metal-organic compounds

catena-Poly[[bis(pyridine-κN)nickel(II)]-di-μ-azido-$κ^4N^1$:N^3-[bis(pyridine-κN)-nickel(II)]-di-μ-azido-$κ^4N^1$:N^1]

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In the structure of the title compound, $[Ni_2(N_3)_4(C_5H_5N)_4]_n$, neutral chains of Ni^{II} atoms are bridged alternately by double end-on and double end-to-end azide bridges. Each Ni^{II} center is located on a crystallographic general position and in a slightly distorted octahedral coordination environment with two pyridine ligands in the *trans* positions. Both end-on and end-to-end double azide bridges become equivalent because of the inversion centers lying between each pair of adjacent Ni^{II} atoms. In the chain, the Ni···Ni separations across the end-on and end-to-end azide bridges are 3.236 (4) and 4.975 (4) Å, respectively, and the end-on azide bridging Ni—N—Ni angle is 100.8 (2)°.

Related literature

For related literature, see: Goher *et al.* (2002); Liu *et al.* (2006); Nelson & Shepherd (1965); Schreiner & Hamm (1973).
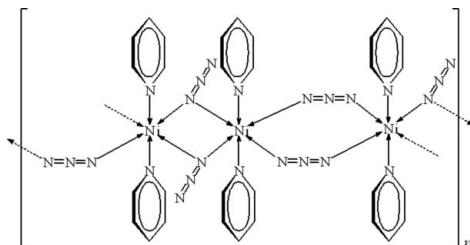
Experimental

Crystal data
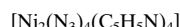
$[Ni_2(N_3)_4(C_5H_5N)_4]$	$γ$ = 65.36 (3)°
M_r = 300.97	V = 649.8 (3) Å³
Triclinic, $P\bar{1}$	Z = 2
a = 8.1354 (16) Å	Mo $Kα$ radiation
b = 9.4770 (19) Å	$μ$ = 1.49 mm⁻¹
c = 10.094 (2) Å	T = 293 (2) K
$α$ = 84.66 (3)°	$0.30 × 0.10 × 0.08$ mm
$β$ = 67.17 (3)°	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	6061 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	2532 independent reflections
T_{min} = 0.913, T_{max} = 1.000	2127 reflections with $I > 2σ(I)$
(expected range = 0.810–0.887)	R_{int} = 0.037

Refinement

$R[F^2 > 2σ(F^2)]$ = 0.061	172 parameters
$wR(F^2)$ = 0.164	H-atom parameters constrained
S = 1.08	$Δρ_{max}$ = 1.66 e Å⁻³
2532 reflections	$Δρ_{min}$ = −0.43 e Å⁻³

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT* and *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2051).

References

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supplementary materials

catena-Poly[[bis(pyridine-*κN*)nickel(II)]-di-*μ*-azido-*κ*^{4}*N*^{1}:*N*^{3}-[bis(pyridine-*κN*)nickel(II)]-di-*μ*-azido-*κ*^{4}*N*^{1}:*N*^{1}]

W.-C. Song, M.-J. Zhang, Y. Tao and J.-R. Li

Comment

Azido-Ni^{II} compounds with mono-N donored pyridine based co-ligands have been investigated early with respect to their metal-to-ligand π-bonding features (Nelson & Shepherd, 1965), magnetic circular dichroism and crystal field (Schreiner & Hamm, 1973). Recently, the crystal structures of two relative compounds, {[Ni(4-ethylpyridine)$_4$(N$_3$)]·(PF$_6$)}$_n$ (Goher *et al.*, 2002) and [Ni(pyridine)$_2$(N$_3$)$_2$] (Liu *et al.*, 2006) have been reported. The former has a single end-to-end azido-bridged cationic chain structure, but the latter is mono-nuclear. Different from them, the title compound, [Ni$_2$(C$_5$H$_5$N)$_4$(N$_3$)$_4$]$_n$ has a neutral chain structure of Ni^{II} atoms bridged alternately by double end-on and double end-to-end azido bridges.

