
C11—C12—C13	126.1 (3)	C18—C17—H17	120.3
N7—C21—C22	108.0 (3)	N4—B1—N1	107.4 (3)
N7—C21—H21	126.0	N4—B1—H1A	110.2
C22—C21—H21	126.0	N7—B1—N4	109.6 (2)
C10—C5—C4	121.7 (2)	N7—B1—N1	109.2 (2)
C10—C5—C6	118.8 (3)	N7—B1—H1A	110.2
C6—C5—C4	119.4 (3)	N1—B1—H1A	110.2
N8—C24—C22	108.9 (2)	N10—O1—Ni1	90.84 (15)
N8—C24—C25	125.5 (2)	N10—O2—Ni1	92.07 (16)
C22—C24—C25	125.5 (2)	O4—C31—H31A	105.2
C4—C2—C3	125.1 (3)	O4—C31—H31B	105.2
C1—C2—C4	106.2 (2)	O4—C31—H31C	106.3
C1—C2—C3	128.7 (3)	O4—C31—H31D	106.3

N5—C14—C12	109.1 (2)	O4—C31—C32A	128.3 (5)
N5—C14—C15	123.4 (2)	O4—C31—C32B	124.3 (6)
C12—C14—C15	127.5 (2)	H31A—C31—H31B	105.9
N2—C4—C5	124.0 (2)	H31C—C31—H31D	106.4
N2—C4—C2	108.9 (2)	C32A—C31—H31A	105.2
C2—C4—C5	127.2 (2)	C32A—C31—H31B	105.2
N4—C11—C12	108.9 (2)	C32B—C31—H31C	106.3
N4—C11—H11	125.6	C32B—C31—H31D	106.3
C12—C11—H11	125.6	C31—C32A—H32A	109.5
C5—C10—H10	119.9	C31—C32A—H32B	109.5
C9—C10—C5	120.2 (3)	C31—C32A—H32C	109.5
C9—C10—H10	119.9	H32A—C32A—H32B	109.5
N1—C1—C2	107.9 (2)	H32A—C32A—H32C	109.5
N1—C1—H1	126.0	H32B—C32A—H32C	109.5
C2—C1—H1	126.0	C31—C32B—H32D	109.5
N9—C23—C22	178.1 (4)	C31—C32B—H32E	109.5
C26—C25—C24	122.3 (2)	C31—C32B—H32F	109.5
C26—C25—C30	118.5 (3)	H32D—C32B—H32E	109.5
C30—C25—C24	118.9 (2)	H32D—C32B—H32F	109.5
C20—C15—C14	121.5 (3)	H32E—C32B—H32F	109.5
C20—C15—C16	118.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···N9^{i}	0.83 (3)	2.17 (3)	2.999 (4)	178 (3)

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