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Dichlorotetrapyridinenickel(II) 0.76-hydrate

Hui Zhang[a,b]* and Liang Fang[a,b]

[a]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China, and [b]Institut für Anorganische Chemie, RWTH Aachen, Professor-Pirlet-Straße 1, 52056 Aachen, Germany

Correspondence e-mail:
hui.zhang@ac.rwth-aachen.de

Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.002 Å
Disorder in solvent or counterion
R factor = 0.022
wR factor = 0.049
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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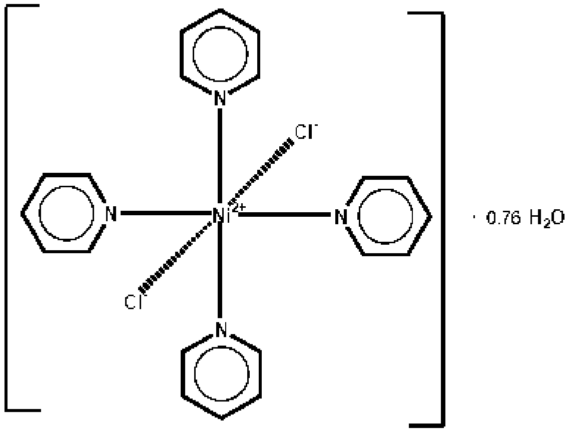
In the title compound, $[NiCl_2(C_5H_5N)_4]\cdot0.76H_2O$, the nickel(II) ion is coordinated in a *trans* fashion by two Cl^- ions and four pyridine molecules. The molecule possesses crystallographic 222 symmetry. The Ni atom has a distorted octahedral geometry, with long Ni—Cl bonds. In the crystal structure, O—H···Cl hydrogen bonding forms a three-dimensional network.

Comment

Many papers have dealt with the electronic and magnetic properties of tetrakis(pyridine)metal(II) chloride complexes, including, for example, the structure of $[Ni(py)_4Cl_2]$ (Long & Clarke, 1978).



(I)

In this paper, we report the crystal structure of the title dichlorotetrakis(pyridine) nickel hydrate complex, (I). A labelled displacement ellipsoid plot of the molecule of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1.

In complex (I), the Ni atom is coordinated by four N atoms of the pyridine ligands and two Cl^- ions. The four pyridine ligands are each bonded to Ni as monodentate ligands through their N atoms. The Ni1—N1 and Ni1—Cl distances are 2.1068 (13) and 2.4219 (10) Å, respectively. The N1—Ni1—N1$(-y+\frac{3}{4}, -x+\frac{3}{4}, -z+\frac{7}{4})$ angle is almost linear, at 179.10 (7)°, and the Cl1—Ni1—Cl1$(-x+1, -y+\frac{1}{2}, z-1)$ angle is linear, at exactly 180°. In comparable compounds, Ni—N distances are in the range 2.0701 (13)–2.1851 (14) Å for the six-coordinate Ni atom of $[Ni(N_3)_2(C_6H_{10}N_4)_2]$ (van Albada *et al.*, 2004) and in the range 2.095 (2)–2.131 (2) Å for the six-coordinate Ni atom of $[Ni(N_3)_2(C_3H_4N_2)_4]$ (Zhang *et al.*, 2002). The Ni—Cl distances are in the range 2.220 (4)–

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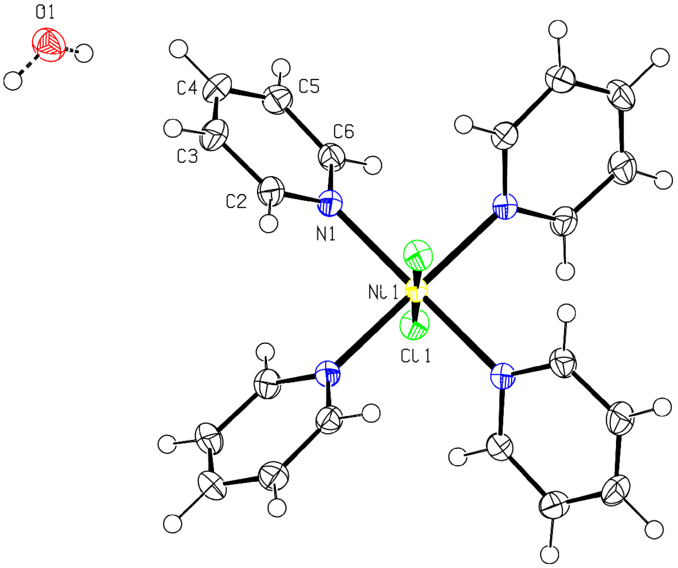

Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

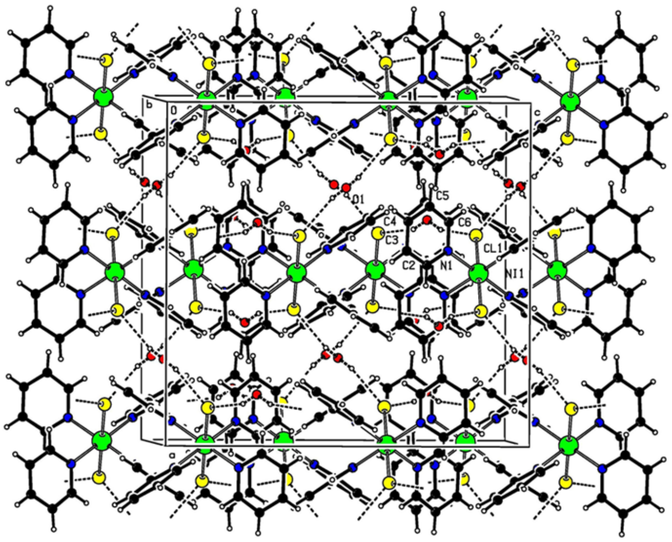

Figure 2
A packing diagram for (I), viewed along the *a* axis. Hydrogen bonds are indicated by thin lines.

2.234 (4) Å for the four-coordinate Ni atom in $(NMe_4)[NiCl_4]$ (Wiesner *et al.*, 1967). The molecule possesses crystallographic 222 symmetry.

The solvent water molecule has partial occupancy; the occupancy factor was allowed to vary in the refinement process and indicated only 76% occupancy. This is the same as that in $[Fe(py)_4Cl_2]\cdot H_2O$ (Long & Clarke, 1978).

Weak intermolecular O—H···Cl hydrogen-bond interactions (Table 2) stabilize the crystal structure of (I). The packing of (I), with the hydrogen bonds, is illustrated in Fig. 2.

The three $[M(py)_4Cl_2]$ structures (M = Fe, Ni and Co) in the work by Long & Clarke (1978) are isostructural with (I). It is possible that their Ni structure may even be identical to (I). Upon investigation of the packing of the so-called anhydrous compound, it was found that there are solvent cavities, in which the water molecules are located in (I). In the earlier data set, water molecules that may have been present were not located.

There is a contraction of the unit cell and of the Ni—N and Ni—Cl bond distances of (I) compared with the earlier structure. This is most likely due to the title structure being derived from low-temperature data [110 (2) K] and, in addition, the fact that the earlier (anhydrous) $[Ni(py)_4Cl_2]$ structure contains 97% Ni and 3% Fe. The Ni—N and Ni—Cl distances in the two compounds are not significantly different.

Experimental

A solution of $NiCl_2\cdot 6H_2O$ (1 g) in ethanol and water (1:1, 20 ml) was added to a solution of *ca* 50% by volume of pyridine dissolved in ethanol. Dilute HCl was added dropwise to this mixture to avoid precipitation. The mixture was then stirred for 1 h and concentrated under vacuum to a volume of 10 ml. Slow evaporation of the solvent allowed the formation of blue prism-shaped crystals of (I) after a few days.

Crystal data

$[NiCl_2(C_5H_5N)_4]\cdot 0.76H_2O$
$M_r = 459.68$
Tetragonal, $I4_1/acd$
$a = 15.815\ (6)$ Å
$c = 16.773\ (9)$ Å
$V = 4195\ (3)$ Å^3
$Z = 8$
$D_x = 1.456$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 814 reflections
$\theta = 2.6$–$28.4°$
$\mu = 1.20$ mm^{-1}
$T = 110\ (2)$ K
Prism, blue
0.21 × 0.15 × 0.13 mm

Data collection

Bruker APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.801$, $T_{max} = 0.857$
26 814 measured reflections
1324 independent reflections
860 reflections with $I > 2\sigma(I)$
$R_{int} = 0.087$
$\theta_{max} = 28.4°$
$h = -21 \rightarrow 21$
$k = -21 \rightarrow 21$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.049$
$S = 0.83$
1324 reflections
72 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.1067 (13)	Ni1—Cl1	2.4219 (10)
N1—Ni1—N1^i	179.10 (7)	N1—Ni1—Cl1	90.45 (3)
N1—Ni1—N1^{ii}	89.98 (7)	N1^{ii}—Ni1—Cl1	89.55 (3)
N1—Ni1—N1	90.02 (7)	Cl1—Ni1—Cl1	180

Symmetry codes: (i) $-y+\frac{3}{4}, -x+\frac{3}{4}, -z+\frac{7}{4}$; (ii) $y+\frac{1}{4}, x-\frac{1}{4}, -z+\frac{7}{4}$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Cl1	0.89 (5)	2.32 (5)	3.1388 (14)	153 (4)

Pyridine H atoms were constrained to an ideal geometry, with C—H distances of 0.95 Å, and refined with fixed isotropic displacement parameters of $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Water H atoms were refined from positions located in a difference Fourier map, with final O1—H1 distances of 0.89 (5) Å and with an isotropic displacement parameter of 0.076 (19) Å^2.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003) and *ATOMS* (Dowty, 2002); software used to prepare material for publication: *SHELXTL*.

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