As shown in Fig. 1, the Ni^{II} center located at the crystallographically general position is coordinated by four azido N and two pyridine N atoms in a slightly distorted octahedral environment, in which two pyridine ligands lie in the *trans* positions. Both end-on and end-to-end double azido bridges become equivalent because of the inversion centers lied on between each two adjacent Ni^{II} atoms, respectively. Based on the (Ni1—N3—Ni1A—N3A) plane, the out-of-plane deviation of the N3—N4—N5 group is *ca* 14.1 (4) °, and the dihedral angles between the mean plane and two pyridyl rings are 99.7 (4) ° for (C1—C5—N1) and 82.9 (4) ° for (C6—C10—N2), respectively. The end-to-end azido-bridged dinuclear unit has a chair configuration with the dihedral angle between the (N6—Ni1—N8B) and (N6—N8—N6B—N8B) mean plane is 143.5 (4) °. In the chain, the Ni—Ni distances across the end-on and end-to-end azido bridges are 3.236 (4) and 4.975 (4) Å, respectively, and the end-on azido bridging Ni1—N3—Ni1A angle is 100.8 (2) °. In addition, in the crystal structure such chains arrange in parallel along the *a* direction to finish the three-dimensional packing (Fig. 2).

Experimental

A mixture of NiCl$_2$·6H$_2$O (24 mg, 0.1 mmol), NaN$_3$ (26 mg, 0.4 mmol) and pyridine (20 mg, 0.25 mmol) in 10 ml of water was sealed in a Teflon-lined stainless-steel Parr bomb that was heated at 413 K for 48 h. Green crystals of the title compound were collected after the bomb was allowed to cool to room temperature spontaneously. Yield, 10% with respect to Cu(II). *Caution*: Azide is potentially explosive, especially in a hydrothermal manipulation. Although we have met no problems in this work, only a small amount of them should be prepared and handled with great caution.

Refinement

H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C, N).

supplementary materials

Figures

Fig. 1. one-dimensional chain structure of the title compound with 30% displacement probability. [Herein, labelled atoms A and B correspond to symmetry oprations i and ii, respectively. (i) = $1 - x$, $1 - y$, $1 - z$; (ii) = $2 - x$, $1 - y$, $1 - z$]
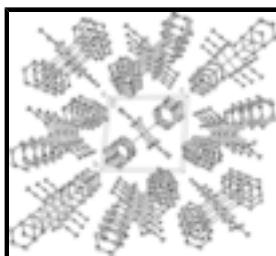

Fig. 2. three-dimensional packing of one-dimensional chains in the title compound.

catena-Poly[[bis(pyridine-κ*N*)nickel(II)]-di-μ-azido-κ^4*N*^{1}:*N*^{3}– [bis(pyridine-κ*N*)nickel(II)]-di-μ-azido-κ^4*N*^{1}:*N*^{1}]
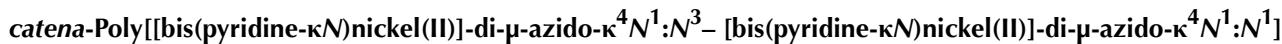
Crystal data

[Ni$_2$(N$_3$)$_4$(C$_5$H$_5$N)$_4$]	$Z = 2$
$M_r = 300.97$	$F_{000} = 308$
Triclinic, $P\bar{1}$	$D_x = 1.538$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.1354$ (16) Å	Cell parameters from 6054 reflections
$b = 9.4770$ (19) Å	$\theta = 2.9–27.6°$
$c = 10.094$ (2) Å	$\mu = 1.49$ mm^{-1}
$\alpha = 84.66$ (3)°	$T = 293$ (2) K
$\beta = 67.17$ (3)°	Block, green
$\gamma = 65.36$ (3)°	$0.30 \times 0.10 \times 0.08$ mm
$V = 649.8$ (3) Å^3	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2532 independent reflections
Radiation source: fine-focus sealed tube	2127 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.037$
$T = 293(2)$ K	$\theta_{max} = 26.0°$
φ and ω scan	$\theta_{min} = 3.0°$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$h = -10 \rightarrow 10$
$T_{min} = 0.913$, $T_{max} = 1.000$	$k = -11 \rightarrow 11$
6061 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.061$

