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Tetraaqua[3-(1*H*-imidazol-4-yl)-2-(6-{*N*-[(1*H*-imidazol-4-yl)-1-carboxylatoethyl]carbamoyl}-2-pyridylcarbonylamino)propionato]nickel(II) pentahydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.041
wR factor = 0.114
Data-to-parameter ratio = 13.3

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

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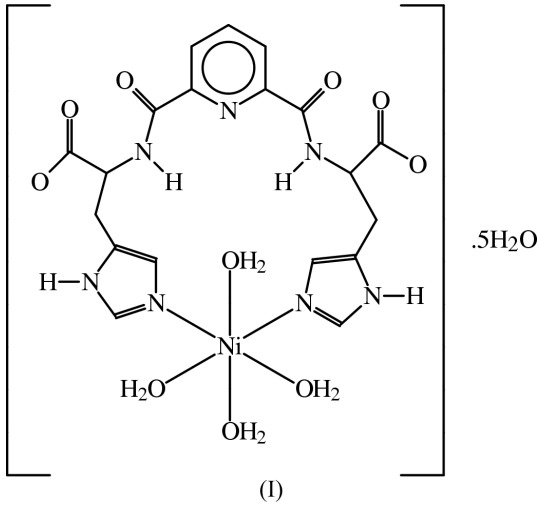
The preparation and crystal structure of the title complex, $[Ni(BHISP)(H_2O)_4]\cdot 5H_2O$, where $BHISP^{2-}$ is 3-(1*H*-imidazol-4-yl)-2-(6-{N-[(1*H*-imidazol-4-yl)-1-carboxylatoethyl]carbamoyl}-2-pyridylcarbonylamino)propionate ($C_{19}H_{17}N_7O_6$), are presented. The Ni^{II} ion is coordinated by two imidazole N atoms of each histidine arm of the $BHISP^{2-}$ ligand, and four water molecules complete the octahedral environment of the complex.

Comment

Urease, a nickel-dependent metalloenzyme, catalyzes the hydrolysis of urea to form ammonia and carbon dioxide (Hausinger, 1993). In 1995, nearly 70 years after urease was first isolated by Summer (1926), Jabri and co-workers announced the X-ray crystal structure of the enzyme from *Klebsiella aerogenes* (Jabri *et al.*, 1995). The active site of urease consists of two Ni atoms 3.5 Å apart bridged by a carbamate group and other ligands comprised of histidine N atoms, a monodentate carboxylate of aspartate and a water molecule.



(I)

As part of a continuing investigation to provide a model for the active site of urease, we prepared the diacid 3-(1*H*-imidazol-4-yl)-2-(6-{N-[(1*H*-imidazol-4-yl)-1-ethoxycarbonylethyl]carbamoyl}-2-pyridylcarbonylamino)propionic acid (H_2BHISP), as a colourless powder in 95% yield, by simple basic hydrolysis of HPH-Pep (Otsuka *et al.*, 1996). The diacid has two histidine units linked to pyridine by amide bonds and it has, in principle, a good chance of forming a binuclear two-coordinate Ni^{II} complex. The reaction of aqueous solutions of H_2BHISP and $Ni(ClO_4)_2$ in the presence of sodium acetate

