metal-organic compounds

A heterometallic polymeric complex: [Cu₂(N₃)₂(medpt)₂{Ni(CN)₄}]ₙ [medpt is bis(3-aminopropyl)methylamine]¹

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The structure of the title compound, catena-poly[[di-μ-azido-κ⁴N¹:N¹-bis[[bis(3-aminopropyl)methylamine-κ³N]copper(II)]]-μ-cyano-[dicyanonickel(II)]-μ-cyano], [Cu₂(N₃)₂(medpt)₂{Ni-(CN)₄}]ₙ [medpt is bis(3-aminopropyl)methylamine, C_7H_{19}-N_2] or [Cu₂Ni(CN)₄(N₃)₂(C₇H₁₉N₃)₂]ₙ, is a one-dimensional heterometallic covalent chain where Ni(CN)₄²⁻ functions as a molecular ion bridge. The Ni atom sits on the centre of inversion. The chain undergoes hydrogen-bonding interactions, forming a three-dimensional supramolecular network.
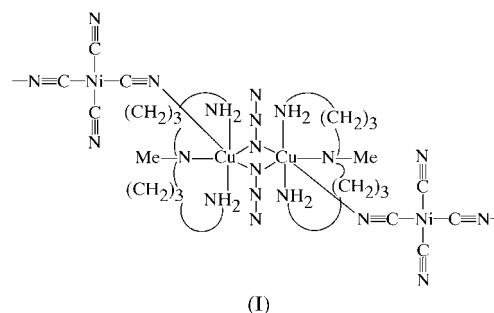
Comment

There are currently several successful examples of self-assembly towards the construction of cyano-bridged complexes, in which cyanometallate anions, e.g. Ag(CN)²⁻, Cu(CN)₃²⁻, Au(CN)₄⁻, M(CN)₄²⁻ (M is Ni^{II}, Pt^{II} and Cd^{II}) and M(CN)₆³⁻ (M is Cr^{III}, Fe^{III}, etc.) (Iwamoto, 1996; Bowmaker et al., 1998; Chesnut & Zubieta, 1998; Falvello & Tomas, 1999; Mondal et al., 2000; Du et al., 2000; Niel et al., 2001; Shorrock et al., 2003; Colacio et al., 2003), behave as bridging moieties to build a multidimensional structure with a second coordination centre, and the resulting complexes demonstrate unique magnetic, host–guest and other properties.

One of the most prominent characteristics of CN⁻ is its ability to act as either a terminal or a bridging ligand. When it acts as a bridging ligand between metal atoms, it usually gives rise to polymeric compounds with a one-, two- or three-dimensional network and often containing guest solvent molecules and/or a complementary ligand. Usually, the second coordination centres are transition metal ions, since $\sigma \rightarrow \pi$ back-bonding stabilizes the resulting complex (Muga et al., 1997). The rigidity and stability of such frameworks allow for shape- and size-selective inclusion of organic solvents, water

molecules, aromatic amines, etc., to fill up the void space, thus stabilizing the crystal structure. Maji et al. (2001) reported a novel porous framework, [{Cu₂(medpt)₂Ni(CN)₄}-(ClO₄)₂]·2.5H₂O, where all the CN groups of the Ni(CN)₄²⁻ anion are involved in bridging. This compound retains single crystallinity upon removal of guest water molecules and the dehydrated species selectively binds organic molecules.

With regard to the Hoffman-type and analogous inclusion compounds, the Hoffman–en-type network [Cd(en)Ni-(CN)₄]·2G (en is ethylenediamine; G is C₄H₄N, C₄H₄S or C₆H₆) has a host structure similar to that of the Hoffman-type network [Cd(NH₃)₂Ni(CN)₄]·2G (G is C₄H₅N, C₄H₄S, C₆H₆ or PhNH₂) (Iwamoto et al., 1974). Similar behaviour was reported for [Ni(en)₂Ni(CN)₄]·2.5H₂O (Černák et al., 1990), where the role of the water molecules was interpreted using a molecular mechanics investigation. Yuge & Iwamoto (1994) reported phenol and aniline as guest molecules accommodated among [M(en)₂Ni(CN)₄]ₙ chains (M is Ni, Cu, Zn or Cd). Moreover, the azide ligand has been used extensively to design molecular-based magnets displaying a huge structural variety, spanning dinuclear, tetranuclear, cubane, and one-, two- and three-dimensional compounds (Ribas et al., 1999). During our ongoing research on mixed bridging ligands, we synthesized the title compound, (I), and this paper reports the synthesis and crystal structure of this novel one-dimensional heterometallic polymeric complex, [Cu₂(medpt)₂(N₃)₂Ni-(CN)₄]ₙ [medpt is bis(3-aminopropyl)methylamine].

