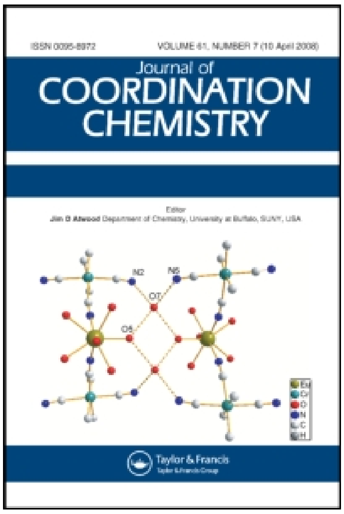

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SYNTHESIS AND X-RAY STRUCTURES OF Ni(II) COMPLEXES OF 1-(2-PYRIDINYL)ETHANONE OXIME

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A study of the complexation of Ni(II) with 1-(2-pyridinyl)ethanone oxime as a function of pH was carried out. A green complex, dibromobis(1-(2-pyridinyl)ethanone oxime)nickel(II), was isolated at pH 3. This octahedral complex (**1**) crystallizes in space group $P2_1/n$ (a = 8.754(2), b = 11.136(3), c = 18.210(4) Å, β = 92.18(2)°, Z = 4) and has *cis* bromide ions (av. Ni–Br = 2.57(2) Å), *cis* pyridine nitrogens (av. Ni–N = 2.091(9) Å), and *trans* oxime nitrogens (av. Ni–N = 2.043(7) Å). An orange octahedral complex, diaquo(1-(2-pyridinyl)ethanone oxime)(1-(2-pyridinyl)ethanone oximato)nickel(II) nitrate, (**2**) crystallized at pH 6 in space group $P2_1/c$ (a = 12.497(3), b = 7.501(2), c = 20.940(5) Å, β = 95.59(2)°, Z = 4) and has *trans* water molecules (av. Ni–O = 2.069(5) Å), *cis* pyridine nitrogens (av. Ni–N = 2.109(5) Å, and *cis* oxime nitrogens (av. Ni–N = 2.037(6) Å). Complex (**2**) has a short intramolecular hydrogen bond between oxime oxygen atoms ($O \cdots O$ = 2.524(3) Å). A dark reddish-brown complex formed at pH ~ 10 was isolated but not fully characterized.

Keywords: Nickel(II), oximes, pH, X-ray structures

INTRODUCTION

Although we have studied[1-5] nickel(II) complexes of a number of aliphatic α-amine oximes, there is little available structural information on aromatic α-amine oxime nickel(II) complexes. Krause and Busch[6] reported synthetic magnetic and conductivity studies on Ni(II), Pd(II) and Pt(II) complexes of 2-pyridinaldoxime. All the Ni(II) complexes were found to be paramagnetic, in contrast to the aliphatic amine oxime complex, bis(3-amino-3-methyl-2-butanone oximato) nickel(II) ($[Ni(AO)_2]^+$).[1,2] A crystal structure of the Pt(II) complex of 1-(2-pyridinyl)ethanone oxime,[7] however, showed square planar coordination as observed with the aliphatic amine oxime ligand in $[Pt(AO)_2]^+$.[8] The oximes were, however, completed deprotonated in the aromatic case and were arranged in a *trans* fashion in the complex instead of the *cis*, hydrogen bonded fashion observed in the aliphatic complex. Because of our continuing interest in short hydrogen bonds, we decided to study Ni(II) complexes of this aromatic amine oxime as a function of pH.

EXPERIMENTAL

Ligand Synthesis

The ligand 1-(2-pyridinyl)-ethanone oxime was prepared essentially as described in the literature.[9] Some 68.2 g of 2-acetylpyridine in 125 cm^3 of ethanol was treated

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with a solution of 51.3 g $NH_2OH \cdot HCl$ and 34.1 g NaOH in 130 cm^3 of water. After 1.5 hours reflux and cooling to room temperature, the solution was treated with dry ice to bring the pH to 7. The precipitate was filtered, washed with H_2O, air dried, and then recrystallized from ethanol to give the product melting at 120–121°C (literature = 121°C).

