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(5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-1,8-diacetato)nickel(II) tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.055
wR factor = 0.139
Data-to-parameter ratio = 19.4

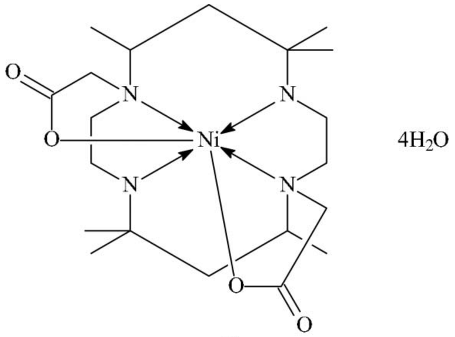
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The Ni atom in the title compound, $[\mathrm{Ni(C_{20}H_{38}N_4O_4)}]\cdot 4H_2O$, is chelated by four N atoms of the macrocycle and also covalently bonded to two carboxylate groups, in a *cis*-N_4O_2Ni octahedral environment. The mononuclear complex interacts with the solvent water molecules to form a three-dimensional network structure.

Comment

Several structural studies have been published to date on the metal complexes of EDTA-like tetraaza macrocycles (EDTA is ethylenediaminetetraacetic acid), the N atoms of which are each joined to an acetate $-CH_2CO_2$ group so that the four N atoms and the four carboxylate arms are able to encapsulate a large metal ion. As the first row transition metals do not usually adopt a coordination higher than six, the extra coordinating acetate arms are not utilized, and this is noted in, for example, the nickel derivative of the 12-membered C_8N_4 ring macrocycle, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid. Only two of the four carboxylic acid units are deprotonated and they bind to the metal atom, which is also coordinated by the four N atoms (Riesen *et al.*, 1986).

The 16-membered $C_{12}N_4$ ring tetraaza macrocycle, γ-*C*-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Hay *et al.*, 1975), reacts with a fivefold excess of ethyl bromoacetate to yield the expected tetraacetic acid, which has been isolated as a hydrochloride hydrate (Wang *et al.*, 2005). When the reaction is carried out with only a twofold equivalent of the acetate, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanium-1,8-diacetic acid is formed (see *Experimental*); this amino acid, when reacted with nickel sulfate, afforded the title compound, (I), in which four N atoms and two carboxylic acid O atoms are able to bond to the metal (scheme, Fig. 1).



(I)

The carboxylate groups each bind through an O atom, and the two O atoms are *cis* to each other in the octahedron surrounding the Ni atom.

The complex and solvent water molecules (Table 2) are linked to form a hydrogen-bonded network structure.

Experimental

5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-1,8-diacetic acid was synthesized from the reaction of the 16-membered-ring tetraaza macrocycle and ethyl bromoacetate in 1:2 molar quantities. 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane (0.28 g, 1 mmol), synthesized using the reported procedure (Hay *et al.*, 1975), and ethyl bromoacetate (0.34 g, 2.05 mmol) were refluxed in 1 *M* sodium hydroxide for 1 h. Hydrochloric acid (1 *M*) was added to give a pH of about 1. To the resulting solution was added nickel sulfate hexahydrate (0.26 g, 1 mmol) to give a purple solution. Deep-blue, almost violet, prisms of (I) formed after several days. The CHN elemental percentages (C 45.4, H8.5, N 10.6%) correspond to an empirical formulation with four water molecules.

Crystal data

$[Ni(C_{20}H_{38}N_4O_4)]\cdot 4H_2O$
$M_r = 529.32$
Monoclinic, $P2_1/n$
$a = 9.1863$ (6) Å
$b = 13.8653$ (9) Å
$c = 19.987$ (1) Å
$\beta = 93.604$ (1)°
$V = 2540.7$ (3) Å^3
$Z = 4$

$D_x = 1.384$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8736 reflections
$\theta = 2.4$–28.3°
$\mu = 0.81$ mm^{-1}
$T = 295$ (2) K
Prism, blue
0.21 × 0.18 × 0.13 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.713$, $T_{max} = 0.902$
21339 measured reflections