(I)

The present X-ray crystal-structure determination reveals that (I) is a one-dimensional heterometallic chain (Fig. 1). In the chain, each pseudo-octahedral Cu^{II} centre is linked to another Cu^{II} centre by a double end-on bridging azide ligand, and these dimeric units are linked alternately by the trans cyanide group of a square-planar Ni(CN)₄²⁻ dianion to form a one-dimensional heterometallic chain along the c axis. The Ni^{II} atom sits on the inversion centre.

All donor N atoms of the triamine (atoms N5, N6 and N7) and one N atom (N1) from the μ-(1,1)-bridging azide ligand form the equatorial plane, where the Cu1—N bond lengths are in the range 2.006 (4)–2.130 (4) Å. The trans axial sites of both Cu^{II} centres are occupied by atom N8 of a cyanide group of the Ni(CN)₄²⁻ anion [Cu1—N8 = 2.223 (4) Å] and another N atom [N1ⁱ; symmetry code: (i) 1 − x, 2 − y, 1 − z] from the end-on bridging azide ligand, with a long Cu1—N bond distance [3.013 (4) Å]. Similarly long Cu—N(azide) distances are also observed in several other systems (Goher et al., 1998; Mautner & Goher, 1994). The Cu1···Cu1 and Cu1···Ni1
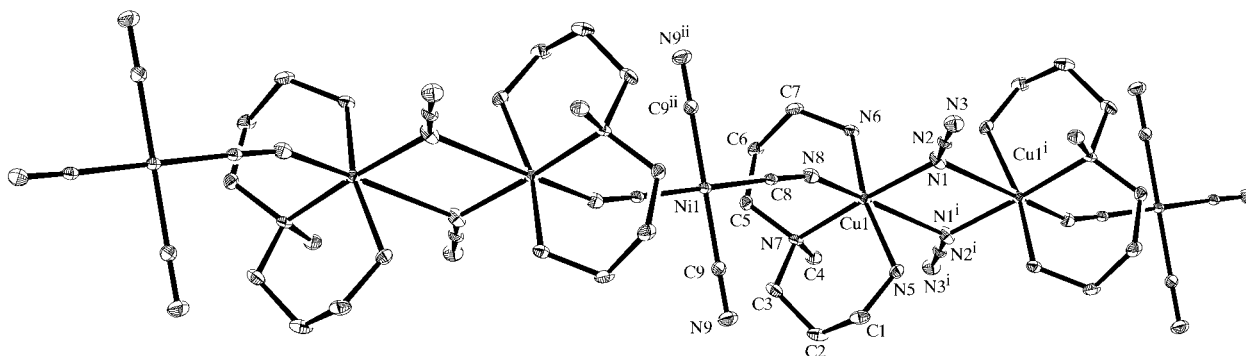
Figure 1
The structure of (I), showing 30% probability displacement ellipsoids. [Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $-x, 2 - y, -z$.]
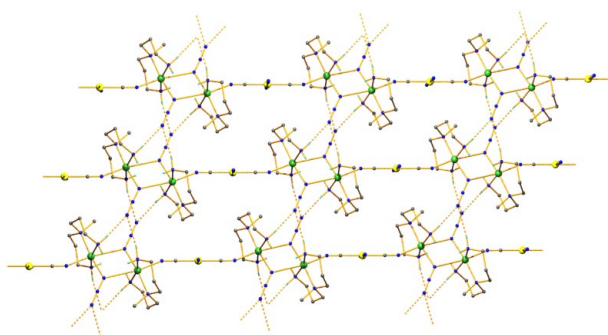

Figure 2
The formation of two-dimensional sheets in the *bc* plane *via* bifurcated hydrogen bonds joining the chains through atom N3 of the bridging azide ligand.

distances are 3.987 and 5.103 Å, respectively. At the Cu^{II} centre, both six-membered chelate rings formed by the medpt ligand possess chair conformations.

