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ISSN 2414-3146

Di-μ-chlorido-bis[(2,2′-bipyridine-κ^2N,N')chlorido-(*N*,*N*-dimethylformamide-κO)nickel(II)]

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Received 5 February 2016
Accepted 13 February 2016

Edited by A. J. Lough, University of Toronto, Canada

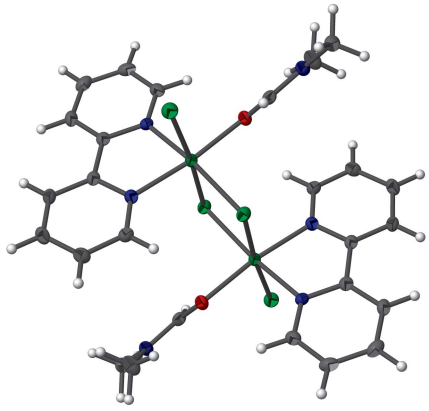
Keywords: crystal structure; bipyridine; nickel(II) complex.

CCDC reference: 1453181

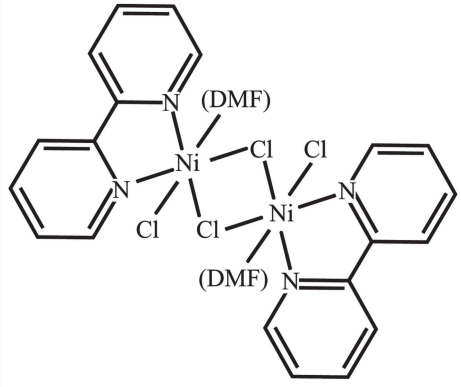
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[Ni_2Cl_2(\mu\text{-}Cl)_2(C_{10}H_8N_2)_2(C_3H_7NO)_2]$, exists as a centrosymmetric dimer of two octahedral nickel centers. In the crystal, two chloride ions bridge the two nickel centers with one terminal chloride ion bound to each nickel atom. Coupled with a chelating bipyridine ligand and an O-bound *N*,*N*-dimethylformamide solvent molecule, each nickel center exhibits an slightly distorted octahedral coordination environment. The meridional chloride ions all sit in equatorial positions, with the bipyridine ligand occupying one equatorial and one axial position, and the *N*,*N*-dimethylformamide ligand occupying the final axial position. The 2,2′-bipyridine ligand binds to nickel in a near planar fashion, with the non-H atoms possessing a mean devation from planarity of 0.046 Å. No π–π interactions are observed in the crystal.

3D view



Chemical scheme



Structure description

The structure of the title compound possesses neutral (bipy)$NiCl_2$(DMF) units which dimerize and are related by a crystallographic inversion center (Fig. 1). Each octahedral Ni^{II} ion is surrounded by two nitrogen atoms from the bipyridine ligand, three chlorine atoms (one terminal and two bridging) and a coordinated *N*,*N*-dimethylformamide molecule. All three chlorine atoms sit on equatorial positions, while the axial positions are occupied by the DMF oxygen atom and a pyridyl nitrogen atom. This is in contrast to the closely related aquo complex, where the bipyridine occupies two equatorial positions and the terminal chlorine sits in an axial site (Ikotun *et al.*, 2007). The arrangement with a terminal equatorial chloride is observed in tridentate bipyridine derivatives (Chen *et al.*, 2009; Hirotsu *et al.*, 2010). The Ni—Cl bond *trans* to the pyridine ring is significantly shorter [2.3971 (7) Å] than the Ni—Cl bond *trans* to the terminal Cl atom [2.5049 (7) Å], consistent with the *trans* influence. Packing of the crystal structure can be seen in Fig. 2. No π–π interactions wer noted in the structure.

