(*meso*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) dibromide dihydrate

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The asymmetric unit of the title compound, [Ni($C_{16}H_{32}N_4$)]$Br_2 \cdot 2H_2O$, consists of one half [Ni($C_{16}H_{32}N_4$)]$^{2+}$ cation, one Br^- anion and one water molecule of crystallization. The Ni^{II} ion lies on an inversion centre in a square-planar environment formed by the four macrocyclic ligand N atoms. In the crystal structure, the cations, anions and water molecules are linked *via* intermolecular N—H···Br and O—H···Br hydrogen bonds, forming discrete chains with set-graph motif $D(2)D_2^2(7)D_2^1(3)D_3^2(8)$. The water molecules and Br^- ions are linked with set-graph motif $R_4^2(8)$.

Related literature

For related structures, see: Ballester *et al.* (2000); Heinlein & Tebbe (1985); Shen *et al.* (1999); Szalda *et al.* (1989); Wang *et al.* (2007); Whimp *et al.* (1970); Yang (2005). For the preparation of the precursor complex $C_{16}H_{32}N_4 \cdot 2HBr \cdot 2H_2O$, see: Hay *et al.* (1975). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).
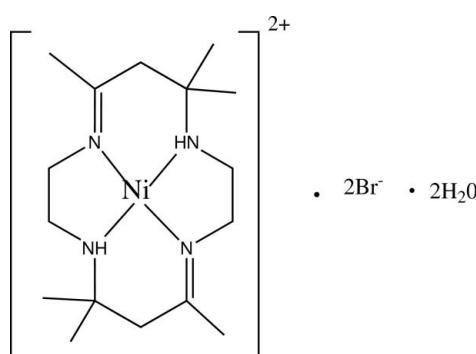
Experimental

Crystal data

[Ni($C_{16}H_{32}N_4$)]$Br_2 \cdot 2H_2O$	V = 1105.3 (4) Å^3
M_r = 535.02	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 8.0349 (16) Å	μ = 4.51 mm^{-1}
b = 15.619 (3) Å	T = 293 K
c = 8.9355 (18) Å	$0.27 \times 0.20 \times 0.20$ mm
β = 99.72 (3)°	

Data collection

Rigaku SCXmini diffractometer	11266 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	2531 independent reflections
	1995 reflections with $I > 2\sigma(I)$
T_{min} = 0.831, T_{max} = 0.862	R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044	116 parameters
$wR(F^2)$ = 0.099	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 0.74 e Å^{-3}
2531 reflections	$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Br1^i	0.91	2.53	3.413 (3)	164
O1—H1E···Br1^{ii}	0.85	2.53	3.374 (3)	169
O1—H1F···Br1^{iii}	0.85	2.55	3.388 (5)	170

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2296).

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supporting information

(*meso*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) dibromide dihydrate

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S1. Comment

The structures of several related macrocyclic complexes have been reported (Whimp *et al.*,1970; Yang, 2005; Heinlein *et al.*, 1985) for many times in the past years. The nickel(II) tetraazamacrocyclic complex cation, $[Ni(C_{16}H_{32}N_4)]^{2+}$ has both *meso* and enantiomeric forms and can combine with different anions to form many kinds of structures (Shen *et al.*, 1999; Ballester *et al.*, 2000; Wang *et al.*, 2007). We herein report the crystal structure of a new compound synthesized by reaction of $Ni(CH_3COO)_2.4H_2O$ and the complex $C_{16}H_{32}N_4.2HBr.2H_2O$ in methanol solution. As shown in Fig.**1**, the Ni^{II} atom is coordinated by four N atoms from the tetraazamacrocycle in a square-planar geometry. The metal atom and the four N atoms are coplanar. The Ni—*N*(amine) and *N*(imine) bond distances are 1.934 (3) Å and 1.916 (3)Å and are similar to those in previously report (Szalda *et al.*,1989). In the crystal structure, the cations, anions and water molecules are linked via intermolecular N—H···Br and O— H···Br hydrogen bonds forming discrete chains with set-graph motif $D_1^1(2)$, $D_2^2(7)$, $D_2^1(3)$ and $D_3^2(8)$. The water molecules and Br⁻ ions are linked forming $R_4^2(8)$ set-graph motif (Bernstein *et al.*, 1995), Fig 2.