When these heterometallic chains line up in the *bc* plane, bifurcated hydrogen bonds (Table 2) from atom N3 join the parallel chains, resulting in a two-dimensional sheet (Fig. 2)
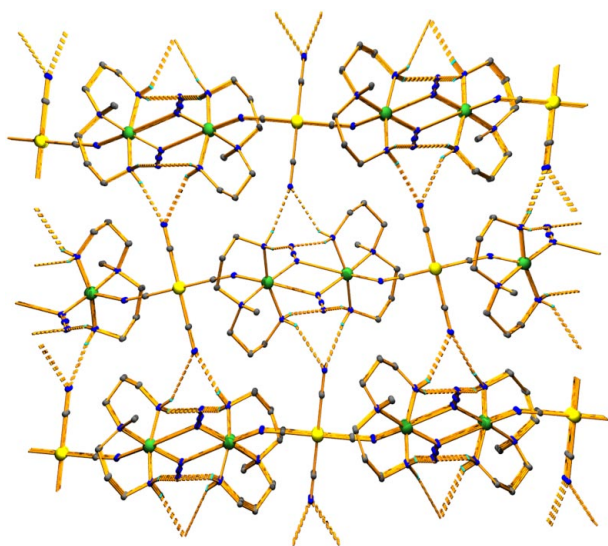

Figure 3
The supramolecular three-dimensional continuum formed by joining the two-dimensional sheets through bifurcated hydrogen bonds generated from the pendant N9 atom of the CN ligand.

with graph-set motif $R_2^1(8)$. The H atoms bound to atoms N6 and N5 are also involved in a bifurcated hydrogen-bonding system with the terminal cyano atom N9. This hydrogen-bonding motif, with graph set $R_4^2(8)$, joins the two-dimensional sheets from above and below to form a three-dimensional supramolecular array (Fig. 3).

Experimental

A methanol solution (5 ml) of medpt (2 mmol, 0.290 g) was added dropwise to an aqueous solution (10 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (2 mmol, 0.741 g). To the resulting deep-blue solution, $K_2[Ni(CN)_4] \cdot 2H_2O$ (1 mmol, 0.276 g) dissolved in water (5 ml) was added. Instantaneously, a crystalline sky-blue complex separated out and was treated with an aqueous solution (5 ml) of NaN_3 (1 mmol, 0.065 g), resulting in a deep-green solution. This was filtered and the filtrate was kept in a $CaCl_2$ desiccator (yield: 60%). Found: C 32.46, H 5.64, N 33.52, Cu 19.56%; calculated for $C_{18}H_{38}Cu_2N_{16}Ni$: C 32.51, H 5.76, N 33.71, Cu 19.11%. Spectroscopic data, IR (ν, cm^{-1}): 3178, 3270, 3300 (N—H), 2859, 2929, 2893, 2963 (CH$_2$), 2117, 2137 (N$_3$), 2036 (CN).

Crystal data

$[Cu_2Ni(CN)_4(N_3)_2(C_7H_{19}N_3)_2]$	$D_x = 1.608$ Mg m^{-3}
$M_r = 664.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 38
$a = 7.4094$ (9) Å	reflections
$b = 14.5472$ (16) Å	$\theta = 2.8$–$20.0°$
$c = 12.8512$ (19) Å	$\mu = 2.26$ mm^{-1}
$\beta = 97.757$ (11)$°$	$T = 160$ (2) K
$V = 1372.5$ (3) Å^3	Plate, green
$Z = 2$	$0.38 \times 0.18 \times 0.08$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.037$
ω scans	$\theta_{max} = 25.0°$
Absorption correction: ψ scan	$h = -8 \rightarrow 1$
(North *et al.*, 1968)	$k = -1 \rightarrow 17$
$T_{min} = 0.595$, $T_{max} = 0.835$	$l = -15 \rightarrow 15$
3235 measured reflections	3 standard reflections
2404 independent reflections	every 97 reflections
1791 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2$
$R(F) = 0.043$	$+ 3.3185P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2404 reflections	$\Delta\rho_{max} = 0.64$ e Å^{-3}
169 parameters	$\Delta\rho_{min} = -0.72$ e Å^{-3}
H-atom parameters constrained	

metal-organic compounds

Table 1
Selected geometric parameters (Å, °).

