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β-meso-(5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Diperchlorate Monohydrate

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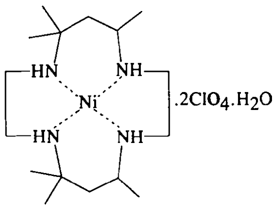
Abstract

In the title compound, $[Ni(C_{16}H_{36}N_4)](ClO_4)_2.H_2O$, the Ni^{II} ion is four-coordinated by the four N atoms of the macrocyclic ligand. The four N atoms are coplanar to within 0.05 Å and the four H atoms attached to the N atoms are located on the same side of the macrocyclic plane. The configuration of the four chiral nitrogen centres and two chiral carbon centres are (1*RS*,4*SR*,8*RS*,11*SR*) and (5*SR*,14*RS*), respectively. The two five-membered chelate rings are in unstable eclipsed forms and the two six-membered chelate rings are in stable chair forms. The two methyl groups attached to the asymmetric C atoms are equatorial. The perchlorate ions and water O atom are not within the bonding distance of the cation.

Comment

The chemistry of macrocyclic compounds has undergone spectacular growth recently, due to their distinctive coordination and biological significance (Cabbiness & Margerum, 1969). The extreme kinetic inertness and very high thermodynamic stability of tetraamine macrocyclic ligand complexes are of particular stereochemical interest, since they greatly enhance the number of potentially isolable isomers (Liang & Chung, 1980; Lee, Lu, Chung & Lee, 1984). In a previous paper (Lee, Wu & Chung, 1984), we reported the synthesis and characterization of five stereoisomers of Ni^{II} complexes of 5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (1,4-CTH), namely, $[Ni(\beta\text{-}rac\text{-}1,4\text{-CTH})(NCS)_2]$, $[Ni(\alpha\text{-}meso\text{-}1,4\text{-CTH})Cl_2]$, $[Ni(\beta\text{-}meso\text{-}1,4\text{-CTH})(NCS)_2]$, $[Ni(\gamma\text{-}meso\text{-}1,4\text{-CTH})(NCS)_2]$ and $[Ni(\delta\text{-}meso\text{-}1,4\text{-CTH})(NCS)_2]$. The present paper concerns the crystal structure of one of these isomers, $[Ni(\beta\text{-}meso\text{-}1,4\text{-CTH})](ClO_4)_2.H_2O$, (I).



(I)

The Ni^{II} ion is four-coordinated by the amine N atoms, with Ni—N distances in the range 1.915 (5)–1.935 (4) Å, which are normal for planar Ni^{II}–tetraamine complexes. The chelate angles subtended at the Ni atom are normal for the five-membered [87.6 (2) and 89.1 (2)°] and six-membered [89.6 (2) and 93.6 (2)°] chelate rings (Fig. 1). These angles are a compromise between the optimum value of the bond angle at Ni (90°), the Ni—N bond distances and the preferred 'bite' of the chelate. Weak hydrogen bonds are formed among the amino group, water molecules and perchlorate O atoms. This hydrogen-bond network stabilizes the crystal packing and is similar to that found in the red macrocyclic ligand complex of copper(II) perchlorate (Lee, Lee, Juang & Chung, 1985), where hydrogen bond lengths range from 3.10 (5) to 3.39 (6) Å.

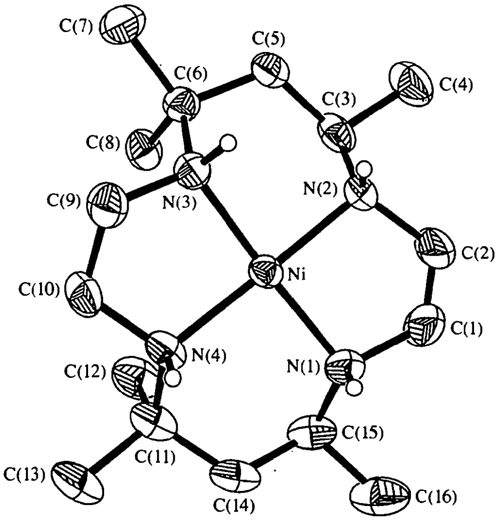


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of a single molecule of (I) with displacement ellipsoids scaled to 30% probability. H atoms attached to N atoms are shown as circles.