H-atom parameters constrained

$wR(F^2) = 0.164$

$w = 1/[\sigma^2(F_o^2) + (0.0999P)^2 + 0.3477P]$
where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.08$

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

2532 reflections

$\Delta\rho_{max} = 1.66$ e Å^{-3}

172 parameters

$\Delta\rho_{min} = -0.43$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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	$U_{iso}*/U_{eq}$
Ni1	0.69698 (7)	0.51940 (6)	0.47848 (5)	0.0358 (2)
N1	0.7466 (6)	0.3698 (5)	0.6423 (4)	0.0435 (9)
N2	0.6740 (6)	0.6716 (5)	0.3143 (4)	0.0453 (9)
N3	0.3937 (5)	0.6239 (5)	0.5965 (4)	0.0423 (9)
N4	0.3021 (5)	0.7109 (4)	0.7033 (4)	0.0392 (8)
N5	0.2148 (8)	0.7941 (6)	0.8059 (5)	0.0725 (14)
N6	0.7515 (6)	0.6794 (5)	0.5723 (5)	0.0498 (10)
N7	0.8790 (5)	0.6417 (4)	0.6133 (4)	0.0423 (9)
N8	1.0035 (5)	0.6082 (5)	0.6582 (4)	0.0501 (10)
C1	0.6961 (8)	0.4251 (7)	0.7757 (5)	0.0545 (13)
H1A	0.6229	0.5315	0.8003	0.065*
C2	0.7475 (9)	0.3319 (7)	0.8788 (6)	0.0622 (14)
H2A	0.7078	0.3749	0.9710	0.075*
C3	0.8581 (9)	0.1744 (7)	0.8438 (6)	0.0687 (16)
H3A	0.8990	0.1093	0.9102	0.082*
C4	0.9060 (11)	0.1169 (7)	0.7085 (7)	0.085 (2)
H4A	0.9752	0.0104	0.6824	0.101*
C5	0.8511 (10)	0.2176 (7)	0.6114 (6)	0.0696 (17)
H5A	0.8893	0.1767	0.5187	0.084*
C6	0.5810 (9)	0.8266 (7)	0.3467 (7)	0.0645 (15)
H6A	0.5188	0.8644	0.4432	0.077*
C7	0.5738 (11)	0.9323 (8)	0.2428 (9)	0.086 (2)

H7A	0.5109	1.0390	0.2685	0.104*
C8	0.6626 (11)	0.8754 (9)	0.0997 (9)	0.085 (2)
H8A	0.6603	0.9436	0.0272	0.102*
C9	0.7538 (9)	0.7183 (9)	0.0657 (7)	0.0781 (19)
H9A	0.8133	0.6778	−0.0299	0.094*
C10	0.7559 (8)	0.6207 (7)	0.1759 (5)	0.0556 (13)
H10A	0.8180	0.5138	0.1520	0.067*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0275 (3)	0.0467 (4)	0.0376 (4)	−0.0149 (3)	−0.0162 (2)	−0.0014 (2)
N1	0.036 (2)	0.055 (2)	0.044 (2)	−0.0173 (18)	−0.0219 (17)	0.0041 (18)
N2	0.043 (2)	0.048 (2)	0.048 (2)	−0.0200 (18)	−0.0191 (18)	0.0057 (18)
N3	0.0319 (19)	0.054 (2)	0.042 (2)	−0.0158 (17)	−0.0140 (17)	−0.0113 (18)
N4	0.040 (2)	0.041 (2)	0.042 (2)	−0.0144 (17)	−0.0242 (18)	0.0033 (18)
N5	0.081 (3)	0.066 (3)	0.053 (3)	−0.017 (3)	−0.018 (3)	−0.018 (2)
N6	0.042 (2)	0.053 (2)	0.065 (3)	−0.0164 (19)	−0.032 (2)	−0.005 (2)
N7	0.035 (2)	0.046 (2)	0.046 (2)	−0.0158 (17)	−0.0142 (17)	−0.0091 (17)
N8	0.0293 (19)	0.075 (3)	0.046 (2)	−0.0179 (19)	−0.0166 (18)	−0.008 (2)
C1	0.047 (3)	0.068 (3)	0.044 (3)	−0.021 (3)	−0.016 (2)	0.002 (2)
C2	0.064 (3)	0.083 (4)	0.041 (3)	−0.030 (3)	−0.021 (3)	0.007 (3)
C3	0.079 (4)	0.075 (4)	0.054 (3)	−0.022 (3)	−0.041 (3)	0.016 (3)
C4	0.110 (6)	0.057 (4)	0.078 (4)	−0.009 (4)	−0.056 (4)	0.005 (3)
C5	0.095 (5)	0.057 (3)	0.058 (3)	−0.017 (3)	−0.044 (3)	−0.005 (3)
C6	0.077 (4)	0.058 (3)	0.076 (4)	−0.032 (3)	−0.043 (3)	0.012 (3)
C7	0.099 (5)	0.063 (4)	0.120 (6)	−0.038 (4)	−0.066 (5)	0.034 (4)
C8	0.093 (5)	0.093 (5)	0.094 (5)	−0.051 (4)	−0.056 (4)	0.047 (4)
C9	0.064 (4)	0.108 (5)	0.056 (4)	−0.035 (4)	−0.022 (3)	0.024 (4)
C10	0.052 (3)	0.070 (3)	0.047 (3)	−0.026 (3)	−0.022 (2)	0.008 (3)