Cu1—N5	2.006 (4)	Cu1—N8	2.222 (4)
Cu1—N6	2.009 (4)	Cu1—N1^i	3.013 (4)
Cu1—N1	2.075 (4)	Ni1—C8	1.868 (4)
Cu1—N7	2.130 (3)	Ni1—C9	1.871 (5)
N5—Cu1—N6	162.23 (16)	N1^i—Cu1—N8	171.33 (13)
N5—Cu1—N1	86.62 (15)	Cu1—N1—Cu1^i	101.55 (14)
N6—Cu1—N1	87.43 (15)	N3—N2—N1	177.1 (5)
N5—Cu1—N7	93.06 (14)	C1—N5—Cu1	121.6 (3)
N6—Cu1—N7	90.63 (14)	C7—N6—Cu1	116.6 (3)
N1—Cu1—N7	172.35 (15)	C4—N7—Cu1	109.2 (3)
N5—Cu1—N8	98.08 (15)	C3—N7—Cu1	113.6 (3)
N6—Cu1—N8	99.19 (15)	C5—N7—Cu1	112.3 (3)
N1—Cu1—N8	96.12 (15)	C8^{ii}—Ni1—C9^{ii}	89.23 (18)
N7—Cu1—N8	91.50 (14)	C8—Ni1—C9^{ii}	90.77 (18)
N2—N1—Cu1	123.2 (3)	C8^{ii}—Ni1—C9	90.77 (18)
N1—Cu1—N1^i	78.45 (13)	C8—Ni1—C9	89.23 (18)
N1^i—Cu1—N5	75.01 (14)	N8—C8—Ni1	177.9 (4)
N1^i—Cu1—N6	87.41 (13)	N9—C9—Ni1	179.3 (4)
N1^i—Cu1—N7	94.07 (13)	C8—N8—Cu1	155.0 (3)

Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $-x, 2 - y, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N5—H5$A\cdots$N9^i	0.90	2.56	3.298 (6)	140
N5—H5$B\cdots$N3^{ii}	0.90	2.62	3.489 (5)	163
N6—H6$A\cdots$N9^{iii}	0.90	2.30	3.154 (6)	158
N6—H6$B\cdots$N3^{iv}	0.90	2.37	3.252 (5)	167

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

H atoms bonded to C and N atoms were placed in geometrically calculated positions, with C—H distances in the range 0.97–0.99 Å and N—H distances of 0.90 Å, and refined as riding, with U_{iso}(H) = $1.2U_{eq}$(C,N) [$1.5U_{eq}$(C) for the methyl H atoms].

