# metal-organic papers

# Hexaaquanickel(II) dichloride bis(hexa-methylenetetramine) tetrahydrate

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In the title compound, $[Ni(H_2O)_6]Cl_2 \cdot 2C_6H_{12}N_4 \cdot 4H_2O$, the $Ni^{II}$ atom lies on a center of inversion, and is coordinated by six O atoms from six water molecules, in a slightly distorted octahedral geometry. In the crystal structure, O, N and Cl atoms act as acceptors (*A*) to form intermolecular O—H⋯*A* hydrogen bonds, giving a three-dimensional network.

## Comment

The structure of the title complex, (I), is similar to that of hexaaquanickel(II) dinitrate bis(hexamethylenetetramine) tetrahydrate (Hu *et al.*, 2002). In (I), the formula unit consists of a hexaaquanickel(II) cation, two chloride anions two hexamethylenetetramine molecules and four uncoordinated water molecules (Fig. 1). The range of Ni—O bond lengths in (I) [2.0227 (18)–2.0554 (18) Å] is similar to the range [2.022 (2)–2.063 (2) Å] in the dinitrate analog (Hu *et al.*, 2002) and is normal for $[Ni(H_2O)_6]^{2+}$ complexes. The $Ni^{II}$ atom lies on a center of inversion and is coordinated by six O atoms from six water molecules. The *cis* angles around the $Ni^{II}$ atom deviate slightly from the ideal angle of 90° [86.61 (8)–93.39 (8)°]; thus the $Ni^{II}$ coordination center has slightly disorted octahedral geometry.



The crystal structure contains intermolecular O—H⋯O, O—H⋯N and O—H⋯Cl hydrogen bonds (Fig. 2 and Table 2) which connect cations, anions and solvent water molecules into a three-dimensional structure.

## Experimental

All reagents and solvents were used as obtained without further purification. $NiCl_2 \cdot 4H_2O$ (1 mmol, 202 mg) and hexamethylenetetramine (2 mmol, 280 mg) were dissolved in ammonia (20 ml). The mixture was stirred for *ca* 5 min to obtain a clear blue solution. After keeping the solution in air for two weeks with ammonia gas escaping, large blue crystals were formed. The product was isolated, washed three times with water, and dried in a vacuum desiccator using $CaCl_2$ (yield: 54%).

## Crystal data

$[Ni(H_2O)_6]Cl_2 \cdot 2C_6H_{12}N_4 \cdot 4H_2O$
$M_r = 590.14$
Triclinic, $P\bar{1}$
$a = 9.330\ (6)$ Å
$b = 9.411\ (6)$ Å
$c = 9.446\ (6)$ Å
$\alpha = 119.551\ (7)°$
$\beta = 94.192\ (8)°$
$\gamma = 100.990\ (8)°$
$V = 694.6\ (8)$ Å$^3$

$Z = 1$
$D_x = 1.411$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2777
    reflections
$\theta = 2.5–26.3°$
$\mu = 0.95$ mm$^{-1}$
$T = 293\ (2)$ K
Block, blue
$0.46 \times 0.32 \times 0.18$ mm

## Data collection

Bruker SMART CCD area-detector
    diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan
    (SADABS; Sheldrick, 1996)
    $T_{min} = 0.670$, $T_{max} = 0.848$
3644 measured reflections

2418 independent reflections
2216 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 11$
$k = -10 \rightarrow 11$
$l = -11 \rightarrow 10$

## Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.089$
$S = 1.05$
2418 reflections
204 parameters
H atoms treated by a mixture of
    independent and constrained
    refinement

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.0662P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å$^{-3}$
$\Delta\rho_{min} = -0.49$ e Å$^{-3}$
Extinction correction: SHELXTL
    (Sheldrick, 1997a)
Extinction coefficient: 0.059 (5)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ni1—O3 | 2.0227 (18) | Ni1—O2 | 2.0554 (18) |
| Ni1—O1 | 2.0460 (17) | | |
| O3—Ni1—O1 | 87.39 (9) | O1—Ni1—O2 | 86.66 (8) |
| O3—Ni1—O1$^i$ | 92.61 (9) | O3—Ni1—O2$^i$ | 89.24 (9) |
| O3—Ni1—O2 | 90.76 (9) | O1—Ni1—O2$^i$ | 93.34 (8) |