Reactions with Ni(II)

A titration curve of an acidified 2 : 1 ligand to metal ($Ni(NO_3)_2$) aqueous solution was generated. A well-defined equivalence point at pH ~3 resulted in a deep green solution which became orange at pH 5 to 6. At pH ~10 there was another equivalence point associated with the formation of a deep red-brown solution. Solids were isolated from solution at pH 3, 6, and 12. That at pH 3 was salted out with NaBr. These were recrystallized to obtain suitable X-ray crystals at pH 3, complex **(1)**, and 6, complex **(2)**, but those from pH 12 were not suitable for diffraction studies. Complex **(1)** was recrystallized (deep green) from ethanol/isopropyl ether while complex **(2)** was recrystallized (deep orange) from ethanol/water.

TABLE I
X-ray data for the complexes.

	Complex 1	Complex 2
Space Group	$P2_1/n$	$P2_1/c$
a(Å)	8.754(2)	12.497(3)
b(Å)	11.136(3)	7.501(2)
c(Å)	18.210(4)	20.940(5)
β(deg)	92.18(2)	95.59(2)
Z	4	4
V(Å^3)	1773.8(7)	1953.4(7)
Formula	$NiBr_2C_{14}H_{16}N_4O_2$	$NiC_{14}H_{19}N_5O_7 1.2H_2O$
d_x (g/cm^3)	1.838(3)	1.529(3)
Formula weight	490.8	449.7
μ (cm^{-1})	55.7	10.4
scan method	$\theta-2\theta$	$\theta-2\theta$
scan range (θ) (deg)	$0.95 + 0.35 \tan\theta$	$0.50 + 0.35 \tan\theta$
data limits (2θ) (deg)	40	45
$h\ k\ l$ range	$\bar{h}\,\bar{k}\,\bar{l}$, $h\,\bar{k}\,\bar{l}$, h k l & h k l (2θ = 2–40°)	$h\,k\,l$ & $\bar{h}\,k\,l$ (2θ = 2–45°) $h\,\bar{k}\,l$ & $\bar{h}\,\bar{k}\,l$ (2θ = 2–30°)
# of refl. measured	3349	3667
# of indep. refl. measured	1646	2433
# of refl. with $I > 2\sigma(I)$	1251	2070
function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
absorption method	none	empirical/scan
rel. range of transmission	95–100%	97.1–100%
w	$4F_o^2/\sigma^2$ counting + $(0.05F_o^2)$)	$4F_o^2/\sigma^2$ counting + $(0.05F_o^2)$)
R	0.042	0.033
R_w	0.049	0.048
s	1.47	1.54
max. shift/error	0.13	0.07
max. dif. density	0.7 e/Å^3 (near Br)	0.5 e/Å^3

X-ray Studies

Complexes (1) and (2) were handled in a parallel fashion. The crystal was mounted in random orientation on an Enraf-Nonius CAD4 diffractometer for data collection. Twenty-five reflections were located by automatic search of reciprocal space and recentred twice. These setting angles were used to obtain the cell dimensions which are included in Table I with other crystal data and structure solution and refinement parameters.

The intensities were collected with MoKα radiation ($\lambda = 0.7107$ Å) obtained from a graphite monochromometer. The data were collected at a rate to obtain 3% counting statistics to a maximum of 90 s. To check instrument and crystal stability, three reflections were recorded every 7200 s of X-ray exposure and showed no significant decay or fluctuation. Three orientation standard reflections were checked every 200 reflections, and all 25 orientation reflections were recentred to obtain a new orientation matrix if necessary. The data were reduced in the normal manner. All calculations were performed using a PDP11/34 or PDP11/24 computer with SDP program.[10]

Structure solution was accomplished by Patterson and Fourier methods, and refinement was by full-matrix least-squares (hydrogen atom positions refined in (1), fixed hydrogen atom contributions in (2), nonhydrogen atoms anisotropic).

TABLE II

Table of positional parameters and estimated standard deviations for complex (1).