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

References

Bowmaker, G. A., Kennedy, B. J. & Reid, J. C. (1998). *Inorg. Chem.* **37**, 3968–3974.
Bruker (1999). *XSCANS*. Release 2.31. Bruker AXS Inc., Madison, Wisconsin, USA.
Černák, J., Chomic, J., Domiano, P., Ori, O. & Andreetti, G. D. (1990). *Acta Cryst.* C**46**, 2103–2107.
Chesnut, D. J. & Zubieta, J. (1998). *Chem. Commun.* pp. 1707–1708.
Colacio, E., Dominguez-Vera, J. M., Lloret, F., Rodriguez, A. & Stoeckli-Evans, H. (2003). *Inorg. Chem.* **42**, 6962–6964.
Du, B., Meyers, E. A. & Shore, S. G. (2000). *Inorg. Chem.* **39**, 4639–4645.
Falvello, L. R. & Tomas, M. (1999). *Chem. Commun.* pp. 273–274.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Goher, M. A. S., Escuer, A., Morsy, A. M. A. Y. & Mautner, F. A. (1998). *Polyhedron*, **17**, 4265–4273.
Iwamoto, T. (1996). *Supramolecular Chemistry in Cyanometallate Systems*, in *Comprehensive Supramolecular Chemistry*, edited by D. D. MacNicol, F. Toda & R. Bishop, Vol. 6, ch. 19. Oxford: Pergamon.
Iwamoto, T., Miyoshi, T. & Sasaki, Y. (1974). *Acta Cryst.* B**30**, 292–295.
Maji, T. K., Mukherjee, P. S., Mostafa, G., Zangrando, E. & Ray Chaudhuri, N. (2001). *Chem. Commun.* pp. 1368–1369.
Mautner, F. A. & Goher, M. A. S. (1994). *Polyhedron*, **13**, 2141–2147.
Mondal, N., Saha, M. K., Bag, B., Mitra, S., Gramlich, V., Ribas, J. & El Fallah, M. S. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1601–1604.
Muga, I., Gutierrez-Zorrila, J. M., Luque, A., Roman, P. & Lloret, F. (1997). *Inorg. Chem.* **36**, 743–745.
Niel, V., Martinez-Agudo, J. M., Munoz, M. C., Gasper, A. B. & Real, J. A. (2001). *Inorg. Chem.* **40**, 3838–3839.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ribas, J., Escuer, A., Monfort, M., Vicente, R., Cortés, R., Lezama, L. & Rojo, T. (1999). *Coord. Chem. Rev.* **193**, 1027–1068.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Shorrock, C. J., Jong, H. & Leznoff, D. B. (2003). *Inorg. Chem.* **42**, 3917–3924.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Yuge, H. & Iwamoto, T. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1237–1242.

supporting information

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Computing details

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

catena-poly[[di-*μ*-azido-*κ⁴N¹*:*N¹*-bis[[bis(3-aminopropyl)methylamine- *κ³N*]copper(II)]]-*μ*-cyano-[dicyanonickel(II)]-*μ*-cyano]

Crystal data

[Cu₂Ni(CN)₄(N₃)₂(C₇H₁₉N₃)₂]	$F(000) = 688$
$M_r = 664.43$	$D_x = 1.608$ Mg m⁻³
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 38 reflections
$a = 7.4094$ (9) Å	$\theta = 2.8$–20.0°
$b = 14.5472$ (16) Å	$\mu = 2.26$ mm⁻¹
$c = 12.8512$ (19) Å	$T = 160$ K
$\beta = 97.757$ (11)°	Plate, green
$V = 1372.5$ (3) Å³	$0.38 \times 0.18 \times 0.08$ mm
$Z = 2$	

Data collection

Bruker P4 diffractometer	2404 independent reflections
Radiation source: fine-focus sealed tube	1791 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.037$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
Absorption correction: ψ scan (North et al., 1968)	$h = -8 \rightarrow 1$
	$k = -1 \rightarrow 17$
$T_{min} = 0.595$, $T_{max} = 0.835$	$l = -15 \rightarrow 15$
3235 measured reflections	3 standard reflections every 97 reflections
	intensity decay: none

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.043$	
$wR(F^2) = 0.115$	Secondary atom site location: difference Fourier map
$S = 1.04$	
2404 reflections	Hydrogen site location: inferred from neighbouring sites
169 parameters	

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 3.3185P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}

