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Acta Cryst. (1998). C54, 1768–1770

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

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(Received 16 January 1998; accepted 11 June 1998)

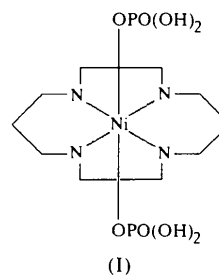
Abstract

The Ni^{II} ion in the title compound, [Ni(H₂PO₄)₂·(C₁₀H₂₄N₄)], is six-coordinate in a distorted square bipyramidal environment. The crystal structure consists of two molecules of the title compound, each residing on a centre of inversion. Four tetramine N atoms of the macrocyclic ligand are equatorial [average Ni—N distance = 2.07 (1) Å] and two O atoms, one from each dihydrogen phosphate ion, are axial [average Ni—O distance = 2.12 (3) Å]. The structure of the title complex consists of a three-dimensional framework, which delimits intersecting *a*-axis, *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 Ni^{II} complexes of cyclic tetramines have been studied extensively because of their diverse stereochemistry. We describe here the crystal structure of the title compound, (I). There are two crystallographically distinct molecules in the asymmetric unit. The coordination geometry around each of the central atoms is the same, while the interatomic distances and angles

differ slightly between the two units centred on Ni1 and Ni2. These units are stacked in alternating sheets normal to the *c* axis at *z* = 0 and *z* = $\frac{1}{2}$, respectively. In each sheet, the molecules centred on Ni1 and Ni2 are connected by strong hydrogen bonds to form ribbons running along [010] and [100], respectively. The sheets are held together by hydrogen bonds established between ribbons in perpendicular directions, giving rise to a three-dimensional framework which delimits intersecting tunnels. Each [Ni(C₁₀H₂₄N₄)] group is anchored by N—H···O hydrogen bonds to different H₂PO₄⁻ tetrahedra. The latter anion is connected to three other anions through strong O—H···O hydrogen bonds to form infinite ribbons spreading in the [001] direction.



The coordination geometry around each Ni^{II} ion is slightly distorted square bipyramidal with four equatorial N atoms and two axial O atoms. The configurations of the four chiral N-atom centres are 1*SR*, 4*SR*, 8*RS* and 11*RS*. The Ni—N distances [2.056 (1)–2.090 (1) Å] agree with corresponding values found in similar nickel complexes (Mukherjee *et al.*, 1995). The observed lengthening of Ni1—O1 [2.099 (1) Å] and Ni2—O5 [2.141 (1) Å] compared with Ni—N may be due to steric constraints introduced by the coordinating bulky H₂PO₄ ligand. These distances are similar to those reported for [*N*-(3-aminopropyl)-1,3-propanedi-

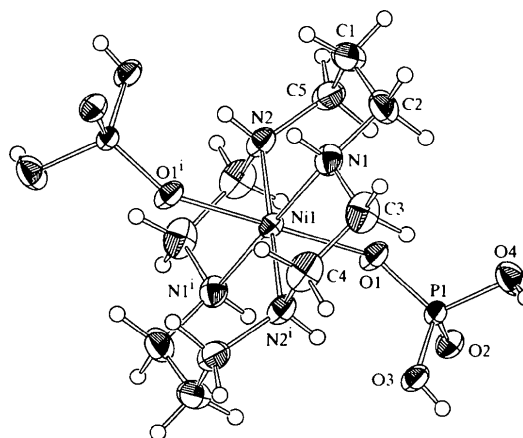


Fig. 1. ZORTEP (Zsolnai, 1994) probability view (50%) of one of the two independent molecules of (I). H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $-x, -y, -z$.]

amine]diaquasulfatonickel(II) monohydrate (Mukherjee *et al.*, 1995).

Each Ni atom lies exactly in the plane defined by the four surrounding N atoms (as required by symmetry). The planarity of this environment is similar to the cases of copper(II) and nickel(II) complexes of 4-methyl-4,7-diazadecane-1,10-diamine (Lu *et al.*, 1997). The geometrical features of the H_2PO_4^- groups are quite regular and can be compared with those observed in similar structures (Abdellahi & Jouini, 1995).

The structure of the title complex delimits intersecting *a*-axis, *b*-axis and *c*-axis tunnels within which the d_{\min} and d_{\max} dimensions are 2.73 (5)/3.82 (5), 2.76 (5)/2.81 (3) and 2.76 (5)/3.82 (5) Å, respectively. It is stabilized by strong O—H...O and weak N—H...O hydrogen bonds.