Experimental

The title Ni^{II} complex was prepared by reduction of (5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,14-diene)nickel(II) diperchlorate, $[Ni(1,4\text{-CT})](ClO_4)_2$ (Curtis, 1964, 1972; Lee, Wu & Chung, 1984). The complex was recrystallized from water.

Crystal data

$[Ni(C_{16}H_{36}N_4)](ClO_4)_2.H_2O$
$M_r = 560.1$
Monoclinic
$P2_1/c$
$a = 17.494\ (3)$ Å
$b = 9.172\ (2)$ Å
$c = 17.388\ (3)$ Å
$\beta = 116.7\ (1)°$
$V = 2492.1\ (13)$ Å^3
$Z = 4$
$D_x = 1.49$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7\text{–}18°$
$\mu = 1.044$ mm^{-1}
$T = 298$ K
Parallelepiped
0.41 × 0.34 × 0.16 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.53$, $T_{\max} = 0.85$
4520 measured reflections
4371 independent reflections

3025 observed reflections $[F > 4\sigma(F)]$
$R_{\text{int}} = 0.021$
$\theta_{\max} = 22.5°$
$h = -20 \rightarrow 18$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 18$
3 standard reflections monitored every 100 reflections intensity decay: 0.08%

Refinement

Refinement on F
$R = 0.0596$
$wR = 0.0581$
$S = 1.81$
3025 reflections
311 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.042$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0.2436 (1)	0.2230 (1)	0.7447 (1)	0.045 (1)
N(1)	0.2508 (3)	0.0484 (6)	0.8099 (3)	0.063 (2)
N(2)	0.1252 (3)	0.1768 (6)	0.6743 (3)	0.068 (2)
N(3)	0.2335 (3)	0.3839 (5)	0.6705 (3)	0.051 (2)
N(4)	0.3624 (3)	0.2738 (6)	0.8144 (3)	0.061 (2)
C(1)	0.1633 (5)	−0.0098 (10)	0.7751 (7)	0.124 (6)
C(2)	0.1111 (6)	0.0377 (12)	0.7044 (7)	0.198 (7)
C(3)	0.0681 (4)	0.2985 (8)	0.6736 (3)	0.064 (3)
C(4)	−0.0264 (4)	0.2531 (10)	0.6294 (5)	0.092 (4)
C(5)	0.0816 (4)	0.4256 (7)	0.6268 (4)	0.058 (3)
C(6)	0.1692 (4)	0.4990 (7)	0.6636 (4)	0.055 (3)
C(7)	0.1665 (5)	0.6191 (8)	0.6018 (4)	0.078 (4)
C(8)	0.1921 (4)	0.5647 (7)	0.7523 (4)	0.065 (3)
C(9)	0.3217 (4)	0.4316 (8)	0.6892 (4)	0.070 (3)
C(10)	0.3793 (4)	0.4168 (8)	0.7852 (4)	0.074 (3)
C(11)	0.3993 (4)	0.2627 (9)	0.9115 (4)	0.075 (3)
C(12)	0.3556 (5)	0.3747 (9)	0.9434 (5)	0.090 (4)
C(13)	0.4960 (4)	0.2897 (10)	0.9505 (4)	0.095 (4)
C(14)	0.3848 (4)	0.1088 (8)	0.9346 (4)	0.075 (3)
C(15)	0.2953 (4)	0.0589 (8)	0.9063 (4)	0.072 (3)
C(16)	0.2921 (5)	−0.0870 (10)	0.9465 (5)	0.110 (5)
Cl(1)	0.4292 (1)	−0.1653 (2)	0.7732 (2)	0.085 (1)
Cl(2)	0.0940 (1)	0.3024 (2)	0.9296 (1)	0.072 (1)
O(1)	0.5032 (5)	−0.2438 (14)	0.8255 (7)	0.232 (7)
O(2)	0.4134 (7)	−0.2147 (10)	0.6943 (6)	0.185 (6)
O(3)	0.4514 (8)	−0.0242 (8)	0.7872 (8)	0.223 (10)
O(4)	0.3655 (4)	−0.2002 (7)	0.7966 (4)	0.120 (4)
O(5)	0.0230 (4)	0.2453 (8)	0.8483 (4)	0.133 (4)
O(6)	0.1460 (4)	0.1810 (8)	0.9725 (4)	0.135 (4)
O(7)	0.1337 (4)	0.3990 (7)	0.9003 (4)	0.120 (4)
O(8)	0.0570 (4)	0.3622 (7)	0.9772 (3)	0.115 (3)
O(9)	0.2662 (9)	0.0672 (16)	0.6146 (7)	0.265 (9)