S2. Experimental

All chemicals were of reagent grade and were used as received without further purification. The precursor complex $C_{16}H_{32}N_4.2HBr.2H_2O$ was prepared by described in the literature method (Hay *et al.*, 1975). To a 10 ml methanol solution of $Ni(CH_3COO)_2.4H_2O$ (0.2 mmol, 0.049 g), a 5 ml methanol solution of $C_{16}H_{32}N_4.2HBr.2H_2O$ (0.2 mmol, 0.0957 g) was added dropwise with stirring. The resulting solution was continuously stirred for about 30 min. Yellow crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature over several days.

S3. Refinement

All hydrogen atoms were placed in calculated positions with C—H = 0.96 to 0.97 Å, N—H = 0.91 Å and O—H = 0.82 Å. They were included in the refinement in the riding-motion approximation with $U_{iso}(H) = 1.2U_{eq}(C, N, O)$ or $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$.
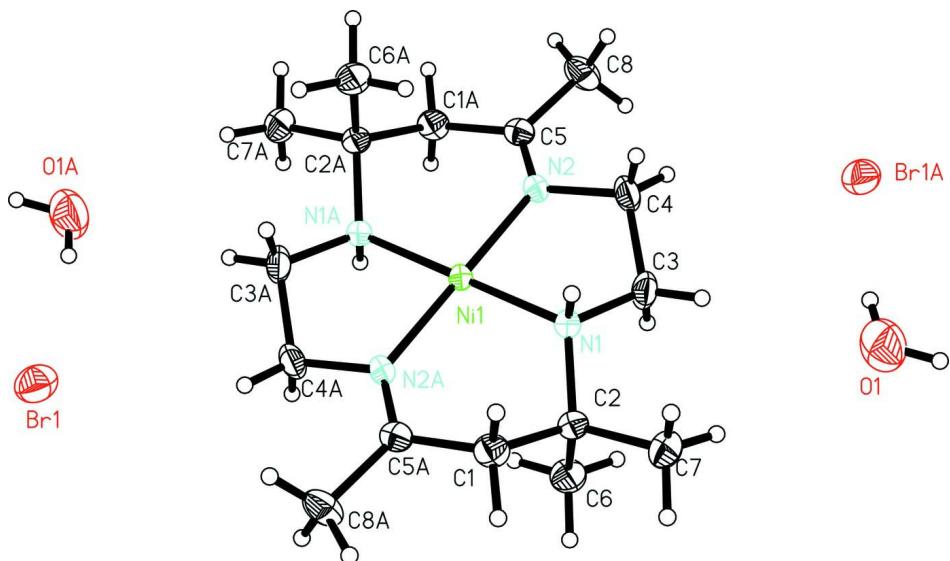
Figure 1

The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabeled atoms are related to labeled atoms by the symmetry code (1-x,1-y,1-z)
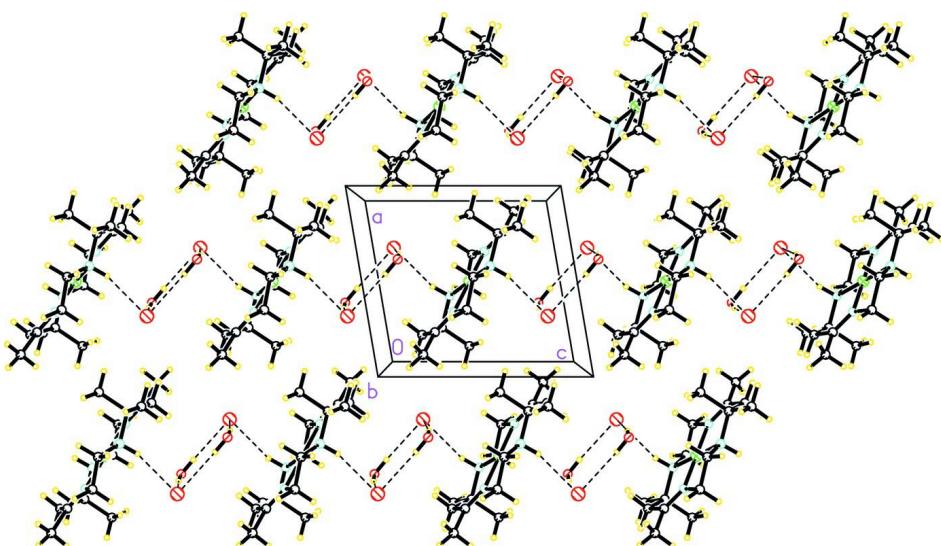
Figure 2