Geometric parameters (Å, °)

Ni1—N1	2.124 (4)	C1—H1A	0.9300
Ni1—N2	2.105 (4)	C2—C3	1.376 (8)
Ni1—N3	2.095 (4)	C2—H2A	0.9300
Ni1—N3[i]	2.103 (4)	C3—C4	1.365 (8)
Ni1—N6	2.132 (4)	C3—H3A	0.9300
Ni1—N8[ii]	2.133 (4)	C4—C5	1.371 (8)
N3—N4	1.195 (5)	C4—H4A	0.9300
N4—N5	1.145 (6)	C5—H5A	0.9300
N6—N7	1.172 (5)	C6—C7	1.382 (8)
N7—N8	1.179 (5)	C6—H6A	0.9300
N1—C5	1.325 (7)	C7—C8	1.382 (11)
N1—C1	1.334 (6)	C7—H7A	0.9300
N2—C10	1.328 (7)	C8—C9	1.364 (10)
N2—C6	1.345 (7)	C8—H8A	0.9300
N3—Ni1[i]	2.103 (4)	C9—C10	1.379 (8)

N8—Ni1ⁱⁱ	2.133 (4)	C9—H9A	0.9300
C1—C2	1.377 (7)	C10—H10A	0.9300
N1—Ni1—N6	88.38 (16)	N1—C1—H1A	118.5
N1—Ni1—N8ⁱⁱ	88.52 (16)	C2—C1—H1A	118.5
N2—Ni1—N1	173.88 (14)	C3—C2—C1	119.3 (5)
N2—Ni1—N6	87.15 (16)	C3—C2—H2A	120.4
N2—Ni1—N8ⁱⁱ	87.70 (16)	C1—C2—H2A	120.4
N3—Ni1—N1	92.67 (15)	C4—C3—C2	117.8 (5)
N3ⁱ—Ni1—N1	91.49 (15)	C4—C3—H3A	121.1
N3—Ni1—N2	91.78 (16)	C2—C3—H3A	121.1
N3ⁱ—Ni1—N2	93.47 (16)	C3—C4—C5	119.3 (6)
N3—Ni1—N3ⁱ	79.16 (16)	C3—C4—H4A	120.3
N3—Ni1—N6	93.68 (15)	C5—C4—H4A	120.3
N3ⁱ—Ni1—N6	172.83 (14)	N1—C5—C4	123.8 (5)
N3—Ni1—N8ⁱⁱ	171.42 (14)	N1—C5—H5A	118.1
N3ⁱ—Ni1—N8ⁱⁱ	92.31 (15)	C4—C5—H5A	118.1
N6—Ni1—N8ⁱⁱ	94.85 (16)	N2—C6—C7	122.9 (6)
N7—N6—Ni1	123.5 (3)	N2—C6—H6A	118.5
N7—N8—Ni1ⁱⁱ	120.3 (3)	C7—C6—H6A	118.5
Ni1—N3—Ni1ⁱ	100.84 (16)	C6—C7—C8	118.2 (7)
C5—N1—C1	116.7 (4)	C6—C7—H7A	120.9
C5—N1—Ni1	120.9 (3)	C8—C7—H7A	120.9
C1—N1—Ni1	121.9 (3)	C9—C8—C7	119.4 (6)
