

# Further refinement of diaqua(1,7,11,17-tetraoxa-2,6,12,16-tetraazacycloeicosane-*N,N',N'',N'''*)-nickel(II) dichloride

Vladimir A. Kuksa,<sup>a</sup>  
Solange M. S. V. Wardell,<sup>b</sup>  
Paul Kong Thoo Lin<sup>c</sup> and R. Alan Howie<sup>d\*</sup>

<sup>a</sup>Department of Ophthalmology, School of Medicine, University of Washington, 1957 NE Pacific Avenue, Seattle, WA 98195-6485, USA,

<sup>b</sup>Departamento de Química Orgânica, Instituto de Química, Universidade Federal Fluminense, 24020-150, Niterói, Rio de Janeiro, Brazil,

<sup>c</sup>School of Life Sciences, The Robert Gordon University, St. Andrew Street, Aberdeen AB25 1HG, Scotland, and

<sup>d</sup>Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: r.a.howie@abdn.ac.uk

## Key indicators

Single-crystal X-ray study

$T = 150\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

Disorder in main residue

$R$  factor = 0.025

$wR$  factor = 0.063

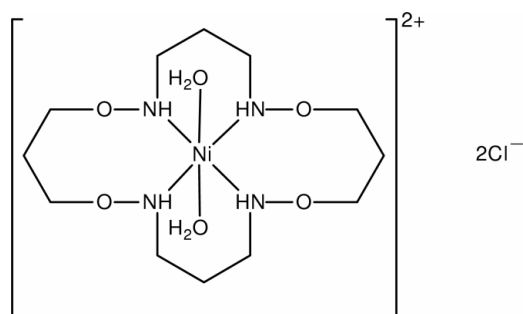
Data-to-parameter ratio = 13.8

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

This further refinement of  $[\text{Ni}(\text{C}_{12}\text{H}_{28}\text{N}_4\text{O}_4)(\text{H}_2\text{O})_2]\text{Cl}_2$  based on the original intensity data improves upon the original by modelling the element of disorder associated with two of the methylene groups of the macrocyclic ligand and reduces  $R$  by about a factor of two in the process. The occupancies [0.256 (3) and 0.190 (5)] of the minor components are, however, low enough to leave the atomic parameters and geometry of the major component little changed from those described in the original publication. The molecule is subject to the operation of a crystallographic mirror plane passing through Ni, O of the water molecules, and two ligand methylene groups.

## Comment

A feature of the structure of the title compound, (I) (Fig. 1), as reported previously by Kuksa *et al.* (2000) was comparatively high residual electron density in the vicinity of C4. Modelling this and a similar but somewhat smaller feature in the vicinity of C7 in terms of disorder of the atoms concerned brought about a significant improvement in the structure determination with the reduction of  $R[F^2 > 2\sigma(F^2)]$  and  $wR2$  (all  $F^2$  data) from 0.050 and 0.136, respectively, to the corresponding values given below. The introduction of disorder into the model, whereby C4 and C7 are both distributed over pairs of sites as C4/C4A and C7/C7A with occupancies of 0.744 (3) and 0.810 (5) for the major (C4 and C7) components, respectively, and with H attached to these and neighbouring atoms treated appropriately, has little effect upon the structural features of the major component such as the coordination of Ni and the internal geometry of the macrocyclic ligand (Table 1) or the hydrogen-bond parameters (Table 2).



(I)