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}
Cu1	0.43217 (6)	0.99616 (3)	0.34460 (4)	0.01568 (17)
N1	0.3096 (5)	1.0570 (3)	0.4633 (3)	0.0260 (9)
N2	0.1533 (5)	1.0811 (3)	0.4520 (3)	0.0205 (8)
N3	0.0026 (5)	1.1055 (3)	0.4455 (3)	0.0291 (9)
N5	0.3363 (5)	0.8764 (3)	0.3917 (3)	0.0216 (8)
H5A	0.4213	0.8538	0.4418	0.026*
H5B	0.2380	0.8896	0.4231	0.026*
N6	0.5784 (5)	1.1121 (2)	0.3399 (3)	0.0195 (8)
H6A	0.5268	1.1559	0.3756	0.023*
H6B	0.6907	1.1017	0.3742	0.023*
N7	0.5887 (5)	0.9311 (2)	0.2383 (3)	0.0176 (8)
C1	0.2837 (6)	0.8011 (3)	0.3173 (4)	0.0272 (11)
H1A	0.1803	0.8211	0.2653	0.033*
H1B	0.2436	0.7475	0.3556	0.033*
C2	0.4425 (7)	0.7738 (3)	0.2610 (4)	0.0310 (11)
H2A	0.4092	0.7173	0.2199	0.037*
H2B	0.5479	0.7588	0.3142	0.037*
C3	0.5005 (7)	0.8468 (3)	0.1874 (4)	0.0271 (11)
H3A	0.5846	0.8189	0.1451	0.032*
H3B	0.3938	0.8657	0.1401	0.032*
C4	0.7695 (6)	0.9054 (3)	0.2953 (4)	0.0249 (10)
H4A	0.8420	0.8754	0.2467	0.037*
H4B	0.7530	0.8630	0.3525	0.037*
H4C	0.8327	0.9608	0.3243	0.037*
C5	0.6174 (6)	0.9924 (3)	0.1480 (3)	0.0211 (9)
H5C	0.4974	1.0044	0.1062	0.025*
H5D	0.6921	0.9586	0.1023	0.025*
C6	0.7088 (6)	1.0845 (3)	0.1766 (4)	0.0252 (11)
H6C	0.8273	1.0731	0.2203	0.030*
H6D	0.7339	1.1152	0.1113	0.030*
C7	0.5975 (7)	1.1485 (3)	0.2352 (4)	0.0258 (11)
H7A	0.6573	1.2094	0.2426	0.031*

H7B	0.4752	1.1566	0.1946	0.031*
Ni1	0.0000	1.0000	0.0000	0.0149 (2)
C8	0.1286 (6)	1.0183 (3)	0.1337 (3)	0.0163 (9)
C9	0.0012 (6)	0.8734 (3)	0.0260 (3)	0.0199 (10)
N8	0.2088 (5)	1.0268 (3)	0.2157 (3)	0.0229 (9)
N9	0.0029 (6)	0.7950 (3)	0.0431 (4)	0.0317 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0149 (3)	0.0135 (3)	0.0195 (3)	−0.0014 (2)	0.00556 (19)	−0.0023 (2)
N1	0.017 (2)	0.031 (2)	0.032 (2)	−0.0036 (18)	0.0095 (17)	−0.0108 (19)
N2	0.024 (2)	0.0160 (18)	0.023 (2)	−0.0029 (16)	0.0077 (15)	−0.0043 (16)
N3	0.023 (2)	0.028 (2)	0.037 (2)	0.0065 (17)	0.0046 (17)	0.001 (2)
N5	0.0216 (19)	0.0207 (19)	0.023 (2)	−0.0041 (16)	0.0069 (15)	0.0043 (17)
N6	0.0191 (19)	0.0145 (18)	0.025 (2)	−0.0023 (15)	0.0043 (15)	−0.0035 (16)
N7	0.0189 (18)	0.0112 (17)	0.0230 (19)	0.0020 (14)	0.0043 (15)	−0.0029 (15)
C1	0.024 (2)	0.018 (2)	0.038 (3)	−0.0068 (19)	−0.001 (2)	0.001 (2)
C2	0.032 (3)	0.016 (2)	0.045 (3)	−0.004 (2)	0.003 (2)	−0.006 (2)
C3	0.033 (3)	0.021 (2)	0.027 (2)	−0.002 (2)	0.002 (2)	−0.010 (2)
C4	0.024 (2)	0.022 (2)	0.029 (2)	0.0070 (19)	0.0042 (19)	0.000 (2)
C5	0.022 (2)	0.023 (2)	0.019 (2)	0.0033 (19)	0.0084 (17)	0.001 (2)
C6	0.023 (2)	0.023 (2)	0.032 (3)	−0.0020 (19)	0.014 (2)	0.005 (2)
C7	0.029 (3)	0.014 (2)	0.036 (3)	0.0020 (19)	0.012 (2)	0.005 (2)
Ni1	0.0156 (4)	0.0120 (4)	0.0175 (4)	0.0005 (3)	0.0035 (3)	−0.0001 (3)
C8	0.017 (2)	0.012 (2)	0.021 (2)	0.0011 (16)	0.0061 (17)	−0.0001 (17)
C9	0.020 (2)	0.020 (2)	0.021 (2)	−0.0027 (18)	0.0065 (19)	−0.0001 (18)
N8	0.0184 (19)	0.022 (2)	0.029 (2)	0.0021 (15)	0.0046 (17)	−0.0023 (17)
N9	0.040 (2)	0.020 (2)	0.035 (2)	−0.0052 (18)	0.0035 (19)	0.0040 (19)