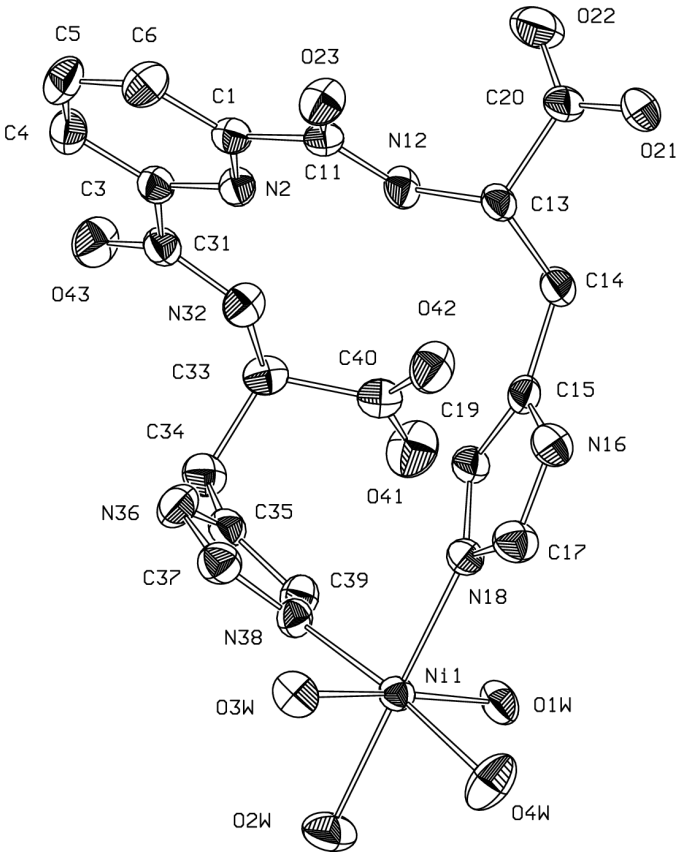


Figure 1
A view of the structure of (I) showing ellipsoids at the 40% probability level and the atom-numbering scheme.

did not lead to the desired binuclear nickel(II) complex but instead led to the title compound, $[Ni(BHISP)(H_2O)_4]\cdot 5H_2O$, (I).

The asymmetric unit of (I) consists of one neutral molecule of $[Ni(BHISP)(H_2O)_4]$ and five molecules of water of crystallization. The coordination environment around the Ni atom is slightly distorted octahedral, and the two imidazole N atoms occupy the *cis* positions (Fig. 1). The Ni—O bond distances are 2.038 (2)–2.110 (2) Å and the *cis*–O—Ni—O angles are 87.63 (10)–89.99 (10)° (Table 1). The Ni—N and Ni—O bond lengths are in agreement with the expected values for Ni^{II} complexes and they are comparable with other tetraaquanickel(II) complexes (McDougall & Hancock, 1980; Palopoli *et al.*, 1988; Cherni *et al.*, 1999). The multidentate $BHISP^{2-}$ ligand shows a particular manner of coordination, *i.e.* only the N atoms from the imidazole rings are coordinated to the Ni atom. The dihedral angle between the imidazole rings is 76.9 (1)°, while the pyridine, amide and carboxylate sites remaining uncoordinated.

There are intramolecular hydrogen bonds from the amide groups (N12 and N32) to the pyridine N2 atom, with N32—H32 forming a bifurcated hydrogen bond to the carboxylate O42 atom (Table 2). In the $BHISP^{2-}$ ligand, the two carboxylate pendant arms are deprotonated. The C—O bond lengths vary from 1.234 (4) to 1.250 (4) Å demonstrating, that the negative charges are delocalized. The presence of several water molecules and several acceptor sites in the ligand framework results in an extensive hydrogen-bond network.

Experimental

A stirred mixture of H_2BHISP, $Ni(ClO_4)_2.6H_2O$ and sodium acetate trihydrate (1:2:12) in water was heated at 353 K for 30 min and the resulting solution cooled to room temperature. The insoluble residue was filtered off to obtain a green solution, from which crystals of (I) were collected after one week. Analysis, calculated for $C_{19}H_{35}N_7NiO_{15}$: C 34.56, H 5.34, N 14.85%; found: C 34.19, H 5.16, N 14.98%.