Table 2. *Selected geometric parameters (Å, °)*

Ni—N(4)	1.935 (4)	N(1)—C(15)	1.500 (9)
Ni—N(3)	1.915 (5)	N(1)—C(1)	1.471 (10)
Ni—N(1)	1.933 (6)	N(2)—C(3)	1.494 (9)
Ni—N(2)	1.921 (5)	N(2)—C(2)	1.442 (13)
Cl(2)—O(8)	1.374 (8)	C(6)—C(8)	1.532 (9)
Cl(2)—O(7)	1.359 (8)	C(6)—C(5)	1.527 (8)
Cl(2)—O(6)	1.419 (7)	C(6)—C(7)	1.526 (10)
Cl(2)—O(5)	1.496 (6)	C(5)—C(3)	1.499 (10)
Cl(1)—O(4)	1.384 (9)	C(3)—C(4)	1.535 (9)
Cl(1)—O(3)	1.342 (8)	C(2)—C(1)	1.235 (13)
Cl(1)—O(2)	1.350 (10)	C(15)—C(14)	1.487 (10)
Cl(1)—O(1)	1.401 (9)	C(15)—C(16)	1.522 (12)
N(4)—C(11)	1.516 (8)	C(9)—C(10)	1.519 (8)
N(4)—C(10)	1.484 (10)	C(11)—C(14)	1.520 (11)
N(3)—C(6)	1.506 (8)	C(11)—C(12)	1.527 (12)
N(3)—C(9)	1.494 (9)	C(11)—C(13)	1.533 (9)
N(4)—Ni—N(3)	89.1 (2)	Ni—N(2)—C(3)	111.4 (4)
N(4)—Ni—N(1)	93.6 (2)	Ni—N(2)—C(2)	106.0 (4)
N(3)—Ni—N(1)	174.4 (2)	C(3)—N(2)—C(2)	116.2 (7)
N(4)—Ni—N(2)	178.7 (2)	N(3)—C(6)—C(8)	110.3 (4)
N(3)—Ni—N(2)	89.6 (2)	N(3)—C(6)—C(5)	107.3 (5)
N(1)—Ni—N(2)	87.6 (2)	C(8)—C(6)—C(5)	110.8 (6)
O(8)—Cl(2)—O(7)	115.1 (5)	N(3)—C(6)—C(7)	110.3 (6)
O(8)—Cl(2)—O(6)	111.2 (4)	C(8)—C(6)—C(7)	109.7 (5)
O(7)—Cl(2)—O(6)	113.2 (5)	C(5)—C(6)—C(7)	108.4 (4)
O(8)—Cl(2)—O(5)	107.1 (4)	C(6)—C(5)—C(3)	119.2 (4)
O(7)—Cl(2)—O(5)	102.7 (4)	N(2)—C(3)—C(5)	108.6 (6)
O(6)—Cl(2)—O(5)	106.6 (4)	N(2)—C(3)—C(4)	111.5 (6)
O(4)—Cl(1)—O(3)	112.0 (8)	C(5)—C(3)—C(4)	109.7 (5)
O(4)—Cl(1)—O(2)	113.4 (6)	N(2)—C(2)—C(1)	120.2 (8)
O(3)—Cl(1)—O(2)	114.7 (8)	N(1)—C(15)—C(14)	109.3 (7)
O(4)—Cl(1)—O(1)	108.8 (6)	N(1)—C(15)—C(16)	110.5 (6)
O(3)—Cl(1)—O(1)	105.6 (7)	C(14)—C(15)—C(16)	111.6 (6)
O(2)—Cl(1)—O(1)	101.2 (7)	N(3)—C(9)—C(10)	108.8 (6)
Ni—N(4)—C(11)	118.8 (5)	N(4)—C(11)—C(14)	108.6 (5)
Ni—N(4)—C(10)	108.8 (3)	N(4)—C(11)—C(12)	109.1 (5)
C(11)—N(4)—C(10)	113.0 (5)	C(14)—C(11)—C(12)	111.0 (7)
Ni—N(3)—C(6)	115.7 (4)	N(4)—C(11)—C(13)	108.4 (6)
Ni—N(3)—C(9)	107.8 (3)	C(14)—C(11)—C(13)	108.4 (6)
C(6)—N(3)—C(9)	118.2 (5)	C(12)—C(11)—C(13)	111.4 (6)
Ni—N(1)—C(15)	117.8 (4)	N(1)—C(1)—C(2)	116.7 (10)
Ni—N(1)—C(1)	106.1 (5)	C(15)—C(14)—C(11)	118.4 (6)
C(15)—N(1)—C(1)	113.9 (7)	N(4)—C(10)—C(9)	108.6 (5)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[1,8-Bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(II) Bis(maleonitriledithiolato)nickelate(II)