Geometric parameters (Å, º)

Cu1—N5	2.006 (4)	C1—H1A	0.99
Cu1—N6	2.009 (4)	C1—H1B	0.99
Cu1—N1	2.075 (4)	C2—H2A	0.99
Cu1—N7	2.130 (3)	C2—H2B	0.99
Cu1—N8	2.222 (4)	C3—H3A	0.97
Cu1—N1^i	3.013 (4)	C3—H3B	0.97
N1—N2	1.200 (5)	C4—H4A	0.98
N2—N3	1.164 (5)	C4—H4B	0.98
N5—C1	1.470 (6)	C4—H4C	0.98
N6—C7	1.470 (6)	C5—H5C	0.99
N7—C4	1.485 (6)	C5—H5D	0.99
N7—C3	1.498 (6)	C6—H6C	0.99
N7—C5	1.500 (5)	C6—H6D	0.99
C1—C2	1.516 (7)	C7—H7A	0.99
C2—C3	1.522 (7)	C7—H7B	0.99
C5—C6	1.524 (6)	Ni1—C8^{ii}	1.868 (4)

C6—C7	1.511 (6)	Ni1—C8	1.868 (4)
N5—H5A	0.90	Ni1—C9ii	1.871 (5)
N5—H5B	0.90	Ni1—C9	1.871 (5)
N6—H6B	0.90	C8—N8	1.145 (6)
N6—H6A	0.90	C9—N9	1.162 (6)
N5—Cu1—N6	162.23 (16)	N5—C1—H1B	109.55
N5—Cu1—N1	86.62 (15)	C2—C1—H1A	109.56
N6—Cu1—N1	87.43 (15)	C2—C1—H1B	109.63
N5—Cu1—N7	93.06 (14)	H1A—C1—H1B	108.09
N6—Cu1—N7	90.63 (14)	C1—C2—H2A	108.58
N1—Cu1—N7	172.35 (15)	C1—C2—H2B	108.60
N5—Cu1—N8	98.08 (15)	C3—C2—H2A	108.58
N6—Cu1—N8	99.19 (15)	C3—C2—H2B	108.68
N1—Cu1—N8	96.12 (15)	H2A—C2—H2B	107.57
N7—Cu1—N8	91.50 (14)	N7—C3—H3A	108.18
N2—N1—Cu1	123.2 (3)	N7—C3—H3B	108.20
N1—Cu1—N1i	78.45 (13)	C2—C3—H3A	108.25
N1i—Cu1—N5	75.01 (14)	C2—C3—H3B	108.22
N1i—Cu1—N6	87.41 (13)	H3A—C3—H3B	107.37
N1i—Cu1—N7	94.07 (13)	N7—C4—H4A	109.47
N1i—Cu1—N8	171.33 (13)	N7—C4—H4B	109.45
Cu1—N1—N2	123.1 (3)	N7—C4—H4C	109.48
Cu1—N1—Cu1i	101.55 (14)	H4A—C4—H4B	109.42
Cu1i—N1—N2	132.1 (3)	H4A—C4—H4C	109.50
N3—N2—N1	177.1 (5)	H4B—C4—H4C	109.51
C1—N5—Cu1	121.6 (3)	N7—C5—H5C	108.27
C7—N6—Cu1	116.6 (3)	N7—C5—H5D	108.20
C4—N7—C3	108.7 (3)	C6—C5—H5C	108.25
C4—N7—C5	108.6 (3)	C6—C5—H5D	108.29
C3—N7—C5	104.4 (3)	H5C—C5—H5D	107.37
C4—N7—Cu1	109.2 (3)	C5—C6—H6C	108.71
C3—N7—Cu1	113.6 (3)	C5—C6—H6D	108.69
C5—N7—Cu1	112.3 (3)	C7—C6—H6C	108.81
N5—C1—C2	110.6 (4)	C7—C6—H6D	108.79
C1—C2—C3	114.5 (4)	H6C—C6—H6D	107.61
N7—C3—C2	116.4 (4)	N6—C7—H7A	109.37
N7—C5—C6	116.1 (4)	N6—C7—H7B	109.32
C7—C6—C5	114.0 (4)	C6—C7—H7A	109.41
N6—C7—C6	111.2 (4)	C6—C7—H7B	109.46
C1—N5—H5A	106.94	H7A—C7—H7B	108.08
Cu1—N5—H5A	106.92	C8ii—Ni1—C8	180.000 (1)
Cu1—N5—H5B	106.92	C8ii—Ni1—C9ii	89.23 (18)
C1—N5—H5B	106.91	C8—Ni1—C9ii	90.77 (18)
H5A—N5—H5B	106.73	C8ii—Ni1—C9	90.77 (18)
C7—N6—H6A	108.15	C8—Ni1—C9	89.23 (18)
Cu1—N6—H6A	108.12	C9ii—Ni1—C9	180.000 (1)
Cu1—N6—H6B	108.10	N8—C8—Ni1	177.9 (4)