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
Br1	−0.0464(1)	0.1633(1)	0.06512(7)	4.17(3)
Br2	0.0790(1)	0.1958(1)	0.26041(6)	3.36(2)
Ni	0.1839(1)	0.2563(1)	0.13448(7)	2.27(3)
O1	0.0120(8)	0.4578(6)	0.2081(4)	3.6(2)
O2	0.2620(8)	0.0128(7)	0.0680(4)	4.1(2)
N1	0.0958(9)	0.4236(7)	0.1485(4)	2.5(2)
N2	0.2560(9)	0.3515(8)	0.0424(4)	2.8(2)
N3	0.3102(9)	0.1065(7)	0.1123(4)	2.7(2)
N4	0.3914(8)	0.2882(7)	0.1907(4)	2.4(2)
C1	0.068(1)	0.633(1)	0.1118(6)	3.7(3)
C2	0.121(1)	0.5069(9)	0.1036(5)	2.5(2)
C3	0.211(1)	0.4683(9)	0.0410(5)	2.6(2)
C4	0.249(1)	0.541(1)	−0.0169(6)	3.6(3)
C5	0.332(1)	0.495(1)	−0.0728(6)	5.1(3)
C6	0.378(1)	0.379(1)	−0.0701(6)	4.8(3)
C7	0.338(1)	0.310(1)	−0.0123(6)	4.0(3)
C8	0.559(1)	0.007(1)	0.1140(6)	3.9(3)
C9	0.452(1)	0.1022(9)	0.1345(5)	2.4(2)
C10	0.498(1)	0.2036(9)	0.1807(5)	2.4(2)
C11	0.640(1)	0.214(1)	0.2164(6)	3.0(2)
C12	0.668(1)	0.308(1)	0.2629(6)	3.8(3)
C13	0.559(1)	0.389(1)	0.2753(6)	3.3(3)
C14	0.420(1)	0.377(1)	0.2367(6)	3.0(2)

The final positional parameters and isotropic equivalent parameters are given in Tables II and III. The molecular structures are illustrated in Figures 1 and 2, and the bond angles and distances are listed in Tables IV and V for compounds (1) and (2), respectively. Least-squares planes, hydrogen atom parameters, anisotropic thermal parameters, and observed and calculated structure factors are available from E.O.S.

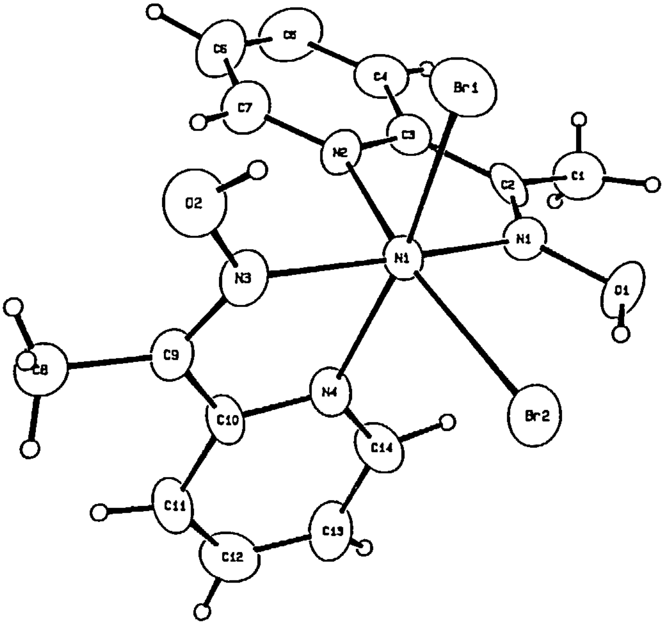

FIGURE 1 Perspective view of complex (1).