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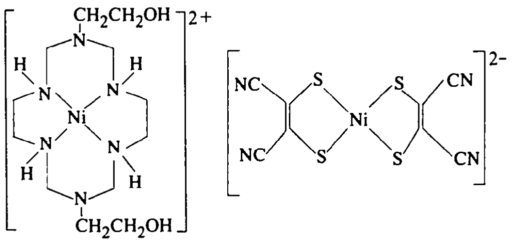
Abstract

In the solid state, the title compound, [1,3,6,8,10,13-hexaazacyclotetradecane-1,8-diylbis(2-ethanol)-N^3,N^6,N^{10},N^{13}]nickel(II) bis(maleonitriledithiolato-S,S')nickelate(II), $[Ni(C_{12}H_{30}N_6O_2)][Ni(C_4N_2S_2)_2]$, forms two-dimensional layers parallel to the (201) plane and its crystal structure is stabilized by N—H···O, N—H···S, C—H···N and O—H···S hydrogen bonds. The short S···Ni anion-to-cation contact of 3.5516 (8) Å is interpreted as a weak interaction between these atoms.

Comment

Salts of the metal dithiolate complex anions $[M(\mathrm{mnt})_2]^{n-}$ [M = Ni, Zn; mnt = maleonitriledithiolato(2−)], with a variety of cations, are found to possess interesting magnetic, electric and optical properties (Manoharan, Noordik, de Boer & Keijzers, 1981; Clemenson, 1990). As part of our work on the synthesis and characterization of such complexes (Shan, Zhang, You, Fun & Sivakumar, 1996), we report the structure determination of the title compound, [1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(II) bis(maleonitriledithiolato)nickelate(II), (I).



(I)

In the macrocyclic nickel cation, the Ni atom, which is located at a centre of inversion, is coordinated to four N atoms of the macrocyclic ligand (Fig. 1). The Ni—N distances of 1.919 (2) and 1.929 (2) Å are similar to those found in other nickel(II) tetraaza macrocycles (Thom, Fox & Boeyens, 1984). The Ni atom in the anion also lies on an inversion centre and is surrounded by a square plane of four S atoms.

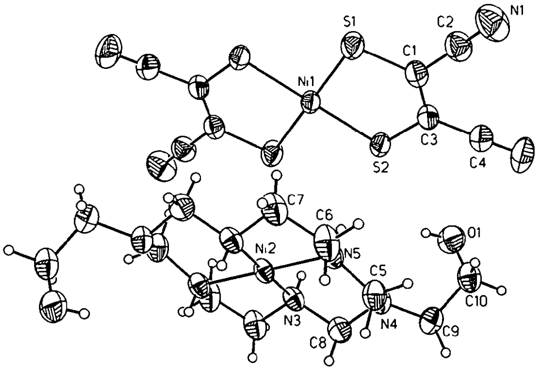


Fig. 1. An ellipsoid plot of the cation and anion of (I) showing the atom-numbering scheme and ellipsoids at the 50% probability level.

A projected view of the packing of the molecules in a unit cell down the b axis is shown in Fig. 2. The molecules are connected through hydrogen bonds forming two-dimensional layers (sheets) parallel to the (201) plane; C—H···N hydrogen bonds link the molecules into chains [C5···N2^{i} 3.377 (4) Å and C5—H5A···N2 162 (3)°; symmetry code: (i) $-x$, y, $\frac{3}{2}-z$]. The N—H···S, N—H···O and O—H···S hydrogen bonds cross-link these chains into sheets and also establish

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