Experimental

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

Crystal data

$[\text{Ni}(\text{H}_2\text{PO}_4)_2(\text{C}_{10}\text{H}_{24}\text{N}_4)]$
 $M_r = 453.01$

Triclinic

$P\bar{1}$

$a = 9.4915 (10) \text{ \AA}$

$b = 10.3342 (8) \text{ \AA}$

$c = 9.1930 (9) \text{ \AA}$

$\alpha = 89.607 (7)^\circ$

$\beta = 90.489 (8)^\circ$

$\gamma = 93.555 (8)^\circ$

$V = 899.93 (15) \text{ \AA}^3$

$Z = 2$

$D_x = 1.672 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical ψ scan (North *et al.*, 1968)

$T_{\min} = 0.77$, $T_{\max} = 0.82$

3760 measured reflections

3529 independent reflections

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.0570$

$S = 1.066$

3529 reflections

342 parameters

All H atoms refined

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 11.66\text{--}15.04^\circ$

$\mu = 1.303 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Cubic

$0.37 \times 0.37 \times 0.15 \text{ mm}$

Brown

3127 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.008$

$\theta_{\max} = 25.97^\circ$

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = 0 \rightarrow 11$

1 standard reflection

frequency: 120 min

intensity decay: 0.6%

$\Delta\rho_{\max} = 0.281 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.282 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0081 (8)

$$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 0.4246P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Ni1—N2	2.072 (1)	P1—O3	1.574 (1)
Ni1—N1	2.075 (1)	P2—O5	1.490 (1)
Ni1—O1	2.099 (1)	P2—O6	1.518 (1)
Ni2—N3	2.056 (1)	P2—O8	1.567 (1)
Ni2—N4	2.090 (1)	P2—O7	1.569 (1)
Ni2—O5	2.141 (1)	O3—HO3	0.72 (2)
P1—O1	1.486 (1)	O4—HO4	0.75 (3)
P1—O2	1.516 (1)	O7—HO7	0.79 (3)
P1—O4	1.571 (1)	O8—HO8	0.83 (3)
N2'—Ni1—N1'	85.09 (6)	O1—P1—O4	110.40 (8)
N2—Ni1—N1'	94.91 (6)	O2—P1—O4	107.96 (8)
N2—Ni1—N1	85.09 (6)	O1—P1—O3	108.28 (7)
N2—Ni1—O1'	92.03 (5)	O2—P1—O3	110.39 (7)
N1—Ni1—O1'	90.33 (5)	O4—P1—O3	105.94 (8)
N2—Ni1—O1	87.97 (5)	O5—P2—O6	115.44 (7)
N1—Ni1—O1	89.67 (5)	O5—P2—O8	106.30 (7)
N3—Ni2—N4''	94.48 (6)	O6—P2—O8	109.74 (7)
N3—Ni2—N4	85.52 (6)	O5—P2—O7	110.26 (8)
N4—Ni2—O5''	94.60 (5)	O6—P2—O7	108.70 (7)
N3''—Ni2—O5	89.91 (6)	O8—P2—O7	105.97 (9)
N3—Ni2—O5	90.09 (6)	P1—O1—Ni1	145.25 (8)
N4—Ni2—O5	85.40 (5)	P2—O5—Ni2	129.71 (7)
O1—P1—O2	113.61 (7)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, 1-z$.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O3—HO3...O2'	0.72 (2)	1.87 (3)	2.596 (2)	174 (3)
O4—HO4...O6'	0.75 (3)	1.87 (3)	2.616 (2)	170 (3)
O7—HO7...O2	0.79 (3)	1.84 (3)	2.628 (2)	171 (3)
O8—HO8...O6''	0.83 (3)	1.78 (3)	2.612 (2)	173 (2)
N1—HN1...O7	0.85 (2)	2.25 (2)	3.087 (2)	165 (2)
N2—HN2...O3	0.84 (2)	2.19 (2)	2.992 (2)	160 (2)
N3—HN3...O6	0.83 (2)	2.42 (2)	3.185 (2)	152 (2)
N3—HN3...O4'	0.83 (2)	2.58 (2)	3.295 (2)	145 (2)
N4—HN4...O8'''	0.80 (2)	2.52 (2)	3.239 (2)	149 (2)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$.

For data collection, the θ -scan width was $(0.75 + 0.5\text{tan}\theta)^\circ$. Data were corrected for Lorentz and polarization effects.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Maciček & Yordanov, 1992; Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL93*.