C10—N2—C6	117.3 (5)	C9—C8—H8A	120.3
C10—N2—Ni1	122.3 (4)	C7—C8—H8A	120.3
C6—N2—Ni1	120.3 (4)	C8—C9—C10	118.7 (6)
N4—N3—Ni1	129.7 (3)	C8—C9—H9A	120.6
N4—N3—Ni1ⁱ	126.7 (3)	C10—C9—H9A	120.6
N5—N4—N3	179.8 (6)	N2—C10—C9	123.4 (6)
N6—N7—N8	177.7 (5)	N2—C10—H10A	118.3
N1—C1—C2	123.0 (5)	C9—C10—H10A	118.3
N3—Ni1—N1—C5	128.9 (4)	N1—Ni1—N3—Ni1ⁱ	−91.00 (17)
N3ⁱ—Ni1—N1—C5	49.6 (4)	N6—Ni1—N3—Ni1ⁱ	−179.55 (16)
N6—Ni1—N1—C5	−137.5 (4)	N2—Ni1—N6—N7	−132.9 (4)
N8ⁱⁱ—Ni1—N1—C5	−42.6 (4)	N1—Ni1—N6—N7	42.9 (4)
N3—Ni1—N1—C1	−59.6 (4)	N8ⁱⁱ—Ni1—N6—N7	−45.5 (4)
N3ⁱ—Ni1—N1—C1	−138.8 (4)	C5—N1—C1—C2	−0.1 (8)
N6—Ni1—N1—C1	34.0 (4)	Ni1—N1—C1—C2	−171.9 (4)
N8ⁱⁱ—Ni1—N1—C1	128.9 (4)	N1—C1—C2—C3	0.9 (9)
N3—Ni1—N2—C10	−129.8 (4)	C1—C2—C3—C4	−2.4 (10)
N3ⁱ—Ni1—N2—C10	−50.6 (4)	C2—C3—C4—C5	3.1 (11)
N6—Ni1—N2—C10	136.6 (4)	C1—N1—C5—C4	0.8 (9)
N8ⁱⁱ—Ni1—N2—C10	41.6 (4)	Ni1—N1—C5—C4	172.8 (6)
N3—Ni1—N2—C6	53.0 (4)	C3—C4—C5—N1	−2.4 (11)

N3^{i}—Ni1—N2—C6	132.3 (4)	C10—N2—C6—C7	−2.2 (8)
N6—Ni1—N2—C6	−40.6 (4)	Ni1—N2—C6—C7	175.1 (5)
N8^{ii}—Ni1—N2—C6	−135.6 (4)	N2—C6—C7—C8	1.5 (10)
N3^{i}—Ni1—N3—N4	161.8 (5)	C6—C7—C8—C9	0.0 (11)
N2—Ni1—N3—N4	−105.0 (4)	C7—C8—C9—C10	−0.6 (10)
N1—Ni1—N3—N4	70.8 (4)	C6—N2—C10—C9	1.6 (8)
N6—Ni1—N3—N4	−17.8 (4)	Ni1—N2—C10—C9	−175.7 (4)
N3^{i}—Ni1—N3—Ni1^{i}	0.0	C8—C9—C10—N2	−0.2 (9)
N2—Ni1—N3—Ni1^{i}	93.19 (17)		

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

Fig. 1

Fig. 2