View of (I) along b, showing chains of organic cations running parallel to the (001) direction, with Br⁻ anions and water molecules lying between them.

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Crystal data

[Ni(C$_{16}$H$_{32}$N$_4$)]Br$_2$·2H$_2$O	$c = 8.9355\,(18)$ Å
$M_r = 535.02$	$\beta = 99.72\,(3)°$
Monoclinic, $P2_1/c$	$V = 1105.3\,(4)$ Å^3
Hall symbol: -P 2ybc	$Z = 2$
$a = 8.0349\,(16)$ Å	$F(000) = 548$
$b = 15.619\,(3)$ Å	$D_x = 1.608$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3476 reflections

$\theta = 2.3$–$27.5°$

$\mu = 4.51$ mm^{-1}

$T = 293$ K

Prism, brown

$0.27 \times 0.20 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 13.6612 pixels mm^{-1}

thin–slice ω scans

Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)

$T_{min} = 0.831$, $T_{max} = 0.862$

11266 measured reflections

2531 independent reflections

1995 reflections with $I > 2\sigma(I)$

$R_{int} = 0.048$

$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$

$h = -10 \rightarrow 10$

$k = -20 \rightarrow 20$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.099$

$S = 1.05$

2531 reflections

116 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 1.6713P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.74$ e Å^{-3}

$\Delta\rho_{min} = -0.74$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ni1	0.5000	0.5000	0.5000	0.02894 (16)
Br1	0.69586 (6)	0.10330 (3)	0.63849 (6)	0.06334 (18)
C1	0.8076 (5)	0.5280 (2)	0.7876 (4)	0.0410 (8)
H1B	0.9228	0.5334	0.8406	0.061*
H1C	0.7344	0.5312	0.8633	0.061*
C2	0.7698 (4)	0.6042 (2)	0.6830 (4)	0.0362 (8)
C3	0.5246 (5)	0.6761 (2)	0.5232 (5)	0.0546 (11)
H3A	0.5877	0.6831	0.4405	0.065*
H3B	0.5384	0.7273	0.5854	0.065*
C4	0.3413 (5)	0.6610 (2)	0.4621 (5)	0.0536 (11)
H4A	0.2748	0.6656	0.5429	0.064*
H4B	0.3003	0.7030	0.3846	0.064*