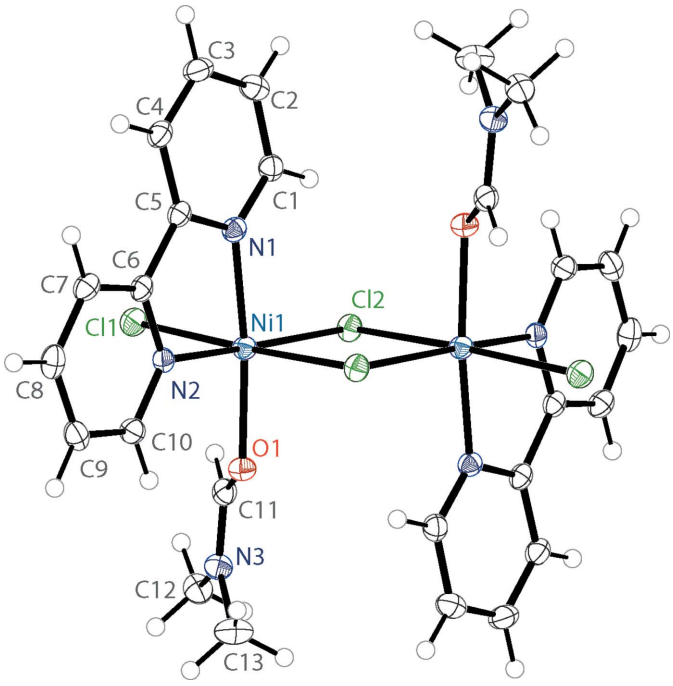


Figure 1
The molecular structure of the title compound. The unlabeled atoms are generated by an inversion center. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres or arbitrary radius.

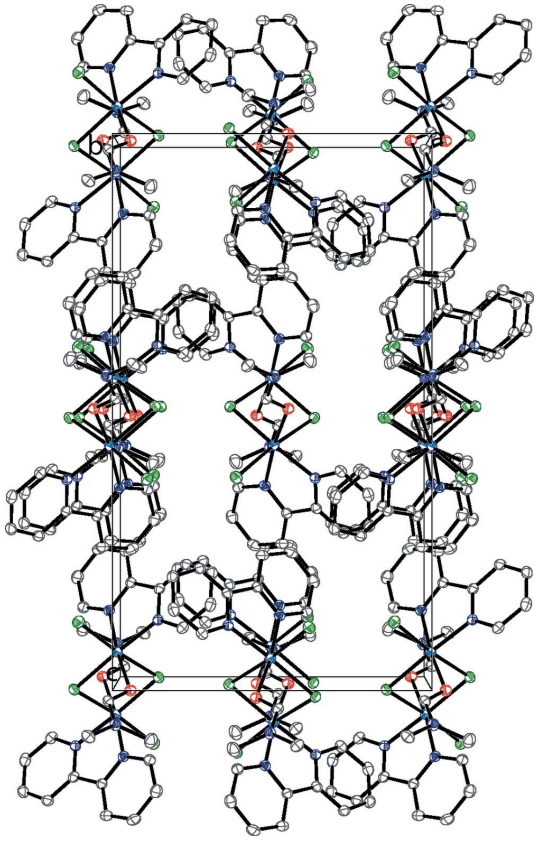


Figure 2
View of the molecular packing of the title compound along the *b* axis.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Ni_2Cl_4(C_{10}H_8N_2)_2(C_3H_7NO)_2]$
M_r	717.78
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	120
a, *b*, *c* (Å)	11.9130 (9), 11.445 (1), 20.7458 (17)
V (Å^3)	2828.6 (4)
Z	4
Radiation type	Cu *Kα*
μ (mm^{-1})	5.44
Crystal size (mm)	0.15 × 0.05 × 0.02
Data collection	
Diffractometer	Bruker D8 Venture CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.240, 0.384
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12752, 2670, 2139
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.032, 0.073, 1.04
No. of reflections	2670
No. of parameters	183
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.30

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010).

Synthesis and crystallization

A mixture of $NiCl_2{\cdot}6H_2O$, 2,2′-bipyridine and *N*,*N*-dimethylformamide was heated in a sealed thick-walled glass tube at 373 K for 48 h. Pale-green needle-shaped crystals suitable for a single-crystal diffraction study were isolated from the tube. The synthesis of closely related complexes is described by Cocker & Bachman (2004).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

We greatly acknowledge support from the National Science Foundation (CHE-1429086).

