metal-organic compounds

Bis(7-amino-2,4-dimethyl-1,8-naph-thyridine)dichloridonickel(II) methanol solvate

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In the title compound, $[NiCl_2(C_{10}H_{11}N_3)_2]\cdot CH_4O$, the Ni^{II} ion lies on a crystallographic twofold axis and is coordinated in a distorted octahedral geometry by four N atoms from two bidentate naphthyridine ligands and two chlorine atoms. The unique methanol solvent molecule has half occupancy. In the crystal structure, intermolecular N—H···Cl and O—H···Cl hydrogen bonds connect molecules into one-dimensional chains which propagate along the c-axis direction.

Related literature

For related literature, see: Bayer (1979); Che *et al.* (2001); Gavrilova & Bosnich (2004); Jin *et al.* (2007); Kukrek *et al.* (2006); Mintert & Sheldrick (1995*a,b*); Oskui & Sheldrick (1999); Oskui, Mintert & Sheldrick (1999); Allen *et al.* (1987).
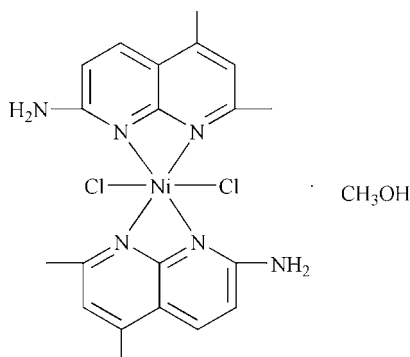
Experimental

Crystal data

$[NiCl_2(C_{10}H_{11}N_3)_2]\cdot CH_4O$
$M_r = 508.09$

Monoclinic, $C2/c$
$a = 13.609\ (10)$ Å
$b = 15.399\ (11)$ Å
$c = 12.632\ (9)$ Å
$\beta = 94.337\ (11)°$
$V = 2640\ (3)$ Å^3
$Z = 4$

Mo $K\alpha$ radiation
$\mu = 0.96$ mm^{-1}
$T = 298\ (2)$ K
$0.18 \times 0.14 \times 0.12$ mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.846$, $T_{max} = 0.894$

6731 measured reflections
2323 independent reflections
1552 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.167$
$S = 1.02$
2323 reflections
150 parameters

19 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Cl1^i	0.82	2.49	3.250 (12)	155
N3—H3B···Cl1^{ii}	0.86	2.49	3.308 (4)	159
N3—H3A···Cl1	0.86	2.57	3.368 (4)	154

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

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

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supplementary materials

Bis(7-amino-2,4-dimethyl-1,8-naphthyridine)dichloridonickel(II) methanol solvate

S. Jin, D. Wang, Y. Sun and **M. Guo**

Comment

The molecular structures and chemical properties (Kukrek *et al.*, 2006; Che *et al.*, 2001) of transition metal complexes of 1,8-naphthyridine (napy) and its derivatives have received much attention, as the ligands can link to metals with several coordination modes such as monodentate, chelating bidentate, and dinuclear bridging binding fashion (Gavrilova & Bosnich, 2004). 5,7-dimethyl-1,8-naphthyridin-2-amine is a potentially tridentate ligand and is capable of linking two to four metal atoms together to form metal aggregates (Oskui *et al.*, 1999; Mintert & Sheldrick, 1995*a*; Oskui & Sheldrick, 1999; Mintert & Sheldrick, 1995*b*). The coordination chemistry of 5,7-dimethyl-1,8-naphthyridine-2-amine (*L*) has not been well studied although an Ni(II) complex (Ni(*L*)$_2$(Cl)$_2$)(Bayer, 1979) has been decribed in a US patent. As an extension of our study (Jin *et al.*, 2007) on naphthyridine coordination chemistry, we have determined the crystal structure of the the title complex (Ni(*L*)$_2$(Cl)$_2$)·(CH$_3$OH).

The title compound was obtained as blue crystals by reacting of nickel chloride hexahydrate and *L* in methanol. The compound is a neutral compound which is air stable and light insensitive. The complex does not dissolve in water and common organic solvent. X-ray structural analysis shows that the complex is mononuclear. The molecular structure of the compound is shown in Fig. 1.