C7—N6—H6B	108.17	N9—C9—Ni1	179.3 (4)
H6A—N6—H6B	107.31	C8—N8—Cu1	155.0 (3)
N5—C1—H1A	109.44		
N5—Cu1—N1—N2	−86.3 (4)	N6—Cu1—N7—C5	−44.6 (3)
N6—Cu1—N1—N2	110.4 (4)	N8—Cu1—N7—C5	54.6 (3)
N8—Cu1—N1—N2	11.4 (4)	Cu1—N5—C1—C2	57.5 (5)
N6—Cu1—N5—C1	−141.2 (4)	N5—C1—C2—C3	−66.9 (5)
N1—Cu1—N5—C1	148.1 (3)	C4—N7—C3—C2	68.4 (5)
N7—Cu1—N5—C1	−39.5 (3)	C5—N7—C3—C2	−175.9 (4)
N8—Cu1—N5—C1	52.4 (3)	Cu1—N7—C3—C2	−53.4 (5)
N5—Cu1—N6—C7	153.3 (4)	C1—C2—C3—N7	69.4 (6)
N1—Cu1—N6—C7	−136.2 (3)	C4—N7—C5—C6	−63.5 (5)
N7—Cu1—N6—C7	51.2 (3)	C3—N7—C5—C6	−179.3 (4)
N8—Cu1—N6—C7	−40.4 (3)	Cu1—N7—C5—C6	57.3 (4)
N5—Cu1—N7—C4	−86.8 (3)	N7—C5—C6—C7	−65.3 (5)
N6—Cu1—N7—C4	75.8 (3)	Cu1—N6—C7—C6	−66.6 (4)
N8—Cu1—N7—C4	175.0 (3)	C5—C6—C7—N6	66.7 (5)
N5—Cu1—N7—C3	34.7 (3)	N5—Cu1—N8—C8	−75.6 (9)
N6—Cu1—N7—C3	−162.7 (3)	N6—Cu1—N8—C8	108.6 (8)
N8—Cu1—N7—C3	−63.5 (3)	N1—Cu1—N8—C8	−163.0 (8)
N5—Cu1—N7—C5	152.8 (3)	N7—Cu1—N8—C8	17.7 (9)

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x, -y+2, -z$.

Hydrogen-bond geometry (Å, º)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N5—H5$A\cdots$N9[iii]	0.90	2.56	3.298 (6)	140
N5—H5$B\cdots$N3[iv]	0.90	2.62	3.489 (5)	163
N6—H6$A\cdots$N9[v]	0.90	2.30	3.154 (6)	158
N6—H6$B\cdots$N3[vi]	0.90	2.37	3.252 (5)	167

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