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full crystallographic data

IUCrData (2016). **1**, x160259 [https://doi.org/10.1107/S2414314616002595]

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Crystal data

$[Ni_2Cl_4(C_{10}H_8N_2)_2(C_3H_7NO)_2]$
M_r = 717.78
Orthorhombic, *Pbca*
Hall symbol: -P 2ab 2ac
a = 11.9130 (9) Å
b = 11.445 (1) Å
c = 20.7458 (17) Å
V = 2828.6 (4) Å^3
Z = 4
F(000) = 1472
D_x = 1.686 Mg m^{-3}
Cu *K*α radiation, λ = 1.54178 Å
Cell parameters from 5383 reflections
θ = 4.3–70.2°
μ = 5.44 mm^{-1}
T = 120 K
Plate, green
0.15 × 0.05 × 0.02 mm

Data collection

Bruker D8 Venture CMOS diffractometer
Radiation source: Cu
HELIOS MX monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.240, T_{max} = 0.384
12752 measured reflections
2670 independent reflections
2139 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 70.2°, θ_{min} = 4.3°
h = −14→13
k = −13→11
l = −19→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.073
S = 1.04
2670 reflections
183 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 1.4865P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 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}
Ni1	0.49476 (3)	0.38808 (4)	0.43948 (2)	0.01585 (12)
Cl2	0.63495 (4)	0.46540 (5)	0.51055 (3)	0.01834 (14)
Cl1	0.61409 (5)	0.25008 (6)	0.38155 (3)	0.02148 (15)
O1	0.45006 (13)	0.26410 (15)	0.50647 (8)	0.0190 (4)
N2	0.36328 (15)	0.34487 (17)	0.37970 (9)	0.0156 (4)
N1	0.52288 (15)	0.50115 (17)	0.36496 (9)	0.0168 (4)
N3	0.49296 (15)	0.10292 (18)	0.56455 (10)	0.0196 (4)
C5	0.45302 (18)	0.4894 (2)	0.31397 (11)	0.0167 (5)
C6	0.35961 (18)	0.4053 (2)	0.32359 (11)	0.0171 (5)
C10	0.28304 (18)	0.2671 (2)	0.39238 (12)	0.0198 (5)
H10	0.2855	0.2259	0.4321	0.024*
C11	0.51802 (19)	0.1879 (2)	0.52417 (11)	0.0191 (5)
H11	0.5923	0.1911	0.5076	0.023*
C1	0.60826 (19)	0.5763 (2)	0.36081 (11)	0.0196 (5)
H1	0.6561	0.5859	0.3971	0.023*
C4	0.4687 (2)	0.5525 (2)	0.25765 (11)	0.0202 (5)
H4	0.4184	0.5435	0.2225	0.024*
C2	0.6298 (2)	0.6409 (2)	0.30573 (12)	0.0231 (6)
H2	0.6922	0.6924	0.3039	0.028*
C8	0.19164 (19)	0.3053 (2)	0.29244 (12)	0.0233 (6)
H8	0.1328	0.2913	0.2625	0.028*
C9	0.19615 (19)	0.2441 (2)	0.34992 (12)	0.0225 (6)
H9	0.1407	0.1873	0.3600	0.027*
C12	0.5762 (2)	0.0156 (2)	0.58366 (12)	0.0242 (6)
H12A	0.6429	0.0231	0.5564	0.036*
H12B	0.5442	−0.0628	0.5786	0.036*
H12C	0.5971	0.0279	0.6288	0.036*
C7	0.27354 (18)	0.3871 (2)	0.27914 (11)	0.0197 (5)
H7	0.2713	0.4305	0.2401	0.024*
C3	0.5587 (2)	0.6290 (2)	0.25328 (12)	0.0237 (6)
H3	0.5714	0.6726	0.2150	0.028*
C13	0.3814 (2)	0.0931 (3)	0.59311 (13)	0.0298 (6)
H13A	0.3298	0.1462	0.5709	0.045*
H13B	0.3852	0.1139	0.6389	0.045*
H13C	0.3545	0.0126	0.5887	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0160 (2)	0.0169 (2)	0.0146 (2)	−0.00102 (17)	−0.00107 (15)	0.00083 (17)
Cl2	0.0161 (3)	0.0210 (3)	0.0179 (3)	0.0006 (2)	−0.0021 (2)	−0.0016 (2)
Cl1	0.0209 (3)	0.0220 (3)	0.0215 (3)	0.0016 (2)	0.0026 (2)	−0.0017 (2)
O1	0.0196 (8)	0.0193 (10)	0.0180 (8)	−0.0006 (7)	0.0003 (6)	0.0032 (7)
N2	0.0158 (9)	0.0149 (11)	0.0160 (10)	0.0000 (8)	0.0001 (8)	−0.0025 (8)
N1	0.0173 (9)	0.0171 (12)	0.0160 (9)	0.0018 (8)	0.0012 (8)	0.0001 (8)