Crystal data

$[Ni(C_{19}H_{17}N_7O_6)(H_2O)_4]\cdot 5H_2O$
M_r = 660.25
Triclinic, $P\overline{1}$
a = 9.610 (2) Å
b = 11.313 (2) Å
c = 13.455 (3) Å
α = 80.96 (3)°
β = 81.45 (3)°
γ = 77.78 (3)°
V = 1401.8 (5) Å^3
Z = 2
D_x = 1.564 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 9.8–15.3°
μ = 0.78 mm^{-1}
T = 293 (2) K
Prismatic, blue
0.47 × 0.33 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (*PLATON*; Spek, 1990)
T_{min} = 0.688, T_{max} = 0.793
5488 measured reflections
5160 independent reflections
3865 reflections with $I > 2\sigma(I)$'
R_{int} = 0.020
θ_{max} = 25.5°
$h = -11 \rightarrow 0$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections every 200 reflections frequency: 120 min intensity decay: 3.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.114
S = 1.04
5160 reflections
388 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 1.1893P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N38	2.038 (3)	Ni1—O2*W*	2.110 (2)
Ni1—O4*W*	2.038 (2)	O21—C20	1.250 (4)
Ni1—O1*W*	2.051 (2)	O22—C20	1.242 (4)
Ni1—O3*W*	2.092 (2)	O41—C40	1.234 (4)
Ni1—N18	2.098 (2)	O42—C40	1.249 (4)
N38—Ni1—O4*W*	174.42 (10)	O3*W*—Ni1—N18	92.56 (10)
N38—Ni1—O1*W*	92.02 (10)	N38—Ni1—O2*W*	87.41 (10)
O4*W*—Ni1—O1*W*	88.96 (10)	O4*W*—Ni1—O2*W*	87.10 (11)
N38—Ni1—O3*W*	91.20 (10)	O1*W*—Ni1—O2*W*	89.99 (10)
O4*W*—Ni1—O3*W*	87.63 (10)	O3*W*—Ni1—O2*W*	88.01 (10)
O1*W*—Ni1—O3*W*	176.13 (9)	N18—Ni1—O2*W*	179.36 (10)
N38—Ni1—N18	92.88 (10)	O22—C20—O21	126.1 (3)
O4*W*—Ni1—N18	92.62 (11)	O41—C40—O42	125.0 (3)
O1*W*—Ni1—N18	89.42 (10)		
N2—C3—C31—N32	7.0 (4)	C11—N12—C13—C14	163.9 (3)
C3—C31—N32—C33	177.1 (3)	C11—N12—C13—C20	−74.1 (4)
N2—C1—C11—N12	4.2 (4)	C31—N32—C33—C34	−78.0 (4)
C1—C11—N12—C13	−179.4 (3)	C31—N32—C33—C40	160.1 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O21^{i}	0.85	1.90	2.748 (3)	177
O1W—H1WB···O21^{ii}	0.81	2.02	2.817 (3)	173
O2W—H2WA···O9W	0.79	2.04	2.800 (11)	162
O2W—H2WA···O9W'	0.79	1.93	2.708 (11)	170
O2W—H2WB···O23^{ii}	0.81	2.14	2.923 (3)	166
O3W—H3WB···O41^{iii}	0.79	1.91	2.691 (3)	171
O3W—H3WA···O7W^{iv}	0.86	1.96	2.803 (4)	168
O4W—H4WA···O5W^{v}	0.87	1.92	2.784 (4)	169
O4W—H4WB···O5W	0.93	1.82	2.713 (4)	161
N12—H12···N2	0.86	2.16	2.653 (4)	116
N16—H16···O8W^{i}	0.85	2.18	2.968 (4)	154
N32—H32···N2	0.83	2.28	2.657 (4)	108
N32—H32···O42	0.83	2.24	2.619 (4)	108
N36—H36···O23^{vi}	0.92	2.35	3.170 (4)	148
O5W—H5WA···O41^{vii}	0.91	2.00	2.836 (4)	153
O5W—H5WB···O22^{i}	0.90	1.85	2.743 (4)	173
O6W—H6WA···O42	1.03	1.69	2.713 (4)	171
O6W—H6WB···O43^{viii}	1.00	1.90	2.877 (4)	164
O7W—H7WA···O43	0.95	1.86	2.789 (4)	166
O7W—H7WB···O22^{viii}	0.93	1.96	2.857 (4)	163
O8W—H8WA···O42	1.06	1.76	2.808 (4)	167
O8W—H8WB···O21^{i}	1.05	1.89	2.920 (4)	167
O9W—H9WA···O8W^{vii}	1.01	1.88	2.871 (12)	167
O9W—H9WB···O6W^{ix}	1.00	1.86	2.831 (12)	165
O9W'—H9WC···O8W^{vii}	0.99	1.83	2.717 (11)	148
O9W'—H9WD···O6W^{ix}	0.99	1.78	2.752 (11)	166

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x, y-1, z$; (iii) $1+x, y, z$; (iv) $-x, -y, 1-z$; (v) $1-x, -y, -z$; (vi) $-x, 1-y, 1-z$; (vii) $-x, -y, -z$; (viii) $-1-x, 1-y, 1-z$; (ix) $1+x, y-1, z$.

H atoms attached to C atoms, clearly revealed in difference syntheses, were added at calculated positions and included in the structure-factor caculations, with C—H distances and U_{iso} values taken from the default settings of the refinement program. H atoms of the water molecules and those bonded to N atoms were found from difference Fourier maps. These atoms were refined with positional constraints and with isotropic displacement parameters were constrained to be 1.2 times the equivalent isotropic displacement parameter of the parent atom. One water molecule of crystallization (O9W) was found disordered and it was split into two positions with 0.5 site occupancy.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET*4 in *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai *et al.*, 1996); software used to prepare material for publication: *SHELXL*97.

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