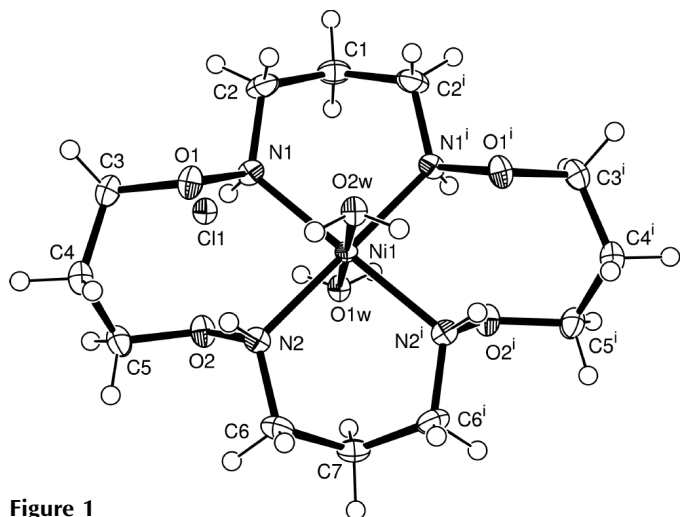
The coordination of Ni is octahedral with equatorial N, with Ni1—N1 and Ni1—N2 2.0990 (12) and 2.1091 (12) Å, respectively, and water molecules in the axial positions, with Ni1—

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Further refinement of structure previously reported (compound 5), by Kuksa, Wardell & Lin [*Inorg. Chem. Commun.* (2000), **3**, 267–270].

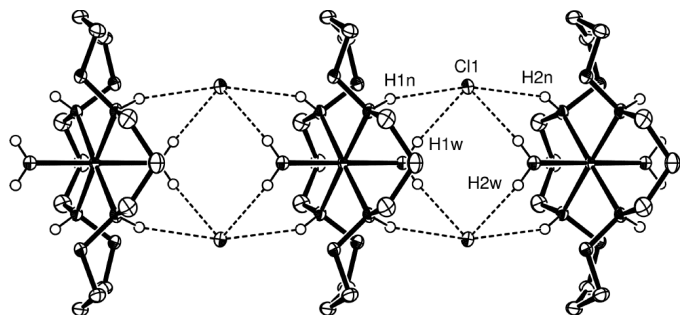


**Figure 1**

The molecule of (I) showing the labelling scheme. Non-H atoms are shown as 50% probability ellipsoids and H as small circles. [Symmetry code: (i)  $x, 1/2-y, z$ .]

O1W and Ni1—O2W at 2.1299 (14) and 2.1061 (14) Å, respectively. The angles at Ni involving *cis*-donor atoms lie in the range 86.52 (5)–93.92 (7)°, while *trans* angles of 178.75 (4) and 179.93 (5)° are observed. The chloride anion does not participate in the coordination of Ni, but is heavily involved as a hydrogen-bond acceptor (see below).

A notable feature of the major component form of the macrocyclic ligand (Fig. 1) is the two-up two-down arrangement of the methylene groups at the points of the envelope flaps of the six- (C1 and C7) and eight-membered [C4 and C4<sup>i</sup>; symmetry code: (i)  $x, 1/2-y, z$ ] chelate rings relative to the plane defined by Ni and its attached N, with C4 and C4<sup>i</sup> above the plane and C1 and C7 below it. In the minor component form with C4A and C7A replacing C4 and C7, the arrangement is now three-up one-down, with only C1 below the reference plane, and is clearly not simply a total inversion of the original two-up two-down arrangement. This further justifies the use, adopted initially on the basis of the magnitudes of the difference map peaks, of two distinct occupancy factors in modelling the disorder. As shown in Table 1, the major and minor forms of the macrocyclic ligand differ



**Figure 2**

A portion of the hydrogen-bonded chain in (I). The representation is the same as that used in Fig. 1, except that H atoms other than those involved in hydrogen bonds to Cl (dashed lines) have been omitted and only selected atoms are labelled, in a generic manner. The direction of view is essentially along  $c$  with  $a$  across the page, *i.e.* the mirror plane running horizontally through the mid-line of the Figure is seen edge-on.

appreciably in terms of the C3—C4, C4—C5 and C6—C7 bond lengths (or their equivalent for the minor component) and also in the angles subtended by non-H atoms at C3, C5 and C6, as well as those at C4, C4A, C7 and C7A.

The hydrogen bonds listed in Table 2, all of which have Cl as acceptor, create infinite chains propagated in the direction of the  $a$  axis (Fig. 2).

## Experimental

The synthesis and growth of crystals of (I) have been described by Kuksa *et al.* (2000).

