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trichloride trihydrate**

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## $\mu$ -Aqua-pentaaqua[ $\mu$ -3,6-bis(6-methyl-2-pyridyl)pyridazine]chlorodinickel(II) trichloride trihydrate

Nack-Do Sung,<sup>a</sup> Ki-Seob Yun,<sup>a</sup> Jin-Gyu Kim<sup>b</sup> and Il-Hwan Suh<sup>b\*</sup>

<sup>a</sup>Division of Applied Biology and Chemistry, Chungnam National University, Taejon 305-764, Korea, and <sup>b</sup>Department of Physics, Chungnam National University, Taejon 305-764, Korea

Correspondence e-mail: ihsuh@cnu.ac.kr

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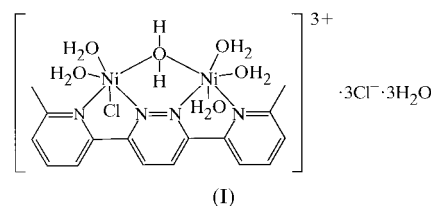
The title compound,  $\mu$ -aqua-1:2 $\kappa^2$ O-pentaaqua-1 $\kappa^2$ O,2 $\kappa^3$ O- $\mu$ -3,6-bis(6-methyl-2-pyridyl)pyridazine-1 $\kappa^2$ N<sup>1</sup>,N<sup>6</sup>:2 $\kappa^2$ N<sup>2</sup>,N<sup>3</sup>-chloro-1 $\kappa$ Cl-dinickel(II) trichloride trihydrate, [Ni<sub>2</sub>Cl(C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>)(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>·3H<sub>2</sub>O, consists of two Ni<sup>II</sup> atoms, a 3,6-bis(6-methyl-2-pyridyl)pyridazine molecule, four Cl atoms and nine water molecules. The two Ni atoms are octahedrally coordinated by N and Cl atoms, and by water molecules, and the three six-membered rings, a pyridazine and two picolines, are planar to within 0.181 (3) Å. The crystal structure is stabilized by an intra- and intermolecular hydrogen-bonding scheme involving water–water and water–chlorine interactions.

### Comment

Complexes of the ligands 3,6-bis(2-pyridyl)pyridazine and 3,6-bis(6-methyl-2-pyridyl)pyridazine (Butte & Case, 1961) with the metal ions Cu<sup>II</sup> (Ghedini *et al.*, 1982), Ni<sup>II</sup> (Ball & Blake, 1969), Co<sup>II</sup> (Andrew *et al.*, 1969), Mg<sup>II</sup> (Andrew *et al.*, 1975), Ru<sup>II</sup> (Denti *et al.*, 1989) and Rh<sup>I</sup> (Rahmouni *et al.*, 1998) have been studied recently. In most of these binuclear complexes, each atom of the N–N group in the pyridazine ring is coordinated to one of the two metal ions. In particular, the Ni<sup>II</sup> complex of 3,6-bis(6-methyl-2-pyridyl)pyridazine, (I), attracted our interest in relation to phosphate receptors because many phosphodiesterases are activated by two or more metal ions in nature. Therefore, we report here the X-ray structure of (I) and discuss the interactions between atoms.

The Ni1 atom in (I) is octahedrally coordinated by the pyridine N1 atom, the pyridazine N2 atom and four water molecules (OW1, OW3, OW4 and OW5). The Ni2 atom is also octahedrally coordinated, by the pyridazine N3 atom, the pyridine N4 atom, three water molecules (OW1, OW6 and OW7) and the Cl1 atom. Therefore, the OW1 water molecule bridges both Ni atoms [Ni1···OW1···Ni2 113.79 (9)°] and the

Ni2···Cl1 distance of 2.3796 (9) Å is 0.2932 Å longer than the mean value 2.0864 (6) Å found for Ni···OW and Ni···N distances. All atomic bond distances in the three six-membered aromatic rings are normal  $sp^2$ -hybridized bond



lengths and each of the three rings is perfectly planar. The three rings as a whole are planar within 0.181 (3) Å and the Ni1, Ni2 and OW1 atoms are 0.415 (2), 0.448 (2) and 0.798 (3) Å out of the plane, respectively. As shown in Table 2, there are 11 intramolecular and seven intermolecular hydrogen bonds, where the four water–water hydrogen-bond lengths range from 2.664 (4) to 2.815 (3) Å [mean value 2.724 (2) Å] and the 14 water–chlorine hydrogen-bond lengths range from 3.066 (2) to 3.300 (4) Å [mean value 3.1764 (7) Å]. This hydrogen-bond scheme stabilizes the three-dimensional molecular packing. The reliability index ( $R = 3.22\%$ ) verifies that all the crystallographic data presented in this report are very close to the standard values given in the *International Tables for Crystallography* (Lonsdale, 1983; Wilson, 1995).

### Experimental

The pale green title complex was prepared by mixing 3,6-bis(6-methyl-2-pyridyl)pyridazine (Butte & Case, 1961) and NiCl<sub>2</sub> (1:2) in absolute ethanol solution. The precipitate was filtered, washed with ethanol and dried at room temperature.