Thanks are due to Mr T. Labassi and Mr S. Barkalah, Faculty of Sciences, Tunis, Tunisia, for assistance with the English in the manuscript.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1017). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1770–1773

Investigations of Complexes of Copper(II) Chloride with Phenylpyrazoles

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(Received 9 April 1998; accepted 25 June 1998)

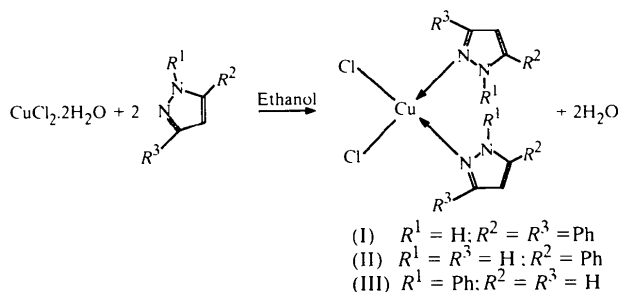
Abstract

The crystal structures of dichlorobis(3,5-diphenylpyrazole-*N*²)copper(II), [CuCl₂(C₁₅H₁₂N₂)₂], (I), dichlorobis(5-phenylpyrazole-*N*²)copper(II), [CuCl₂(C₉H₈N₂)₂], (II), and dichlorobis(1-phenylpyrazole-*N*²)copper(II), [CuCl₂(C₉H₈N₂)₂], (III), have been determined from X-ray diffraction data. There are significant differences in the coordination of the Cl[−] ions to the Cu²⁺ ion. The coordination of the Cu²⁺ ion is distorted square pyramidal in compounds (I) and (II), and distorted tetrahedral in (III). All available N—H groups form hydrogen bonds, which are intra- and intermolecular in (I), and intramolecular in (II). An N—H group in (I) forms a bifurcated hydrogen bond. Intermolecular interactions between neighbouring molecules form dimers and chains in (I) and (II), respectively.

Comment

This paper deals with X-ray crystal structure studies on copper(II) chloride complexes of phenylpyrazoles. Previous studies on copper(II)-substituted pyrazole complexes were undertaken on their protolytic properties and on the influence of the nature and position of substituents on metal complexation (Kostka & Strawiak, 1982; Goslar *et al.*, 1987, 1988; Nasiadek, 1985).

The X-ray structure analyses of dichlorobis(3,5-diphenylpyrazole)copper(II), (I), dichlorobis(5-phenylpyrazole)copper(II), (II), and dichlorobis(1-phenylpyrazole)copper(II), (III), were undertaken to elucidate the geometry around the Cu²⁺ ion.



In (I), there is a five-coordinated Cu²⁺ ion with distorted square-pyramidal coordination. The basal plane is defined by two *cis*-N atoms of two phenylpyrazole ligands and two Cl[−] ions, with the apical Cl¹ ligand being shared by two adjacent complexes [symmetry code: (i) $-x, 1-y, -z$]; thus, the molecules form dimers. Moreover, an intermolecular N21—H21...Cl2¹ hydrogen bond also leads to dimerization. The N21 atom is also involved in an intramolecular N21—H21...Cl1 hydrogen bond, but this three-centre interaction is weak, as indicated by the long H...Cl distances. A stronger intramolecular hydrogen bond is formed by the H11 atom (N11—H11...Cl2; see Table 2 and Fig. 1). The base of the distorted square pyramid is not planar; the deviations of the N12, N22, Cl1 and Cl2 atoms from their weighted least-squares plane (Nardelli, 1996) are $-0.374(3)$, $0.530(4)$, $-0.038(1)$ and $0.052(1)$ Å, respectively, and $-0.226(1)$ Å for Cu1. The C255 atom is disordered over two positions, the most populated site having an occupation factor of 0.68 (5).

In (II), the geometry around the Cu²⁺ ion is best described as square pyramidal with the basal plane formed by the two *trans*-N atoms of the phenylpyrazole ligands and two Cl[−] ions; the fifth apical site is occupied by one Clⁱⁱ ion from a neighbouring molecule [symmetry code: (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$]. Thus, the molecules form chains running along the *a* axis. The base of the pyramid is not planar; the deviations of the N12, Cl1, N22 and Cl2 atoms from their weighted least-squares plane (Nardelli, 1996) are $0.463(4)$, $-0.050(1)$, $0.451(4)$ and $-0.062(1)$ Å, respectively, with Cu1 displaced by $0.359(1)$ Å. The N11 and N21 atoms form intramolecular hydrogen bonds (N11—H11...Cl2 and N21—H21...Cl2; see Table 4 and Fig. 2).

In (III) (Fig. 3), the four-coordinated Cu²⁺ ion lies on a twofold axis, with a distorted tetrahedral geometry, being bonded to two Cl[−] ions and two N atoms of two phenylpyrazole ligands. The dihedral angle between the N12/Cu1/Cl1 plane and its symmetry related plane at $(2-x, 1-y, z)$ is $123.0(1)^\circ$.