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

Hg—N	2.35 (1)	Hg—Br	2.837 (1)
N^i—Hg—N	180	Br—Hg—Br^{ii}	88.08 (4)
N—Hg—Br	90.03 (2)	Br—Hg—Br^{iii}	180
N—Hg—Br^{ii}	89.99 (2)	Br^i—Hg—Br^{iii}	180

Symmetry codes: (i) $-x, y, z$; (ii) $x, y, -z$; (iii) $x, -y, -z$.

The major residual difference electron-density features lie 0.96 Å from the Hg atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: local programs.

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Bis(dihydrogen phosphato-*O*)[(1*RS*,4*RS*,8*SR*,11*SR*)-1,4,8,11-tetraazacyclotetradecane-κ^4N]nickel(II) monohydrate

Saoussen Namouchi-Cherni, Ahmed Driss and Tahar Jouini

Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisia. E-mail: tahar.jouini@fst.rnu.tn

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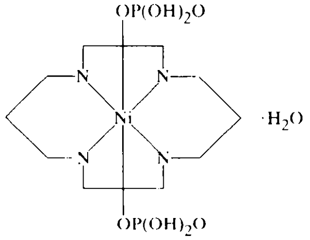
Abstract

The Ni^{II} ion in the title compound, $[Ni(H_2PO_4)_2(C_{10}H_{24}N_4)]\cdot H_2O$, is six-coordinate in a distorted square-bipyramidal environment. Four N atoms from the tetraaza-macrocycle are in a square-planar arrangement [average Ni—N distance = 2.071 (2) Å] and two O atoms, one from each dihydrogen phosphate ion, are axial [average Ni—O distance = 2.144 (2) Å]. The structure of the title complex forms a three-dimensional framework, which delimits intersecting *b*-axis and *c*-axis tunnels. Two types of hydrogen bonds, O—H···O and N—H···O, ensure the cohesion and stability of the molecular packing.

Comment

The title compound belongs to the family of 14-membered macrocyclic amines. Their coordination behavior with transition metals has been widely studied both chemically and crystallographically, but the reported crystal structures of macrocyclic amines and their salts are rather few in number. The crystal structure of bis(dihydrogen phosphato-*O*)(1,4,8,11-tetraazacyclotetradecane-κ^4N)nickel(II) monohydrate, (I), is composed of nickel complex molecules. Each complex is connected to six others by means of hydrogen bonding, strong enough to form a three-dimensional framework, which delimits intersecting tunnels where water molecules are located (Fig. 1). The coordination geometry around the Ni^{II} ion is slightly distorted square bipyramidal with four equatorial N atoms and two axial O atoms, one



(I)

from each dihydrogen phosphate ion (Fig. 2). The configurations of the four chiral N-atom centers are 1*RS*, 4*RS*, 8*SR* and 11*SR*. Each $[Ni(C_{10}H_{24}N_4)]$ group is anchored by N—H···O hydrogen bonds to neighboring $H_2PO_4^-$ tetrahedra. The latter anion is connected to three others through strong O—H···O hydrogen bonds to form infinite ribbons spreading in the [001] direction.

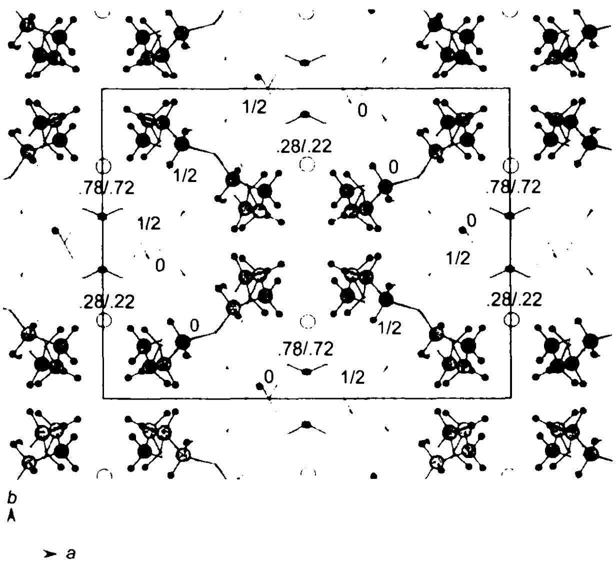


Fig. 1. Projection of the structure of (I) along [001]. The hydrogen bonds in the *a* direction between the phosphate groups are shown as dashed lines, but those along **c** are obscured.