#### Crystal data

[Ni <sub>2</sub> Cl(C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> )(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub> ·3H <sub>2</sub> O	$Z = 2$
$M_r = 683.68$	$D_x = 1.685 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.1807 (11) \text{ \AA}$	Cell parameters from 25 reflections
$b = 11.626 (3) \text{ \AA}$	$\theta = 11.3\text{--}14.9^\circ$
$c = 11.7904 (16) \text{ \AA}$	$\mu = 1.845 \text{ mm}^{-1}$
$\alpha = 112.119 (13)^\circ$	$T = 289 (2) \text{ K}$
$\beta = 103.677 (10)^\circ$	Block, light green
$\gamma = 96.013 (14)^\circ$	$0.56 \times 0.50 \times 0.33 \text{ mm}$
$V = 1347.2 (4) \text{ \AA}^3$	

#### Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.017$
Non-profiled $\omega/2\theta$ scans	$\theta_{\text{max}} = 24.97^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = -13 \rightarrow 12$
$T_{\text{min}} = 0.281$ , $T_{\text{max}} = 0.544$	$k = -13 \rightarrow 12$
4975 measured reflections	$l = 0 \rightarrow 14$
4725 independent reflections	3 standard reflections
3927 reflections with $I > 2\sigma(I)$	frequency: 300 min
	intensity decay: 1%

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 1.2395P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.080$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.033$	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
4725 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
316 parameters	
H atoms: see below	

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

Ni1—OW3	2.013 (2)	Ni2—OW7	2.033 (2)
Ni1—OW4	2.048 (2)	Ni2—N3	2.057 (2)
Ni1—N2	2.051 (2)	Ni2—OW6	2.063 (2)
Ni1—OW5	2.083 (2)	Ni2—N4	2.115 (2)
Ni1—N1	2.102 (2)	Ni2—OW1	2.153 (2)
Ni1—OW1	2.169 (2)	Ni2—Cl1	2.3796 (9)
OW3—Ni1—OW4	88.47 (9)	OW7—Ni2—OW6	90.62 (9)
OW3—Ni1—N2	172.94 (9)	N3—Ni2—OW6	93.56 (10)
OW4—Ni1—N2	95.14 (9)	OW7—Ni2—N4	104.26 (9)
OW3—Ni1—OW5	85.24 (9)	N3—Ni2—N4	79.05 (9)
OW4—Ni1—OW5	173.63 (9)	OW6—Ni2—N4	89.59 (9)
N2—Ni1—OW5	91.22 (9)	OW7—Ni2—OW1	87.81 (8)
OW3—Ni1—N1	106.99 (10)	N3—Ni2—OW1	88.97 (8)
OW4—Ni1—N1	90.20 (10)	OW6—Ni2—OW1	89.42 (8)
N2—Ni1—N1	79.11 (9)	N4—Ni2—OW1	167.89 (9)
OW5—Ni1—N1	90.67 (9)	OW7—Ni2—Cl1	86.88 (7)
OW3—Ni1—OW1	84.67 (8)	N3—Ni2—Cl1	88.81 (7)
OW4—Ni1—OW1	92.54 (9)	OW6—Ni2—Cl1	176.49 (7)
N2—Ni1—OW1	89.10 (8)	N4—Ni2—Cl1	93.40 (7)
OW5—Ni1—OW1	87.88 (8)	OW1—Ni2—Cl1	88.03 (6)
N1—Ni1—OW1	168.09 (9)	Ni2—OW1—Ni1	113.79 (9)
OW7—Ni2—N3	174.70 (9)		

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

D—H...A	D—H	H...A	D...A	D—H...A
OW1—HW1A...OW2	0.86	1.84	2.705 (3)	180
OW1—HW1B...Cl2	0.89	2.41	3.232 (2)	153
OW2—HW2A...Cl3	0.89	2.28	3.163 (3)	169
OW2—HW2B...Cl4	1.00	2.14	3.126 (3)	170
OW3—HW3A...OW2 <sup>i</sup>	0.80	2.06	2.815 (3)	157
OW3—HW3B...Cl2 <sup>i</sup>	0.84	2.23	3.066 (2)	170
OW4—HW4A...Cl4	0.93	2.26	3.171 (3)	167
OW4—HW4B...Cl4 <sup>ii</sup>	0.96	2.16	3.097 (2)	166
OW5—HW5A...Cl1 <sup>iii</sup>	0.85	2.24	3.089 (2)	173
OW5—HW5B...Cl2	0.91	2.24	3.140 (2)	172
OW6—HW6A...Cl4	0.84	2.42	3.257 (2)	176
OW6—HW6B...OW8	0.94	1.78	2.715 (4)	172
OW7—HW7B...Cl3	0.81	2.35	3.092 (2)	153
OW7—HW7A...OW9	0.80	1.86	2.661 (4)	175
OW8—HW8B...Cl3 <sup>iv</sup>	1.09	2.22	3.300 (4)	172
OW8—HW8A...Cl2 <sup>v</sup>	1.08	2.24	3.294 (3)	167
OW9—HW9A...Cl3 <sup>vi</sup>	0.88	2.41	3.235 (3)	156
OW9—HW9B...Cl2	0.91	2.39	3.208 (3)	150

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

The positional parameters of the H atoms in the pyridazine and picoline rings were calculated geometrically and constrained to ride on their attached atoms. Water H atoms were located from difference density maps and their positions were fixed. Their isotropic displacement parameters were fixed at 1.2 or 1.5 (for methyl group) times the equivalent isotropic displacement parameters of their parent atoms. The highest peak and deepest hole in the final difference density map are 0.66 e Å<sup>-3</sup> at 1.47 Å from OW8 and -0.34 e Å<sup>-3</sup> at 0.82 Å from Cl4.

Data collection: *CAD-4 EXPRESS Software* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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