C5	0.2117 (4)	0.5591 (2)	0.2827 (4)	0.0343 (7)
C6	0.8765 (5)	0.6034 (3)	0.5571 (5)	0.0503 (10)
H6A	0.8525	0.5525	0.4972	0.075*
H6B	0.9941	0.6044	0.6013	0.075*
H6C	0.8503	0.6528	0.4937	0.075*
C7	0.8061 (5)	0.6849 (3)	0.7812 (5)	0.0561 (11)
H7A	0.7833	0.7348	0.7184	0.084*
H7B	0.9225	0.6851	0.8290	0.084*
H7C	0.7353	0.6853	0.8576	0.084*
C8	0.0896 (5)	0.6244 (3)	0.2077 (5)	0.0528 (10)
H8A	0.0147	0.5984	0.1252	0.079*
H8B	0.1504	0.6702	0.1695	0.079*
H8C	0.0252	0.6468	0.2802	0.079*
N1	0.5857 (3)	0.60021 (16)	0.6151 (3)	0.0332 (6)
H1A	0.5300	0.6015	0.6957	0.040*
N2	0.3276 (3)	0.57404 (17)	0.3970 (3)	0.0333 (6)
O1	0.6240 (6)	0.8913 (2)	0.6616 (5)	0.0923 (12)
H1E	0.6525	0.9438	0.6665	0.111*
H1F	0.5421	0.8854	0.5885	0.111*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0263 (3)	0.0225 (3)	0.0368 (3)	0.0004 (2)	0.0016 (2)	0.0001 (3)
Br1	0.0521 (3)	0.0655 (3)	0.0752 (4)	−0.0076 (2)	0.0189 (2)	−0.0112 (2)
C1	0.041 (2)	0.046 (2)	0.0338 (19)	0.0010 (16)	−0.0019 (16)	−0.0021 (16)
C2	0.0299 (17)	0.0349 (19)	0.042 (2)	−0.0014 (14)	0.0011 (15)	−0.0035 (15)
C3	0.057 (3)	0.0238 (17)	0.075 (3)	−0.0031 (17)	−0.012 (2)	0.0055 (19)
C4	0.050 (2)	0.0277 (19)	0.074 (3)	0.0112 (17)	−0.013 (2)	−0.0055 (19)
C5	0.0321 (17)	0.0398 (19)	0.0319 (18)	0.0022 (14)	0.0079 (14)	0.0059 (15)
C6	0.043 (2)	0.051 (2)	0.061 (3)	−0.0022 (18)	0.021 (2)	0.008 (2)
C7	0.051 (2)	0.041 (2)	0.071 (3)	−0.0062 (18)	−0.004 (2)	−0.012 (2)
C8	0.048 (2)	0.057 (3)	0.048 (2)	0.019 (2)	−0.0043 (19)	0.003 (2)
N1	0.0299 (14)	0.0264 (14)	0.0430 (17)	−0.0001 (11)	0.0051 (12)	−0.0013 (12)
N2	0.0321 (15)	0.0257 (14)	0.0407 (16)	0.0040 (11)	0.0025 (13)	0.0021 (12)
O1	0.103 (3)	0.070 (2)	0.097 (3)	0.013 (2)	−0.001 (2)	0.019 (2)

Geometric parameters (Å, º)

Ni1—N2	1.916 (3)	C4—H4B	0.9700
Ni1—N2^i	1.916 (3)	C5—N2	1.282 (4)
Ni1—N1	1.934 (3)	C5—C8	1.494 (5)
Ni1—N1^i	1.934 (3)	C5—C1^i	1.494 (5)
C1—C5^i	1.494 (5)	C6—H6A	0.9600
C1—C2	1.513 (5)	C6—H6B	0.9600
C1—H1B	0.9700	C6—H6C	0.9600
C1—H1C	0.9700	C7—H7A	0.9600
C2—N1	1.503 (4)	C7—H7B	0.9600

C2—C6	1.525 (5)	C7—H7C	0.9600
C2—C7	1.535 (5)	C8—H8A	0.9600
C3—N1	1.477 (4)	C8—H8B	0.9600
C3—C4	1.501 (5)	C8—H8C	0.9600
C3—H3A	0.9700	N1—H1A	0.9100
C3—H3B	0.9700	O1—H1E	0.8500
C4—N2	1.475 (5)	O1—H1F	0.8500
C4—H4A	0.9700		