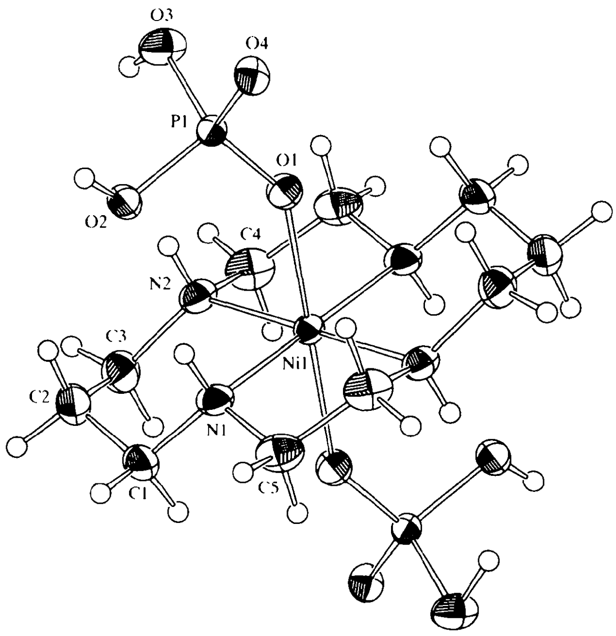


Fig. 2. *ZORTEP* (Zsolnai, 1994) probability view (50%) of $[Ni(H_2PO_4)_2(C_{10}H_{24}N_4)]$ complex molecule. H atoms are shown as spheres of arbitrary radii and the hydrate molecule has been omitted.

Electronic spin resonance measurements shows that this material is diamagnetic. This behavior is expected because of the square-planar geometry of the nickel complex, the Ni atom being surrounded by the four secondary N atoms of the tetraazamacrocycle. The values for the Ni—N bond lengths [2.063 (2) and 2.079 (2) Å for Ni—N1 and Ni—N2, respectively] lie in the normal range for low-spin nickel(II) complexes with four coplanar N-donor atoms (Ruiz *et al.*, 1993; Hübener *et al.*, 1995; Namouchi-Cherni *et al.*, 1998). The observed lengthening of Ni—O [2.144 (2) Å] compared with Ni—N may be due to steric constraints introduced by the coordinating bulky H_2PO_4 ligand. This distance is similar to that reported for [*N*-(3-aminopropyl)-1,3-propanediamine]diaquasulfatonickel(II) monohydrate (Mukherjee *et al.*, 1995) and in the similar structure of bis(dihydrogen phosphato-*O*)[1,4,8,11-tetraazacyclotetradecane-κ^4N]nickel(II) (Namouchi-Cherni *et al.*, 1998). The geometrical features of the $H_2PO_4^-$ groups are quite regular and can be compared to those observed in the latter structure (Namouchi-Cherni *et al.*, 1998).

The structure of the title complex delimits intersecting *b*-axis and *c*-axis tunnels, where water molecules are located. The H atoms of N—H and O—H of $H_2PO_4^-$ form hydrogen bonds to neighboring O atoms and therefore stabilize the complex.

Experimental

The title complex was prepared by hydrothermal crystallization in a sealed vessel from ethanolic solutions of nickel nitrate, 1,4,8,11-tetraazacyclotetradecane, phosphoric acid and water.