The Ni atom lies on a crystallographic twofold axis and is coordinated to two *L* ligands, and two chloride ions. The Cl atoms are in a *cis* orientation with respect to each other (Cl1—Ni1—Cl1^i = 96.55 (10)°; symmetry code: (i) −*x* + 2, *y*, −*z* + 3/2). Both *L* ligands coordinate through N atoms in a bidentate chelate fashion to form two four-membered Ni/N/C/N rings. Two chloride anions coordinate to the Ni^{II} ion to complete the distorted octahedral geometry. The amine group of the 5,7-dimethyl-1,8-naphthyridin-2-amine ligand does not form any bonding interactions with Ni atoms. All the bond lengths and bond angles in the ligand are in the normal ranges (Allen *et al.*, 1987). The N2—C2 bond distance is 1.340 (5) Å, typical for a C—N double bond. The two naphthyridine rings are almost perpendicular to each other with the N1^i—Ni1—N1—C8, N2^i—Ni1—N1—C8 torsion angles of 75.41 (16), and 14.39 (14)°. N2—Ni1—N1^i, and N1^i—Ni1—N1 are 100.08 (14), and 85.1 (2) ° respectively. The solvent methanol molecules are bonded to the corresponding (Ni$_{(L)}$2(Cl)2) moiety through hydrogen bonds and a (Ni(*L*)$_2$(Cl)$_2$) moiety is bonded to two neighbouring (Ni(*L*)$_2$(Cl)$_2$) moieties *via* hydrogen bonds. Hence, in the crystal structure, the compound forms 1-D chains along the *c* axis *via* intermolecular hydrogen bonds, (Fig. 2).

Experimental

All reagents and solvents were used as obtained without further purification. The CH,*N* elemental analyses were performed on a Perkin-Elmer model 2400 elemental analyzer.

To an methanol solution of nickel chloride hexahydrate (24 mg, 0.1 mmol), was added *L* (17.4 mg, 0.1 mmol) in 10 ml of methanol. The solution was stirred for a few minutes, then the solution was filtered. The solution was left standing at

room temperature for several days. Light blue crystals were isolated after slow evaporation of its solution in air. Yield: 33 mg, 65%. Anal. Calcd for $C_{21}H_{26}Cl_2N_6Ni_O$: C, 49.60; H, 5.12; N, 16.53; Found: C, 49.52; H, 5.05; N, 16.47.

Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with N—H = 0.86, C—H = 0.93–0.96 and O—H = 0.82 Å. They were included in the refinement in the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(O and methyl C atoms)
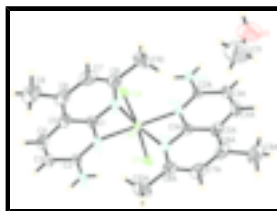
Figures

Fig. 1. The molecular structure, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level [symmetry code: (A): $-x + 2$, y, $-z + 3/2$].
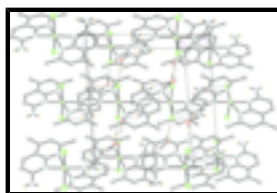
Fig. 2. Part of the crystal structure showing hydrogen bonds as dashed lines.

Bis(7-amino-2,4-dimethyl-1,8-naphthyridine)dichloridonickel(II) methanol solvate

Crystal data

$[NiCl_2(C_{10}H_{11}N_3)_2]\cdot CH_4O$	$F_{000} = 1056$
$M_r = 508.09$	$D_x = 1.278$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 1560 reflections
$a = 13.609$ (10) Å	$\theta = 2.5$–$21.3°$
$b = 15.399$ (11) Å	$\mu = 0.96$ mm^{-1}
$c = 12.632$ (9) Å	$T = 298$ (2) K
$\beta = 94.337$ (11)°	Block, blue
$V = 2640$ (3) Å^3	$0.18 \times 0.14 \times 0.12$ mm
$Z = 4$	

Data collection

Bruker SMART-APEX diffractometer	2323 independent reflections
Radiation source: fine-focus sealed tube	1552 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.053$
$T = 298(2)$ K	$\theta_{max} = 25.0°$

φ and ω scans	$\theta_{min} = 2.0°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -16 \rightarrow 16$
$T_{min} = 0.846$, $T_{max} = 0.894$	$k = -18 \rightarrow 14$
6731 measured reflections	$l = -15 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.052$	H-atom parameters constrained
$wR(F^2) = 0.167$	$w = 1/[\sigma^2(F_o^2) + (0.097P)^2 + 0.4954P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2323 reflections	$\Delta\rho_{max} = 0.57$ e Å^{-3}
150 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
19 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 $F^2 > 2\text{sigma}(F^2)$ 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	1.0000	0.12244 (5)	0.7500	0.0366 (3)	
Cl1	1.13154 (9)	0.01906 (8)	0.76050 (9)	0.0498 (4)	
N1	0.9035 (3)	0.2275 (3)	0.7978 (3)	0.0450 (10)	
N2	0.9990 (3)	0.1486 (2)	0.9113 (3)	0.0362 (9)	
N3	1.1018 (3)	0.0618 (3)	1.0176 (3)	0.0492 (11)	
H3A	1.1205	0.0366	0.9618	0.059*	
H3B	1.1261	0.0460	1.0794	0.059*	
O1	0.8427 (10)	0.3836 (8)	0.3032 (12)	0.142 (5)	0.50
H1	0.7837	0.3941	0.3035	0.213*	0.50
C1	0.9341 (3)	0.2147 (3)	0.9013 (3)	0.0392 (11)	
C2	1.0359 (3)	0.1249 (3)	1.0084 (3)	0.0373 (11)	
C3	1.0054 (4)	0.1694 (4)	1.0990 (4)	0.0533 (14)	