### Crystal data

[Ni(C<sub>12</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>  
 $M_r = 458.03$   
 Monoclinic,  $P2_1/m$   
 $a = 7.4288$  (3) Å  
 $b = 13.1426$  (5) Å  
 $c = 10.2527$  (3) Å  
 $\beta = 102.2480$  (18)°  
 $V = 978.22$  (6) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.555$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 15576 reflections  
 $\theta = 2.0$ – $26.4$ °  
 $\mu = 1.30$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block, light violet  
 $0.60 \times 0.15 \times 0.15$  mm

### Data collection

Delft Instruments FAST area-detector diffractometer  
 $\varphi$  scans  
 Absorption correction: refined from  $\Delta F$  (DIFABS; Walker & Stuart, 1983)  
 $T_{\min} = 0.710$ ,  $T_{\max} = 0.823$   
 15576 measured reflections

2090 independent reflections  
 1892 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$   
 $\theta_{\max} = 26.4$ °  
 $h = -9 \rightarrow 9$   
 $k = -16 \rightarrow 16$   
 $l = -12 \rightarrow 12$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.025$   
 $wR(F^2) = 0.063$   
 $S = 1.05$   
 2090 reflections  
 152 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 0.4373P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.64$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ni1—N1	2.0990 (12)	N2—C6	1.4792 (18)
Ni1—O2W	2.1061 (14)	C1—C2	1.5130 (19)
Ni1—N2	2.1091 (12)	C3—C4A	1.484 (6)
Ni1—O1W	2.1299 (14)	C3—C4	1.521 (2)
O1—C3	1.4404 (17)	C4—C5	1.488 (2)
O1—N1	1.4451 (14)	C4A—C5	1.514 (6)
O2—C5	1.4381 (18)	C6—C7A	1.443 (5)
O2—N2	1.4457 (14)	C6—C7	1.504 (2)
N1—C2	1.4776 (18)		
N1—Ni1—N1 <sup>i</sup>	93.02 (7)	O2—N2—C6	109.60 (11)
N1—Ni1—O2W	89.69 (4)	C2 <sup>i</sup> —C1—C2	113.13 (18)
N1—Ni1—N2 <sup>i</sup>	178.75 (4)	N1—C2—C1	111.34 (13)
N1—Ni1—N2	86.52 (5)	O1—C3—C4A	123.0 (2)
O2W—Ni1—N2	91.47 (4)	O1—C3—C4	105.85 (13)
N2 <sup>i</sup> —Ni1—N2	93.92 (7)	C5—C4—C3	115.67 (16)
N1—Ni1—O1W	90.26 (4)	C3—C4A—C5	116.4 (4)
O2W—Ni1—O1W	179.93 (5)	O2—C5—C4	116.16 (13)
N2 <sup>i</sup> —Ni1—O1W	88.58 (4)	O2—C5—C4A	104.3 (2)
C3—O1—N1	114.59 (10)	C7A—C6—N2	116.6 (4)
C5—O2—N2	113.93 (10)	N2—C6—C7	113.13 (15)
O1—N1—C2	107.27 (10)	C6—C7—C6 <sup>i</sup>	115.0 (2)

Symmetry code: (i)  $x, \frac{1}{2}-y, z$ .

**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>
O1W—H1W...Cl1	0.796 (18)	2.375 (18)	3.1571 (11)	167.7 (18)
O2W—H2W...Cl1 <sup>1</sup>	0.820 (18)	2.339 (18)	3.1493 (11)	169.9 (17)
N1—H1N...Cl1	0.883 (18)	2.529 (18)	3.3597 (12)	156.9 (14)
N2—H2N...Cl1 <sup>1</sup>	0.890 (17)	2.546 (17)	3.3351 (12)	148.0 (13)

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

A more complete account of the data collection process is given by Darr *et al.* (1993). H atoms attached to C (methylene groups) were placed in calculated positions, with C—H = 0.99 Å and refined as riding atoms with  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ . H atoms attached to N and O were located in a difference map and refined isotropically.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989); cell refinement: *MADNES*; data reduction: *ABSMAD* (Karaulov, 1992); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick,

1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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