Table 1. Selected geometric parameters (Å, °)

Pr1—O2^i	2.4881 (16)	O1—Pr1^{iv}	2.5313 (15)
Pr1—O5	2.4883 (18)	O2—C1	1.263 (2)
Pr1—O7	2.5006 (18)	O2—Pr1^v	2.4881 (16)
Pr1—O4	2.5070 (15)	O2—Pr1^{iv}	2.7607 (16)
Pr1—O8	2.5298 (18)	O3—C4	1.259 (2)
Pr1—O1^{ii}	2.5313 (15)	O3—Pr1^{vi}	2.5313 (16)
Pr1—O3^{iii}	2.5313 (16)	O4—C4	1.248 (3)
Pr1—O6	2.6352 (19)	N1—C3	1.485 (3)
Pr1—O3	2.7603 (17)	N1—C2	1.487 (3)
Pr1—O2^{ii}	2.7607 (16)	C1—C2	1.510 (3)
O1—C1	1.245 (2)	C3—C4	1.507 (3)

O2^i—Pr1—O5	73.43 (6)	O4—Pr1—O6	84.77 (6)
O2^i—Pr1—O7	136.02 (6)	O8—Pr1—O6	135.42 (6)
O5—Pr1—O7	135.51 (6)	O1^{ii}—Pr1—O6	65.98 (6)
O2^i—Pr1—O4	111.10 (5)	O3^{iii}—Pr1—O6	140.11 (6)
O5—Pr1—O4	142.20 (6)	O2^i—Pr1—O3	62.11 (5)
O7—Pr1—O4	68.17 (6)	O5—Pr1—O3	121.29 (6)
O2^i—Pr1—O8	81.54 (6)	O7—Pr1—O3	103.18 (6)
O5—Pr1—O8	69.08 (7)	O4—Pr1—O3	48.99 (5)
O7—Pr1—O8	134.31 (6)	O8—Pr1—O3	68.26 (6)
O4—Pr1—O8	74.47 (6)	O1^{ii}—Pr1—O3	128.23 (5)
O2^i—Pr1—O1^{ii}	80.07 (5)	O3^{iii}—Pr1—O3	120.12 (6)
O5—Pr1—O1^{ii}	74.00 (6)	O6—Pr1—O3	68.33 (6)
O7—Pr1—O1^{ii}	79.66 (6)	O2^i—Pr1—O2^{ii}	121.08 (6)
O4—Pr1—O1^{ii}	143.33 (6)	O5—Pr1—O2^{ii}	66.60 (6)
O8—Pr1—O1^{ii}	142.09 (6)	O7—Pr1—O2^{ii}	69.03 (6)
O2^i—Pr1—O3^{iii}	150.17 (6)	O4—Pr1—O2^{ii}	127.16 (5)
O5—Pr1—O3^{iii}	82.57 (6)	O8—Pr1—O2^{ii}	119.17 (5)
O7—Pr1—O3^{iii}	73.80 (6)	O1^{ii}—Pr1—O2^{ii}	48.83 (5)
O4—Pr1—O3^{iii}	77.75 (5)	O3^{iii}—Pr1—O2^{ii}	61.61 (5)
O8—Pr1—O3^{iii}	73.38 (6)	O6—Pr1—O2^{ii}	104.90 (5)
O1^{ii}—Pr1—O3^{iii}	110.38 (5)	O3—Pr1—O2^{ii}	171.64 (5)
O2^i—Pr1—O6	69.70 (6)	Pr1^v—O2—Pr1^{iv}	118.90 (6)
O5—Pr1—O6	128.96 (6)	Pr1^{vi}—O3—Pr1	117.37 (6)
O7—Pr1—O6	66.43 (6)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H5···C11^i	0.91 (3)	2.40 (3)	3.248 (2)	155 (3)
N1—H6···C11	0.81 (3)	2.47 (3)	3.259 (2)	165 (3)
O5—H7···C12^{ii}	0.76 (4)	2.37 (4)	3.118 (2)	173 (3)
O5—H8···O6^{iii}	0.80 (4)	1.96 (4)	2.744 (3)	165 (4)
O6—H9···C11^{iv}	0.84 (5)	2.60 (4)	3.354 (2)	149 (4)
O6—H10···C12^i	0.77 (4)	2.39 (5)	3.128 (2)	161 (4)
O7—H11···O8^{iii}	0.72 (5)	2.42 (5)	2.870 (3)	123 (5)
O7—H11···C12^v	0.72 (5)	2.71 (5)	3.312 (2)	143 (5)
O7—H12···C11	0.81 (4)	2.40 (4)	3.202 (2)	169 (4)
O8—H13···C12^{vi}	0.75 (4)	2.39 (4)	3.140 (2)	172 (4)
O8—H14···O9	0.79 (4)	1.99 (4)	2.778 (3)	175 (3)
O9—H15···C11^{vii}	0.93 (5)	2.38 (5)	3.219 (2)	151 (4)
O9—H16···C11^{vi}	0.96 (5)	2.30 (5)	3.249 (3)	168 (4)

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

All H atoms were located by difference Fourier synthesis and refined isotropically. The refinement gives X—H (X = C, N, O) distances in the range 0.72 (5)–0.92 (4) Å and all bond angles involving H atoms are reasonable. U_{iso} values for H atoms are in the range 0.025 (7)–0.078 (15) Å^2.

