Bis(2-pyridiniomethyleneaminoguanidinium) *trans*-tetraaquadichloronickel(II) dichloride tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.044
wR factor = 0.142
Data-to-parameter ratio = 16.7

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

In the title compound, $(C_7H_{11}N_4)_2[Ni(H_2O)_4Cl_2]Cl_2\cdot4H_2O$, the Ni complex occupies a special position on the twofold axis; both cation and anions, as well as the water molecules, are in general positions. The multiple crystallographically independent hydrogen bonds form an infinite three-dimensional network in the crystal.

Comment

In an attempt to obtain the tetrachloronickelate(II) analogues of tetrachlorocuprate(II) aminoguanidinium compounds (Alstrum-Acevedo *et al.*, 2001), the title compound, (I), was obtained (Fig. 1).

(I)
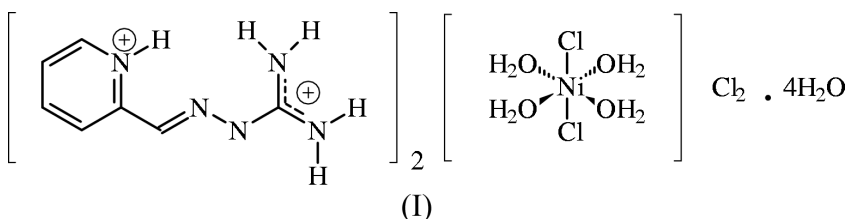
Both pyridyl and guanyl N atoms in (I) are protonated, thus giving rise to a dicationic species. Due to the protonation of the guanyl nitrogen, two NH_2 groups are attached to the C atom of the guanidine moiety. The C—N bond distances involving the two NH_2 groups, *viz.* C8—N4 and C8—N5, as well as the N4—C8—N5 angle (Table 1), indicate considerable π-character in the bonding. Delocalization and the intramolecular N1—H1···N2 and N5—H5A···N2 hydrogen bonds (Table 2) are responsible for the planarity of the molecule.

Experimental

1.0 mmol of aminoguanidine bicarbonate was neutralized by the dropwise addition of concentrated H_2SO_4 until the evolution of CO_2 ceased and then added to a solution of 1.0 mmol of 2-formylpyridine in ethanol, followed by 2–3 drops of H_2SO_4 to catalyze the reaction. The mixture was refluxed for 5 h and slowly evaporated at *ca* 308 K to give a yellow solid, m.p. 463–465 K. Compound (I) was prepared by dissolving 1 mmol of the aminoguanidine in approximately 50 ml of a 3:1 EtOH–HCl (12 *N*) mixture by volume, adding an equimolar amount of $NiCl_2\cdot6H_2O$, and subsequent heating of the reaction mixture under reflux for 1 h. The solution was then filtered and the filtrate left until crystals formed.
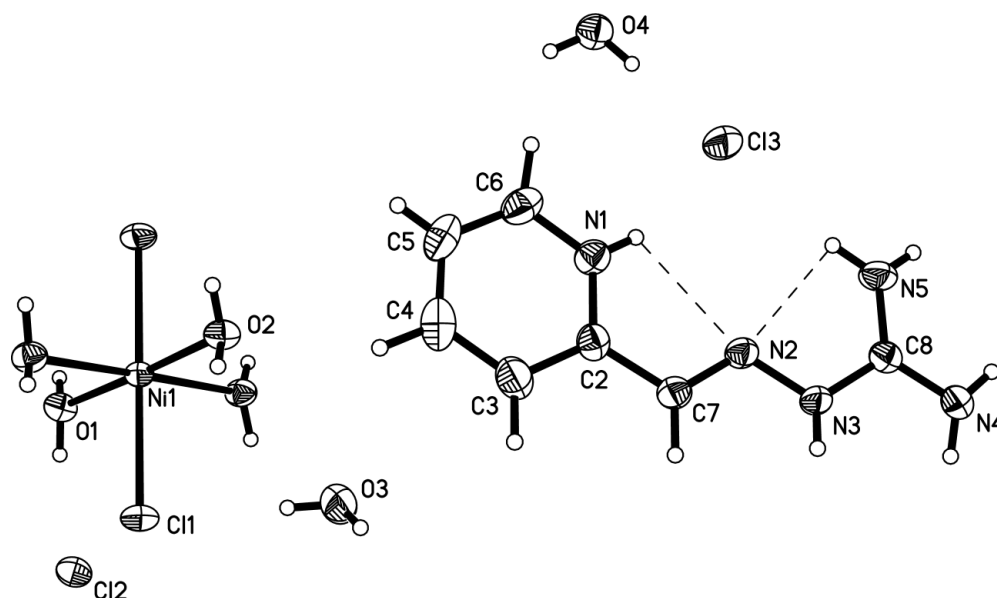
Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Crystal data