H3	1.0298	0.1519	1.1664	0.064*	
C4	0.9421 (4)	0.2359 (4)	1.0888 (4)	0.0597 (15)	
H4	0.9239	0.2645	1.1492	0.072*	
C5	0.9021 (4)	0.2635 (3)	0.9862 (4)	0.0498 (13)	
C6	0.8347 (4)	0.3297 (4)	0.9603 (5)	0.0669 (16)	
C7	0.8050 (5)	0.3422 (4)	0.8555 (5)	0.0712 (17)	
H7	0.7608	0.3867	0.8370	0.085*	
C8	0.8387 (4)	0.2902 (4)	0.7755 (4)	0.0604 (15)	
C9	0.7974 (5)	0.3884 (4)	1.0462 (6)	0.096 (2)	
H9A	0.8501	0.4251	1.0745	0.143*	
H9B	0.7744	0.3533	1.1021	0.143*	
H9C	0.7443	0.4237	1.0161	0.143*	
C10	0.8065 (5)	0.3040 (5)	0.6585 (5)	0.096 (2)	
H10A	0.8608	0.2923	0.6165	0.144*	
H10B	0.7853	0.3630	0.6476	0.144*	
H10C	0.7530	0.2654	0.6379	0.144*	
C11	0.8902 (16)	0.4248 (14)	0.3805 (17)	0.155 (7)	0.50
H11A	0.9272	0.4714	0.3524	0.233*	0.50
H11B	0.9343	0.3855	0.4192	0.233*	0.50
H11C	0.8442	0.4480	0.4271	0.233*	0.50

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0416 (5)	0.0413 (6)	0.0266 (4)	0.000	0.0006 (3)	0.000
Cl1	0.0544 (8)	0.0553 (9)	0.0388 (7)	0.0143 (6)	−0.0016 (5)	−0.0065 (5)
N1	0.045 (2)	0.049 (3)	0.041 (2)	0.010 (2)	0.0026 (17)	0.0066 (19)
N2	0.041 (2)	0.037 (2)	0.0300 (18)	0.0033 (18)	0.0014 (16)	−0.0001 (16)
N3	0.059 (3)	0.058 (3)	0.029 (2)	0.010 (2)	−0.0054 (18)	0.0034 (19)
O1	0.130 (8)	0.148 (8)	0.146 (8)	0.055 (6)	−0.005 (7)	−0.023 (7)
C1	0.041 (3)	0.039 (3)	0.037 (2)	0.000 (2)	0.005 (2)	0.002 (2)
C2	0.038 (3)	0.044 (3)	0.030 (2)	−0.002 (2)	0.0023 (19)	0.002 (2)
C3	0.060 (3)	0.069 (4)	0.031 (2)	0.000 (3)	0.006 (2)	−0.002 (2)
C4	0.071 (4)	0.067 (4)	0.043 (3)	0.001 (3)	0.021 (3)	−0.012 (3)
C5	0.053 (3)	0.043 (3)	0.056 (3)	0.001 (3)	0.016 (2)	−0.006 (2)
C6	0.059 (4)	0.059 (4)	0.085 (4)	0.014 (3)	0.022 (3)	−0.007 (3)
C7	0.066 (4)	0.056 (4)	0.093 (5)	0.027 (3)	0.010 (4)	0.015 (4)
C8	0.055 (3)	0.063 (4)	0.064 (3)	0.017 (3)	0.007 (3)	0.019 (3)
C9	0.093 (5)	0.074 (5)	0.123 (6)	0.026 (4)	0.032 (5)	−0.027 (4)
C10	0.099 (5)	0.106 (6)	0.080 (4)	0.035 (4)	−0.020 (4)	0.025 (4)
C11	0.153 (11)	0.141 (10)	0.167 (11)	0.034 (8)	−0.018 (8)	−0.025 (9)