N3	0.0186 (9)	0.0192 (12)	0.0209 (10)	0.0006 (9)	−0.0008 (8)	0.0023 (9)
C5	0.0166 (11)	0.0180 (14)	0.0156 (11)	0.0036 (10)	0.0008 (9)	−0.0015 (10)
C6	0.0173 (11)	0.0171 (14)	0.0169 (11)	0.0036 (10)	0.0024 (9)	−0.0026 (10)
C10	0.0204 (11)	0.0181 (14)	0.0208 (12)	0.0003 (10)	0.0037 (9)	−0.0005 (10)
C11	0.0178 (11)	0.0222 (14)	0.0174 (11)	−0.0032 (11)	−0.0019 (9)	−0.0023 (11)
C1	0.0195 (11)	0.0200 (14)	0.0192 (12)	−0.0008 (10)	−0.0003 (10)	−0.0023 (10)
C4	0.0245 (12)	0.0212 (15)	0.0148 (11)	0.0023 (11)	−0.0003 (9)	−0.0003 (10)
C2	0.0215 (12)	0.0215 (15)	0.0263 (13)	−0.0029 (11)	0.0025 (10)	0.0025 (11)
C8	0.0177 (11)	0.0291 (17)	0.0230 (13)	0.0020 (11)	−0.0019 (10)	−0.0091 (12)
C9	0.0182 (11)	0.0200 (15)	0.0294 (13)	−0.0023 (10)	0.0029 (10)	−0.0067 (12)
C12	0.0264 (13)	0.0218 (15)	0.0242 (13)	0.0013 (11)	−0.0058 (10)	0.0020 (11)
C7	0.0206 (11)	0.0225 (15)	0.0161 (11)	0.0043 (11)	−0.0003 (9)	0.0005 (10)
C3	0.0284 (13)	0.0240 (16)	0.0187 (12)	0.0011 (11)	0.0054 (10)	0.0048 (11)
C13	0.0247 (13)	0.0319 (17)	0.0329 (15)	−0.0003 (12)	0.0052 (11)	0.0109 (13)

Geometric parameters (Å, º)

Ni1—Cl2	2.3971 (7)	C11—H11	0.9500
Ni1—Cl2^{i}	2.5049 (7)	C1—H1	0.9500
Ni1—Cl1	2.4413 (7)	C1—C2	1.385 (3)
Ni1—O1	2.0563 (17)	C4—H4	0.9500
Ni1—N2	2.0582 (19)	C4—C3	1.387 (4)
Ni1—N1	2.044 (2)	C2—H2	0.9500
Cl2—Ni1^{i}	2.5049 (7)	C2—C3	1.385 (3)
O1—C11	1.246 (3)	C8—H8	0.9500
N2—C6	1.355 (3)	C8—C9	1.384 (4)
N2—C10	1.332 (3)	C8—C7	1.380 (3)
N1—C5	1.353 (3)	C9—H9	0.9500
N1—C1	1.335 (3)	C12—H12A	0.9800
N3—C11	1.318 (3)	C12—H12B	0.9800
N3—C12	1.463 (3)	C12—H12C	0.9800
N3—C13	1.459 (3)	C7—H7	0.9500
C5—C6	1.484 (3)	C3—H3	0.9500
C5—C4	1.387 (3)	C13—H13A	0.9800
C6—C7	1.395 (3)	C13—H13B	0.9800
C10—H10	0.9500	C13—H13C	0.9800
C10—C9	1.385 (3)		
Cl2—Ni1—Cl2^{i}	85.88 (2)	O1—C11—H11	118.1
Cl2—Ni1—Cl1	97.81 (2)	N3—C11—H11	118.1
Cl1—Ni1—Cl2^{i}	174.92 (2)	N1—C1—H1	118.7
O1—Ni1—Cl2^{i}	91.29 (5)	N1—C1—C2	122.6 (2)
O1—Ni1—Cl2	91.12 (5)	C2—C1—H1	118.7
O1—Ni1—Cl1	92.13 (5)	C5—C4—H4	120.4
O1—Ni1—N2	92.55 (7)	C5—C4—C3	119.2 (2)
N2—Ni1—Cl2^{i}	86.61 (6)	C3—C4—H4	120.4
N2—Ni1—Cl2	171.71 (6)	C1—C2—H2	120.6
N2—Ni1—Cl1	89.49 (6)	C1—C2—C3	118.8 (2)