$(C_7H_{11}N_4)_2[Ni(H_2O)_4Cl_2]Cl_2 \cdot 4H_2O$
$M_r = 745.95$
Monoclinic, $C2/c$
$a = 24.698\ (4)$ Å
$b = 7.106\ (1)$ Å
$c = 18.538\ (2)$ Å
$\beta = 99.59\ (1)°$
$V = 3208.0\ (8)$ Å^3
$Z = 4$

$D_x = 1.544$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33
reflections
$\theta = 2.5–12.5°$
$\mu = 1.16$ mm^{-1}
$T = 293\ (2)$ K
Prism, yellow
$0.30 \times 0.16 \times 0.10$ mm

Data collection

Siemens $P4/PC$ diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
(North et al., 1968)
$T_{min} = 0.325$, $T_{max} = 0.367$
4547 measured reflections
3656 independent reflections
2222 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 32$
$k = -1 \rightarrow 9$
$l = -24 \rightarrow 23$
3 standard reflections
every 97 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.142$
$S = 1.02$
3656 reflections
219 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.075 (3)	C7—N2	1.286 (6)
Ni1—O2	2.092 (4)	C8—N3	1.368 (5)
Ni1—Cl1	2.3923 (9)	C8—N4	1.324 (6)
N1—C6	1.334 (6)	C8—N5	1.304 (6)
N1—C2	1.356 (6)	N2—N3	1.360 (5)
O1—Ni1—O2	178.04 (13)	N5—C8—N4	123.2 (4)
O1—Ni1—Cl1	88.83 (9)	N5—C8—N3	119.9 (4)
O2—Ni1—Cl1	92.79 (9)	N4—C8—N3	116.9 (4)
N1—C2—C7	119.2 (4)	C7—N2—N3	117.7 (4)
N2—C7—C2	118.1 (4)	N2—N3—C8	116.9 (3)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1$A\cdots$O4^i	0.84	1.99	2.775 (5)	156
O1—H1$B\cdots$Cl2	0.84	2.30	3.132 (4)	169
O2—H2$A\cdots$O4^{ii}	0.85	1.97	2.795 (6)	163
O2—H2$B\cdots$Cl2^{iii}	0.84	2.30	3.131 (4)	169
O3—H3$A\cdots$Cl1	0.82	2.35	3.163 (4)	172
O3—H3$B\cdots$Cl3^{ii}	0.85	2.42	3.180 (6)	147
O4—H4$A\cdots$Cl3	0.86	2.26	3.096 (4)	167
O4—H4$B\cdots$Cl2^{iv}	0.83	2.31	3.107 (4)	161
N1—H1$\cdots$N2	0.85	2.42	2.717 (5)	101
N1—H1$\cdots$Cl3	0.85	2.29	3.096 (4)	160
N3—H3$C\cdots$Cl1^v	0.82	2.48	3.231 (4)	153
N4—H4$C\cdots$O2^{vi}	0.84	2.43	3.207 (6)	155
N4—H4$C\cdots$O1^{vii}	0.84	2.49	3.119 (5)	132
N4—H4$D\cdots$Cl2^v	0.84	2.35	3.187 (4)	168
N5—H5$A\cdots$N2	0.86	2.37	2.634 (5)	98
N5—H5$A\cdots$Cl3	0.86	2.39	3.225 (4)	162
N5—H5$B\cdots$O3^{vi}	0.84	1.98	2.778 (6)	157

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, 1-y, \frac{1}{2}+z$; (iii) $-x, 1+y, \frac{3}{2}-z$; (iv) $x, -y, z-\frac{1}{2}$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

H-atom positions were located in difference Fourier maps and a riding model with fixed displacement parameters [$U_{ij} = 1.2U_{ij}$(eq) of the atom to which they are bonded] was used for subsequent refinements. H atoms attached to N and O atoms were refined with fixed bond lengths r(D—H) = 0.85 Å.

Data collection: *P4 Software* (Siemens, 1995); cell refinement: *P4 Software*; data reduction: *P4 Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

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