Geometric parameters (Å, °)

Ni1—N2^i	2.078 (4)	C3—H3	0.9300
Ni1—N2	2.078 (4)	C4—C5	1.432 (7)
Ni1—N1^i	2.197 (4)	C4—H4	0.9300
Ni1—N1	2.197 (4)	C5—C6	1.394 (8)

Ni1—Cl1^i	2.3918 (18)	C6—C7	1.368 (9)
Ni1—Cl1	2.3918 (18)	C6—C9	1.529 (8)
N1—C8	1.323 (6)	C7—C8	1.393 (8)
N1—C1	1.356 (6)	C7—H7	0.9300
N2—C2	1.340 (5)	C8—C10	1.524 (8)
N2—C1	1.348 (6)	C9—H9A	0.9600
N3—C2	1.322 (6)	C9—H9B	0.9600
N3—H3A	0.8600	C9—H9C	0.9600
N3—H3B	0.8600	C10—H10A	0.9600
O1—C11	1.295 (15)	C10—H10B	0.9600
O1—H1	0.8200	C10—H10C	0.9600
C1—C5	1.405 (6)	C11—H11A	0.9600
C2—C3	1.422 (6)	C11—H11B	0.9600
C3—C4	1.338 (7)	C11—H11C	0.9600
N2^i—Ni1—N2	157.6 (2)	C3—C4—C5	120.8 (5)
N2^i—Ni1—N1^i	62.57 (14)	C3—C4—H4	119.6
N2—Ni1—N1^i	100.08 (14)	C5—C4—H4	119.6
N2^i—Ni1—N1	100.08 (14)	C6—C5—C1	116.6 (5)
N2—Ni1—N1	62.57 (14)	C6—C5—C4	128.9 (5)
N1^i—Ni1—N1	85.1 (2)	C1—C5—C4	114.4 (5)
N2^i—Ni1—Cl1^i	97.75 (10)	C7—C6—C5	118.1 (5)
N2—Ni1—Cl1^i	97.07 (11)	C7—C6—C9	121.0 (6)
N1^i—Ni1—Cl1^i	159.27 (10)	C5—C6—C9	120.9 (6)
N1—Ni1—Cl1^i	92.59 (12)	C6—C7—C8	122.1 (5)
N2^i—Ni1—Cl1	97.07 (11)	C6—C7—H7	119.0
N2—Ni1—Cl1	97.75 (10)	C8—C7—H7	119.0
N1^i—Ni1—Cl1	92.59 (12)	N1—C8—C7	121.0 (5)
N1—Ni1—Cl1	159.27 (10)	N1—C8—C10	116.5 (5)
Cl1^i—Ni1—Cl1	96.55 (9)	C7—C8—C10	122.4 (5)
C8—N1—C1	117.5 (4)	C6—C9—H9A	109.5
C8—N1—Ni1	151.8 (4)	C6—C9—H9B	109.5
C1—N1—Ni1	90.7 (3)	H9A—C9—H9B	109.5
C2—N2—C1	119.3 (4)	C6—C9—H9C	109.5
C2—N2—Ni1	144.6 (3)	H9A—C9—H9C	109.5
C1—N2—Ni1	96.2 (3)	H9B—C9—H9C	109.5
C2—N3—H3A	120.0	C8—C10—H10A	109.5
C2—N3—H3B	120.0	C8—C10—H10B	109.5
H3A—N3—H3B	120.0	H10A—C10—H10B	109.5
C11—O1—H1	109.5	C8—C10—H10C	109.5
N2—C1—N1	110.6 (4)	H10A—C10—H10C	109.5
N2—C1—C5	124.8 (4)	H10B—C10—H10C	109.5
N1—C1—C5	124.6 (4)	O1—C11—H11A	109.5
N3—C2—N2	119.1 (4)	O1—C11—H11B	109.5
N3—C2—C3	121.4 (4)	H11A—C11—H11B	109.5
N2—C2—C3	119.6 (4)	O1—C11—H11C	109.5
C4—C3—C2	121.1 (5)	H11A—C11—H11C	109.5

C4—C3—H3	119.4	H11B—C11—H11C		109.5
C2—C3—H3	119.4			

Symmetry codes: (i) −*x*+2, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯Cl1[ii]	0.82	2.49	3.250 (12)	155
N3—H3B⋯Cl1[iii]	0.86	2.49	3.308 (4)	159
N3—H3A⋯Cl1	0.86	2.57	3.368 (4)	154

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

Fig. 1

Fig. 2