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

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1—H1⋯N1$^{ii}$ | 0.77 (3) | 2.06 (3) | 2.823 (3) | 172 (3) |
| O1—H2⋯O4 | 0.85 (3) | 1.90 (3) | 2.739 (3) | 166 (3) |
| O2—H3⋯N2 | 0.76 (4) | 2.08 (4) | 2.814 (3) | 164 (3) |
| O2—H4⋯Cl1 | 0.84 (4) | 2.39 (4) | 3.191 (2) | 158 (3) |
| O3—H5⋯N4$^{iii}$ | 0.85 (3) | 1.98 (3) | 2.799 (3) | 161 (3) |
| O3—H6⋯O5 | 0.71 (3) | 2.00 (3) | 2.714 (3) | 172 (3) |
| O4—H7⋯Cl1$^{iv}$ | 0.88 (5) | 2.37 (5) | 3.253 (3) | 176 (4) |
| O4—H8⋯Cl1$^v$ | 0.77 (5) | 2.44 (5) | 3.210 (3) | 173 (4) |
| O5—H9⋯N3$^{vi}$ | 0.79 (3) | 2.05 (3) | 2.838 (3) | 170 (3) |
| O5—H10⋯Cl1$^{vii}$ | 0.82 (4) | 2.35 (4) | 3.168 (3) | 174 (3) |

Symmetry codes: (ii) $1 - x, 2 - y, 1 - z$; (iii) $x, y, 1 + z$; (iv) $1 - x, 1 - y, -z$; (v) $x - 1, y, z$; (vi) $2 - x, 2 - y, 1 - z$; (viii) $x, 1 + y, 1 + z$.

H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.97 Å, and included in the refinement in riding-model approximation with $U_{iso} = 1.2U_{eq}$ of the carrier atom. H atoms bonded to O atoms were refined independently with isotropic displacement parameters.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); program(s) used to
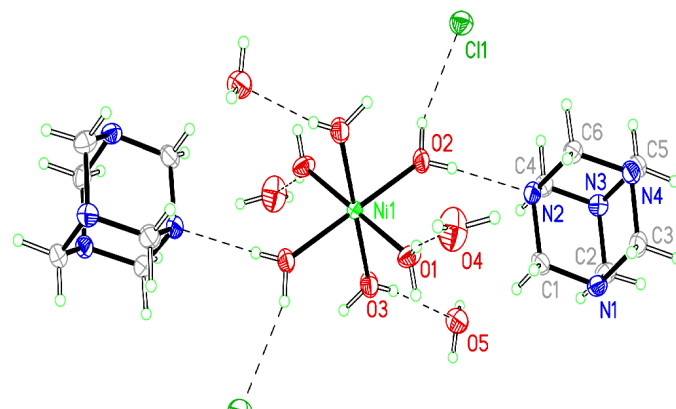


**Figure 1**
View of the centrosymmetric formula unit of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Unlabeled atoms are related to the corresponding labeled atoms by the symmetry code $1 - x, 1 - y, 1 - z$.
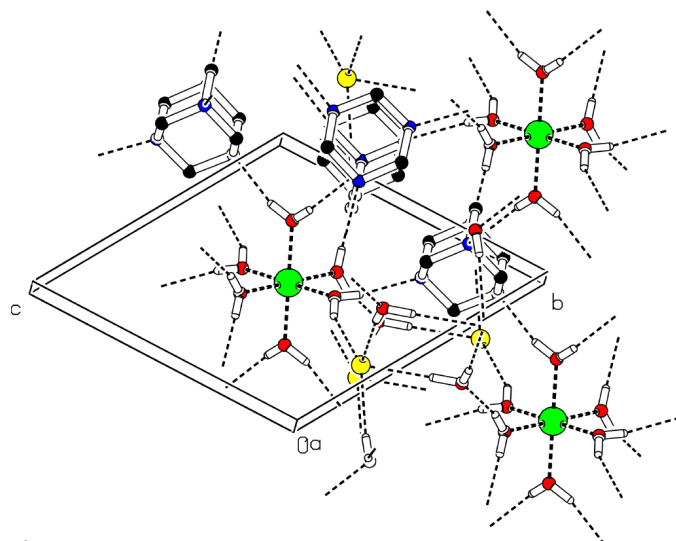


**Figure 2**
View along the $a$ axis of the three-dimensional structure in (I), with the hydrogen bonds shown as dashed lines.

solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

## References

Hu, M.-L., Ye, M.-D. & Ng, S. W. (2002). Acta Cryst. E**58**, m486–m487.
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (1997a). SHELXL97 and SHELXS97. University of Göttingen, Germany.
Sheldrick, G. M. (1997b). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.