N2—Ni1—N2[i]	180.000 (1)	N2—C5—C1[i]	120.7 (3)
N2—Ni1—N1	86.01 (12)	C8—C5—C1[i]	114.8 (3)
N2[i]—Ni1—N1	93.99 (12)	C2—C6—H6A	109.5
N2—Ni1—N1[i]	93.99 (12)	C2—C6—H6B	109.5
N2[i]—Ni1—N1[i]	86.01 (12)	H6A—C6—H6B	109.5
N1—Ni1—N1[i]	180.0	C2—C6—H6C	109.5
C5[i]—C1—C2	117.5 (3)	H6A—C6—H6C	109.5
C5[i]—C1—H1B	107.9	H6B—C6—H6C	109.5
C2—C1—H1B	107.9	C2—C7—H7A	109.5
C5[i]—C1—H1C	107.9	C2—C7—H7B	109.5
C2—C1—H1C	107.9	H7A—C7—H7B	109.5
H1B—C1—H1C	107.2	C2—C7—H7C	109.5
N1—C2—C1	107.3 (3)	H7A—C7—H7C	109.5
N1—C2—C6	109.9 (3)	H7B—C7—H7C	109.5
C1—C2—C6	111.7 (3)	C5—C8—H8A	109.5
N1—C2—C7	110.1 (3)	C5—C8—H8B	109.5
C1—C2—C7	107.1 (3)	H8A—C8—H8B	109.5
C6—C2—C7	110.6 (3)	C5—C8—H8C	109.5
N1—C3—C4	106.8 (3)	H8A—C8—H8C	109.5
N1—C3—H3A	110.4	H8B—C8—H8C	109.5
C4—C3—H3A	110.4	C3—N1—C2	113.8 (3)
N1—C3—H3B	110.4	C3—N1—Ni1	107.4 (2)
C4—C3—H3B	110.4	C2—N1—Ni1	119.1 (2)
H3A—C3—H3B	108.6	C3—N1—H1A	105.1
N2—C4—C3	106.9 (3)	C2—N1—H1A	105.1
N2—C4—H4A	110.3	Ni1—N1—H1A	105.1
C3—C4—H4A	110.3	C5—N2—C4	118.5 (3)
N2—C4—H4B	110.3	C5—N2—Ni1	129.9 (2)
C3—C4—H4B	110.3	C4—N2—Ni1	111.5 (2)
H4A—C4—H4B	108.6	H1E—O1—H1F	108.1
N2—C5—C8	124.5 (3)		

C5[i]—C1—C2—N1	64.1 (4)	N2—Ni1—N1—C2	−154.2 (3)
C5[i]—C1—C2—C6	−56.4 (4)	N2[i]—Ni1—N1—C2	25.8 (3)
C5[i]—C1—C2—C7	−177.6 (3)	N1[i]—Ni1—N1—C2	79 (100)
N1—C3—C4—N2	−48.4 (5)	C8—C5—N2—C4	1.2 (5)
C4—C3—N1—C2	179.0 (3)	C1[i]—C5—N2—C4	180.0 (3)
C4—C3—N1—Ni1	45.0 (4)	C8—C5—N2—Ni1	−176.6 (3)
C1—C2—N1—C3	173.5 (3)	C1[i]—C5—N2—Ni1	2.2 (5)

C6—C2—N1—C3	−64.9 (4)	C3—C4—N2—C5	−148.4 (4)
C7—C2—N1—C3	57.2 (4)	C3—C4—N2—Ni1	29.8 (4)
C1—C2—N1—Ni1	−58.4 (3)	N2^{i}—Ni1—N2—C5	−65 (100)
C6—C2—N1—Ni1	63.2 (3)	N1—Ni1—N2—C5	173.9 (3)
C7—C2—N1—Ni1	−174.7 (3)	N1^{i}—Ni1—N2—C5	−6.1 (3)
N2—Ni1—N1—C3	−23.2 (3)	N2^{i}—Ni1—N2—C4	117 (100)
N2^{i}—Ni1—N1—C3	156.8 (3)	N1—Ni1—N2—C4	−4.0 (3)
N1^{i}—Ni1—N1—C3	−150 (100)	N1^{i}—Ni1—N2—C4	176.0 (3)

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Br1^{ii}	0.91	2.53	3.413 (3)	164
O1—H1*E*···Br1^{iii}	0.85	2.53	3.374 (3)	169
O1—H1*F*···Br1^{i}	0.85	2.55	3.388 (5)	170

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x+1, y+1/2, −z+3/2; (iii) x, y+1, z.