5770 independent reflections
5188 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -17 \rightarrow 18$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.139$
$S = 1.15$
5770 reflections
298 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 2.6926P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.106 (2)	Ni1—N4	2.097 (2)
Ni1—N2	2.098 (2)	Ni1—O1	2.108 (2)
Ni1—N3	2.090 (2)	Ni1—O3	2.112 (2)
N1—Ni1—N2	91.8 (1)	N2—Ni1—O3	95.7 (1)
N1—Ni1—N3	176.9 (1)	N3—Ni1—N4	92.5 (1)
N1—Ni1—N4	85.6 (1)	N3—Ni1—O1	103.5 (1)
N1—Ni1—O1	79.1 (1)	N3—Ni1—O3	79.1 (1)
N1—Ni1—O3	103.1 (1)	N4—Ni1—O1	94.7 (1)
N2—Ni1—N3	85.7 (1)	N4—Ni1—O3	169.5 (1)
N2—Ni1—N4	89.9 (1)	O1—Ni1—O3	81.4 (1)
N2—Ni1—O1	169.5 (1)		

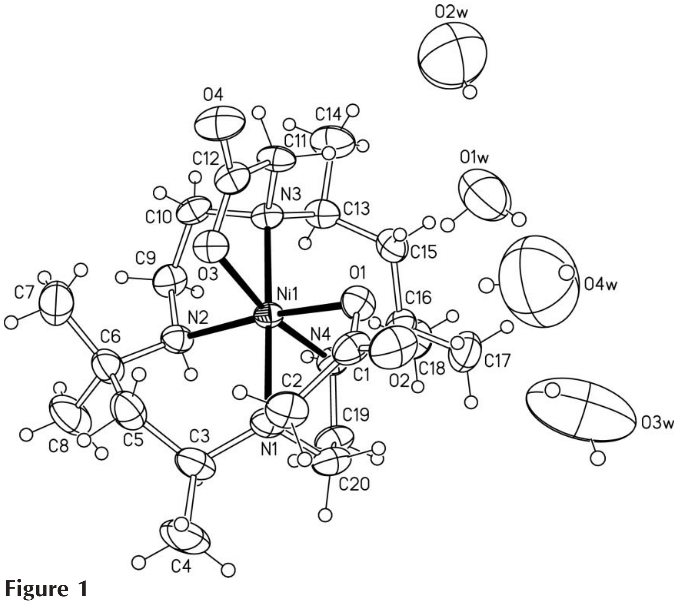


Figure 1
A plot of (I), showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O4^{i}	0.86	2.43	3.160 (4)	143
N4—H4N···O4^{i}	0.86	2.22	2.993 (3)	150
O1*W*—H1*W*1···O1	0.85	2.07	2.903 (4)	167
O1*W*—H1*W*2···O4*W*	0.85	2.24	2.949 (9)	142
O2*W*—H2*W*1···O1*W*	0.85	1.99	2.822 (7)	164
O2*W*—H2*W*2···O3*W*^{ii}	0.86	1.85	2.57 (1)	141
O3*W*—H3*W*1···O4^{iii}	0.86	2.19	2.817 (6)	129
O3*W*—H3*W*2···O4*W*	0.88	1.78	2.37 (1)	123
O4*W*—H4*W*2···O2	0.88	2.05	2.693 (8)	129

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

The C– and N-bound H atoms were positioned geometrically [N—H = 0.86 Å and C—H = 0.96–0.98 Å; $U_{iso}(H) = 1.2U_{eq}$(C or N); or $1.5U_{eq}$(C) for methyl H atoms] and included in the refinement in the riding-model approximation. The methyl groups were rotated to fit the electron density. The water H atoms were placed at chemically sensible positions on the basis of hydrogen bonds and their positions were fixed; such a scheme had one water molecule forming only one hydrogen bond. All distances between H atoms exceed 2 Å.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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References

Bruker (2002). *SADABS*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Hay, R. W., Lawrence, G. A. & Curtis, N. F. (1975). *J. Chem. Soc. Perkin Trans. I*, pp. 591–593.

m1482 Wang *et al.* • $[Ni(C_{20}H_{38}N_4O_4)]\cdot 4H_2O$ *Acta Cryst.* (2005). E**61**, m1481–m1483

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

Riesen, A., Zehnder, M. & Kaden, T. A. (1986). *Helv. Chim. Acta*, **69**, 2067–2073.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Wang, S.-F., Li, H.-Q., Ruan, B.-F., Zhu, H.-L. & Ng, S. W. (2005). *Acta Cryst.* E**61**, o2413–o2414.

Acta Cryst. (2005). E**61**, m1481–m1483 Wang *et al.* • $[Ni(C_{20}H_{38}N_4O_4)]\cdot 4H_2O$ **m1483**