N1—Ni1—Cl2	96.73 (6)	C3—C2—H2	120.6
N1—Ni1—Cl2^{i}	89.44 (6)	C9—C8—H8	120.4
N1—Ni1—Cl1	86.66 (6)	C7—C8—H8	120.4
N1—Ni1—O1	172.15 (7)	C7—C8—C9	119.2 (2)
N1—Ni1—N2	79.69 (8)	C10—C9—H9	120.6
Ni1—Cl2—Ni1^{i}	94.12 (2)	C8—C9—C10	118.7 (2)
C11—O1—Ni1	120.95 (15)	C8—C9—H9	120.6
C6—N2—Ni1	114.81 (15)	N3—C12—H12A	109.5
C10—N2—Ni1	125.98 (16)	N3—C12—H12B	109.5
C10—N2—C6	119.2 (2)	N3—C12—H12C	109.5
C5—N1—Ni1	115.31 (16)	H12A—C12—H12B	109.5
C1—N1—Ni1	125.58 (16)	H12A—C12—H12C	109.5
C1—N1—C5	118.8 (2)	H12B—C12—H12C	109.5
C11—N3—C12	121.5 (2)	C6—C7—H7	120.4
C11—N3—C13	121.4 (2)	C8—C7—C6	119.3 (2)
C13—N3—C12	117.0 (2)	C8—C7—H7	120.4
N1—C5—C6	114.9 (2)	C4—C3—H3	120.6
N1—C5—C4	121.6 (2)	C2—C3—C4	118.9 (2)
C4—C5—C6	123.5 (2)	C2—C3—H3	120.6
N2—C6—C5	115.0 (2)	N3—C13—H13A	109.5
N2—C6—C7	121.0 (2)	N3—C13—H13B	109.5
C7—C6—C5	124.0 (2)	N3—C13—H13C	109.5
N2—C10—H10	118.7	H13A—C13—H13B	109.5
N2—C10—C9	122.5 (2)	H13A—C13—H13C	109.5
C9—C10—H10	118.7	H13B—C13—H13C	109.5
O1—C11—N3	123.8 (2)		

Ni1—O1—C11—N3	−176.70 (18)	C5—C4—C3—C2	−0.6 (4)
Ni1—N2—C6—C5	1.9 (3)	C6—N2—C10—C9	0.9 (4)
Ni1—N2—C6—C7	−178.44 (18)	C6—C5—C4—C3	−180.0 (2)
Ni1—N2—C10—C9	179.02 (18)	C10—N2—C6—C5	−179.8 (2)
Ni1—N1—C5—C6	6.5 (3)	C10—N2—C6—C7	−0.1 (3)
Ni1—N1—C5—C4	−173.88 (18)	C1—N1—C5—C6	−179.0 (2)
Ni1—N1—C1—C2	172.30 (19)	C1—N1—C5—C4	0.6 (3)
N2—C6—C7—C8	−0.6 (4)	C1—C2—C3—C4	−0.3 (4)
N2—C10—C9—C8	−0.9 (4)	C4—C5—C6—N2	174.8 (2)
N1—C5—C6—N2	−5.6 (3)	C4—C5—C6—C7	−4.8 (4)
N1—C5—C6—C7	174.8 (2)	C9—C8—C7—C6	0.6 (4)
N1—C5—C4—C3	0.5 (4)	C12—N3—C11—O1	180.0 (2)
N1—C1—C2—C3	1.4 (4)	C7—C8—C9—C10	0.1 (4)
C5—N1—C1—C2	−1.5 (4)	C13—N3—C11—O1	−1.2 (4)
C5—C6—C7—C8	179.0 (2)		

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