Crystal data

$[Ni(H_2PO_4)_2(C_{10}H_{24}N_4)]\cdot H_2O$
$M_r = 471.03$
Monoclinic
*C*2/*c*
$a = 16.991\ (2)$ Å
$b = 12.307\ (1)$ Å
$c = 9.500\ (2)$ Å
$\beta = 107.50\ (2)^\circ$
$V = 1894.6\ (5)$ Å^3
$Z = 4$
$D_x = 1.651$ Mg m^{-3}
$D_m = 1.653\ (3)$ Mg m^{-3}
D_m measured by flotation in C_2H_5I/C_6H_6

Mo *K*α radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.32\text{–}14.78^\circ$
$\mu = 1.24$ mm^{-1}
$T = 293\ (2)$ K
Hexagonal
0.65 × 0.29 × 0.11 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer

1840 reflections with $I > 2\sigma(I)$

$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{\min} = 0.69$, $T_{\max} = 0.87$
2192 measured reflections
2062 independent reflections

$R_{\rm int} = 0.008$
$\theta_{\max} = 26.97°$
$h = -21 \rightarrow 20$
$k = -15 \rightarrow 0$
$l = 0 \rightarrow 12$
1 standard reflection
frequency: 120 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.067$
$S = 1.08$
2062 reflections
175 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.4068P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni1—N1	2.063 (2)	P1—O2	1.581 (2)
Ni1—N2	2.079 (2)	O2—HO2	0.78 (4)
Ni1—O1	2.144 (2)	O3—HO3	0.76 (5)
P1—O1	1.486 (2)	N1—HN1	0.87 (4)
P1—O4	1.514 (2)	N2—HN2	0.83 (3)
P1—O3	1.571 (2)		
N1$^{\rm i}$—Ni1—N1	180.0	O1$^{\rm i}$—Ni1—O1	180.0
N1—Ni1—N2$^{\rm i}$	85.56 (9)	O1—P1—O4	116.2 (1)
N1—Ni1—N2	94.44 (9)	O1—P1—O3	112.4 (1)
N2$^{\rm i}$—Ni1—N2	180.0	O4—P1—O3	104.7 (1)
N1—Ni1—O1$^{\rm i}$	90.87 (8)	O1—P1—O2	106.5 (1)
N2—Ni1—O1$^{\rm i}$	90.16 (8)	O4—P1—O2	110.4 (1)
N1—Ni1—O1	89.13 (8)	O3—P1—O2	106.3 (1)
N2—Ni1—O1	89.84 (8)	P1—O1—Ni1	145.1 (1)

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

The θ-scan width was $(0.6 + 0.6\tan\theta)°$. Data were corrected for Lorentz–polarization effects. The structure was solved by heavy-atom methods and refined by full-matrix least squares. The O atom of the water molecule is disordered. It was refined isotropically and the corresponding H atoms were not located. H atoms of the organic molecule and the phosphate group were located from difference Fourier syntheses and were refined isotropically. The C—H distances are in the range 0.91 (4)–0.99 (4) Å. The two N—H distances are 0.83 (3) and 0.87 (4) Å, and the two O—H distances are 0.76 (5) and 0.78 (4) Å. The $U_{\rm iso}$ values of the H atoms vary from 0.03 (1) to 0.07 (1) Å^2.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992; Enraf-Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1417). Services for accessing these data are described at the back of the journal.

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Chiral bisphosphanes. V.† Chloro{*rac*,*trans*-1-[chloro(piperidin-1-yl)phosphino]-2-[bis(piperidin-1-yl)phosphino]cyclopentane-*P*,*P*′}neopentylplatinum(II) acetone solvate

LUTZ DAHLENBURG AND STEFAN MERTEL

Institut für Anorganische Chemie, Universität Erlangen–Nürnberg, Egerlandstraße 1, 91058 Erlangen, Germany. E-mail: dahlbg@anorganik.chemie.uni-erlangen.de

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Abstract

In the title compound, $[\mathrm{PtCl(C_5H_{11})(C_{20}H_{38}ClN_3P_2)]\cdot(CH_3)_2CO}$, coordination about the central metal deviates slightly from ideal square-planar geometry. The $-\mathrm{P(Cl)}$-$\mathrm{NC_5H_{10}}$ substituent resides in a *trans* position with respect to the neopentyl group, with the two remaining *trans* coordination sites being occupied by the chloro ligand and the $-\mathrm{P(NC_5H_{10})_2}$ residue of the chelating bisphosphane ligand.

Comment

The title complex, (I), was prepared as part of our continuing studies of Group 8 metal complexes derived

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† Part IV: Dahlenburg & Kaunert (1998).