Data collection: *CAD-4 ARGUS* (Enraf–Nonius, 1996). Cell refinement: *CAD-4 ARGUS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELX97*.

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Diaqua{hydrogen bis[1-(2-pyridyl)ethanone oximato-N,N']}nickel(II) perchlorate hydrate

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Abstract

In the title compound, $[Ni(C_7H_8N_2O)(C_7H_9N_2O)(H_2O)_2]ClO_4 \cdot H_2O$, the Ni atom lies on a twofold axis

and is in a distorted octahedral environment. The coordination consists of two planar bidentate oxime ligands with *cis* oxime groups and two *trans* water molecules above and below this plane. The two oxime molecules have lost one proton to give a very short symmetrical hydrogen bond between the oxime O atoms. The O· · ·O separation is 2.432 (3) Å.

Comment

In the course of structural and equilibrium studies on transition metal complexes formed by different oxime ligands, we have shown that pyridine-2-carboxaldehyde oxime compounds of the type shown in the Scheme below readily form polynuclear complexes which are potential model compounds in the study of redox and magnetic exchange interactions of metal ions (Orama & Saarinen, 1996). The best known examples are the trinuclear copper(II) complexes characterized by the presence of a highly stable trinuclear Cu_3OH central core both in the solid state and in aqueous solution (Orama *et al.*, 1990). With nickel(II), on the other hand, most of the complexes formed by ligands $HL1$ and $HL2$ have been found to belong to the mononuclear series $Ni(HL)_n^{2+}$ ($n = 1$, 2 or 3) or are oximate members of the series derived from the stepwise dissociation of the oxime protons from the parent bis- and tris-complexes (Orama *et al.*, 1989). The 6-methyl group on the pyridine ring, however, seems to have a decisive effect on the polymerization reactions of nickel(II), and binuclear, trinuclear and nonanuclear complexes of compositions $Ni_2L_3^{3+}$, $Ni_3L_3(OH)_2^-$ and $Ni_9L_{10}(OH)_6^{2+}$ are readily formed as major species in aqueous solution with $HL3$ (Saarinen & Orama, 1998; Pajunen *et al.*, 1999). To facilitate interpretation of the coordination models in these systems we have now isolated the title complex, (I), with an aqueous composition $NiL(HL)^+$ formed between nickel(II) and $HL2$ in the solid state. The crystal structures of two further Ni^{II} complexes of the ligand 1-(2-pyridyl)ethanone oxime have been reported by Riggle *et al.* (1992).
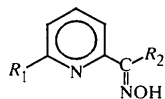
HL1: $R_1 = R_2 = H$
HL2: $R_1 = H$, $R_2 = Me$
HL3: $R_1 = Me$, $R_2 = H$

$ClO_4^- \cdot H_2O$
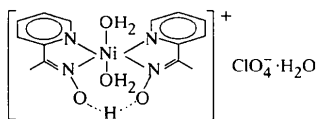
(I)

Most of the complexes formed between nickel(II) and bidentate oxime ligands have been found to possess a

square-planar four-coordination stabilized by an intramolecular hydrogen bond between *cis* oxime atoms (Chakravorty, 1974). In the present case, the Ni^{II} atom is in a distorted octahedral environment. The six-coordination consists of two planar bidentate oxime ligands with *cis* oxime groups and two *trans* water molecules above and below this plane. The molecule of (I) is oriented around a crystallographic twofold axis which passes through the central atom. The Ni—N_{oxime} [2.0375 (18) Å], Ni—$N_{pyridine}$ [2.0971 (19) Å] and Ni—O [2.1236 (16) Å] bond lengths are comparable with those observed in the corresponding nitrate complex (Riggle *et al.*, 1992) and with those observed in other similar complexes (Pearse *et al.*, 1989; Ansell *et al.*, 1982). As expected, all these bond lengths are considerably longer than the respective distances in the square-planar complexes (Saarinen *et al.*, 1979).
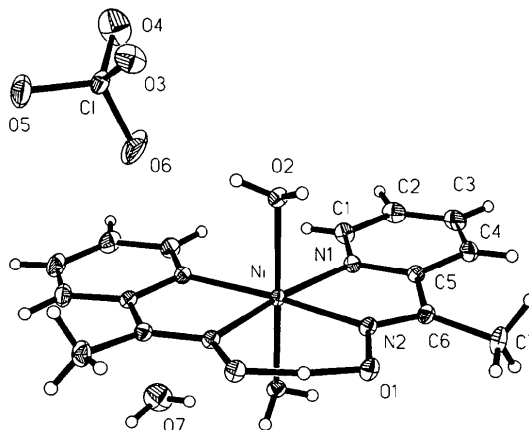

Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

The two oxime NOH groups in (I) have lost one proton to give a very short hydrogen bond between the oxime O atoms. The trend proposed by Chakravorty (1974) suggests that with O· · ·O separations larger than 2.5 Å, the hydrogen bond is unsymmetrical, whereas O· · ·O distances approaching 2.40 Å result in a symmetrical hydrogen bond. The major difference between the present perchlorate and the aforementioned nitrate complexes is in this intramolecular hydrogen bond. In the nitrate complex, the O· · ·O separation is 2.524 (3) Å and the hydrogen bond is unsymmetrical (O1—H = 1.52 and O2—H = 1.07 Å). In (I), the O· · ·O separation is 2.432 (3) Å and the hydrogen bond, with an O—H distance of 1.22 Å, is symmetrical as a result of crystallographic requirements. The perchlorate ion is disordered around the twofold axis and the distance between the two partially occupied Cl positions is 0.536 Å. The hydrogen bond distances between the water, perchlorate and complex molecules are given in Table 2.

Experimental

The title complex was obtained when the pH of an aqueous solution containing nickel(II) chloride and H*L*2 in a 1:2 molar ratio was adjusted to 5 with NaOH. Attempts to isolate a crystalline compound from such solutions were unsuccessful, but when the chloride counter-ion was changed to perchlorate by adding solid NaClO$_4$ to the solution, a light-green crystalline compound was obtained.

Crystal data
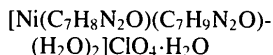
[Ni(C$_7$H$_8$N$_2$O)(C$_7$H$_9$N$_2$O)-
(H$_2$O)$_2$]ClO$_4$·H$_2$O
M_r = 483.50
Monoclinic
$P2/c$
a = 10.586 (2) Å
b = 11.925 (2) Å
c = 7.803 (2) Å
β = 105.64 (3)°
V = 948.6 (3) Å^3
Z = 2
D_x = 1.693 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 6.40–12.01°
μ = 1.221 mm^{-1}
T = 193 (2) K
Prismatic
0.45 × 0.45 × 0.45 mm
Light green

Data collection

Rigaku AFC-7S diffractom-
eter
$2\theta/\omega$ scans
Absorption correction: none
2108 measured reflections
1962 independent reflections
1934 reflections with
$I > 2\sigma(I)$
R_{int} = 0.013

θ_{max} = 26.50°
h = -13 → 12
k = -14 → 0
l = 0 → 9
3 standard reflections
every 200 reflections
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.084
S = 1.115
1962 reflections
197 parameters
H atoms treated by a
mixture of independent
and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 1.0452P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.292 e Å^{-3}
$\Delta\rho_{min}$ = -0.819 e Å^{-3}
Extinction correction:
SHELXL97 (Sheldrick, 1997a)
Extinction coefficient:
0.0154 (16)
Scattering factors from
International Tables for
Crystallography (Vol. C)

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

Ni—N2	2.0375 (18)	Ni—O2	2.1236 (16)
Ni—N1	2.0971 (19)	O1—N2	1.373 (2)
N2—Ni—N2^i	93.20 (10)	N2—Ni—O2	90.45 (7)
N2—Ni—N1	77.91 (7)	N1—Ni—O2	88.90 (7)
N1^i—Ni—N1	110.98 (10)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O1^i	1.22	1.22	2.432 (3)	169
O2—H2A···O5^{ii}	0.85	2.01	2.799 (4)	153
O2—H2A···O6	0.85	2.00	2.851 (5)	175
O2—H2B···O1^{iii}	0.85	1.84	2.692 (2)	178
O7—H7···O2^{iv}	0.85	2.17	3.007 (3)	168

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

Analysis of the systematic absences suggested two possible space groups, $P2/c$ and Pc. The refinement suggested that $P2/c$ was the proper choice. The perchlorate ion is disordered in both space groups and refinement in the non-centrosymmetric space group Pc resulted in a strongly correlated structure; the largest correlation coefficients between 'symmetry-related' parameters vary from 0.83 to 0.87. H atoms were located in difference maps and were refined isotropically, except for those of the water molecules, which were refined as riding with an O—H bond length of 0.85 Å. The refined C—H distances are in the range 0.87 (3)–1.07 (4) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL97*.

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