

Aquachloro(1,4,8,11-tetraazaundecane)-
nickel(II) chlorideAlexandr E. Oblezov,* Daniel R.
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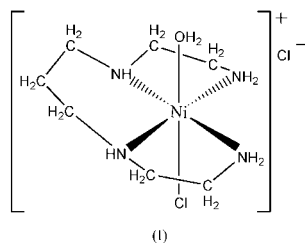
Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.034
 wR factor = 0.090
Data-to-parameter ratio = 21.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $[\text{NiCl}(\text{C}_7\text{H}_{20}\text{N}_4)(\text{H}_2\text{O})]\text{Cl}$, has the Ni atom in a distorted octahedral coordination with the four amino N atoms occupying a square plane while the chloro and aqua ligands occupy the axial positions. The Ni–N bond distances range from 2.079 (1) to 2.088 (2) Å.

Comment

Complexes of transition metals with long alkyl chains are widely used to build Langmuir–Blodgett monolayers with specific magnetic properties (Culp *et al.*, 2002, 2003). An attempt to synthesize a nickel(II) pentaazamacrocyclic complex with an attached 1-dodecyl chain, as described in Choi & Suh (2003), was not successful. The result of this reaction was the title complex, (I). Lavender-colored prismatic crystals were collected and characterized by single-crystal X-ray diffraction.



The tetradentate 1,4,8,11-tetraazaundecane ligand is coordinated to the Ni center in a wrap-around fashion, occupying the four square-planar positions. The Ni–N bond distances [average 2.080 (2) Å] are significantly longer than their counterparts in the (1,4,8,11-tetraazaundecane)nickel(II) cation [average 1.923 (5) Å] (Bernard *et al.*, 2001). In the latter, the Ni center is in a square-planar coordination with vacant axial positions.

The H atoms of the coordinated water and the uncoordinated counter-ion Cl^- are involved in hydrogen bonding with their inversion-symmetry equivalents, creating a diamond-shaped motif. As a result, hydrogen-bonding chains are formed along the b axis. These chains are linked together by hydrogen bonds between the amino groups on the one hand and both (coordinated and uncoordinated) Cl^- ions, thus creating two-dimensional layers in the ab plane.

Experimental

To a refluxing solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.2 g, 5 mmol) in MeOH (50 ml) was added 1,4,8,11-tetraazaundecane (0.8 g, 5 mmol). After 3 h of reflux, the solvent was evaporated and a light-purple product of the reaction was dissolved in EtOH (20 ml). Slow evaporation of the solvent over 5 d, at room temperature, yielded light-purple prismatic crystals.

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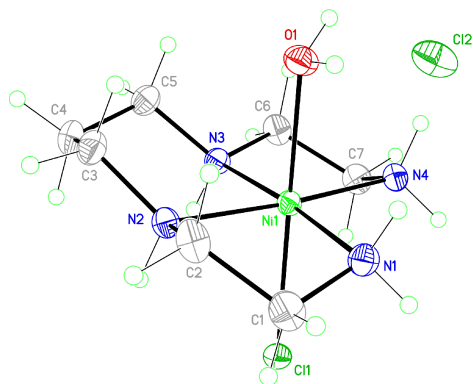


Figure 1
View of the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

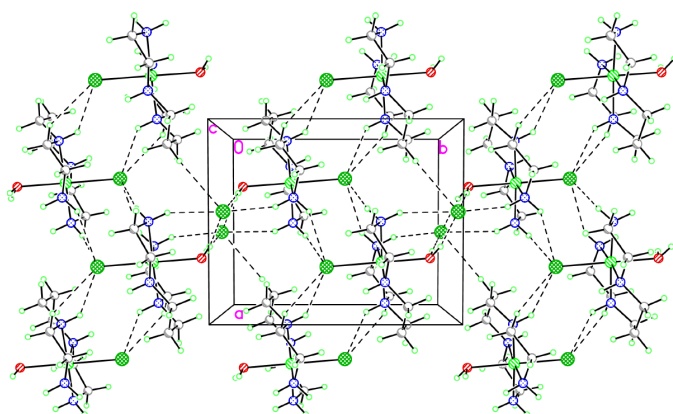


Figure 2
View of the two-dimensional layer in the crystal structure of the title compound.

Crystal data

[NiCl(C₇H₂₀N₄)(H₂O)]Cl
M_r = 307.90
 Monoclinic, *P*₂₁/*n*
a = 8.3029 (6) Å
b = 10.2497 (7) Å
c = 15.6829 (11) Å
 β = 94.470 (2)°
V = 1330.59 (16) Å³
Z = 4

D_x = 1.537 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 112 reflections
 θ = 2.0–28.0°
 μ = 1.84 mm⁻¹
T = 173 (2) K
 Plate, purple
 0.26 × 0.24 × 0.23 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: by integration based on measured indexed crystal faces (*SHELXTL*; Bruker, 2000)
T_{min} = 0.536, *T_{max}* = 0.753

7715 measured reflections
 2944 independent reflections
 2798 reflections with *I* > 2 σ (*I*)
R_{int} = 0.089
 θ_{\max} = 27.5°
h = -5 → 10
k = -12 → 13
l = -20 → 19

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.034
wR(*F*²) = 0.090
S = 1.02
 2944 reflections
 136 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.4679P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.53 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.94 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—N1	2.0788 (14)	Ni1—N4	2.0878 (16)
Ni1—N2	2.0805 (16)	Ni1—O1	2.1821 (13)
Ni1—N3	2.0825 (13)	Ni1—Cl1	2.4777 (5)
N1—Ni1—N2	84.41 (6)	N3—Ni1—O1	93.46 (5)
N1—Ni1—N3	175.50 (6)	N4—Ni1—O1	90.26 (5)
N2—Ni1—N3	92.08 (6)	N1—Ni1—Cl1	88.33 (4)
N1—Ni1—N4	99.99 (6)	N2—Ni1—Cl1	90.84 (4)
N2—Ni1—N4	175.18 (5)	N3—Ni1—Cl1	88.91 (4)
N3—Ni1—N4	83.62 (6)	N4—Ni1—Cl1	91.25 (4)
N1—Ni1—O1	89.23 (5)	O1—Ni1—Cl1	177.32 (3)
N2—Ni1—O1	87.82 (5)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...Cl2	0.96	2.28	3.2359 (13)	174
N1—H1 <i>D</i> ...Cl2	0.92	2.44	3.3123 (16)	159
O1—H2...Cl2 ⁱ	0.97	2.15	3.1066 (14)	167
N4—H4 <i>C</i> ...Cl2 ⁱ	0.92	2.64	3.4766 (14)	151
N1—H1 <i>C</i> ...Cl1 ⁱⁱ	0.92	2.68	3.4699 (17)	144
N4—H4 <i>D</i> ...Cl1 ⁱⁱ	0.92	2.57	3.4356 (15)	157
N4—H4 <i>C</i> ...Cl2 ⁱ	0.92	2.64	3.4766 (14)	151

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

The C—H and N—H H atoms were placed in idealized positions and refined riding on their parent atoms. A C—H distance of 0.99 Å was used for *Csp*³ atoms. N—H distances of 0.93 and 0.92 Å were used for N—H and N—H₂ amino groups, respectively. The H-atom displacement parameters were set at 1.2*U*_{eq} of the parent C or N atoms. The water molecule H atoms were obtained from a difference Fourier map, but did not refine satisfactorily. Thus, they were constrained in a riding model on the O atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART* and *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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