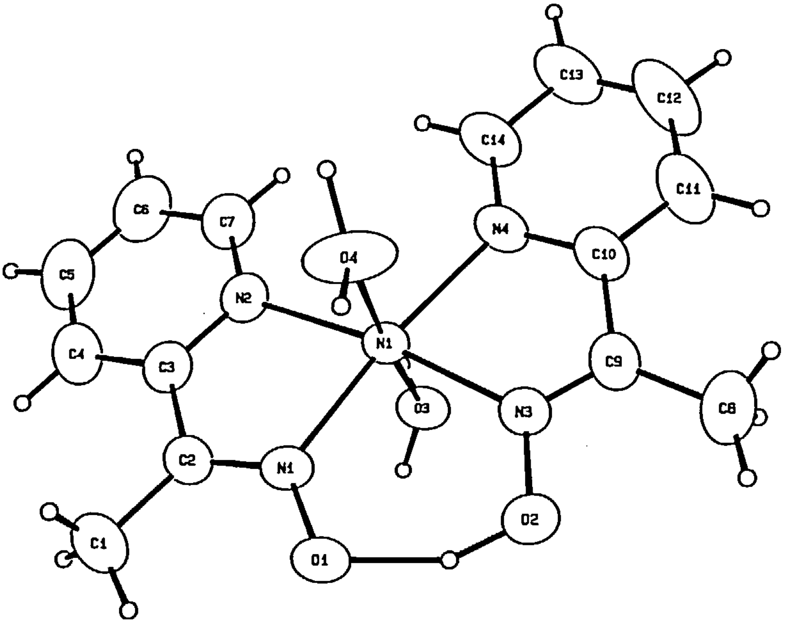

FIGURE 2 Perspective view of complex (2).

TABLE III
Table of positional parameters and estimated standard deviations for complex (**2**).

Atom	x/a	y/b	z/c	B(Å^2)
Ni	0.32979(3)	−0.13544(5)	−0.19688(2)	2.595(8)
O1	0.5312(2)	−0.1238(3)	−0.2626(1)	3.29(5)
O2	0.3613(2)	−0.1161(4)	−0.3384(1)	4.57(6)
O3	0.3089(2)	−0.4085(3)	−0.2069(1)	3.37(5)
O4	0.3388(2)	0.1379(3)	−0.1862(1)	5.35(6)
N1	0.4902(2)	−0.1471(3)	−0.2053(1)	2.80(5)
N2	0.3931(2)	−0.1746(4)	−0.1011(1)	3.31(6)
N3	0.2879(2)	−0.1105(4)	−0.2932(1)	3.29(6)
N4	0.1608(2)	−0.1101(3)	−0.2030(1)	3.41(6)
C1	0.6742(3)	−0.1475(5)	−0.1533(2)	4.70(9)
C2	0.5547(2)	−0.1595(4)	−0.1542(2)	3.08(7)
C3	0.5014(3)	−0.1871(4)	−0.0953(2)	3.35(7)
C4	0.5565(3)	−0.2253(6)	−0.0370(2)	4.76(9)
C5	0.5020(4)	−0.2520(7)	0.0158(2)	6.0(1)
C6	0.3932(3)	−0.2387(6)	0.0099(2)	5.8(1)
C7	0.3418(3)	−0.2000(6)	−0.0492(2)	4.60(9)
C8	0.1508(4)	−0.0909(8)	−0.3834(2)	7.2(1)
C9	0.1902(3)	−0.0983(5)	−0.3143(2)	4.02(8)
C10	0.1148(3)	−0.0933(5)	−0.2635(2)	3.88(8)
C11	0.0070(3)	−0.0704(7)	−0.2773(2)	5.8(1)
C12	−0.0584(3)	−0.0664(8)	−0.2284(2)	7.2(1)
C13	−0.0138(3)	−0.0837(7)	−0.1669(2)	6.2(1)
C14	0.0955(3)	−0.1048(6)	−0.1565(2)	4.80(9)
N5	0.8094(3)	0.6330(4)	0.0721(2)	4.78(8)
O5	0.8619(6)	0.6275(8)	0.0280(3)	9.6(2)
O6	0.8057(5)	0.5084(7)	0.1086(3)	6.7(2)
O7	0.7596(5)	0.7728(8)	0.0820(3)	7.0(2)
O8	0.8155(7)	0.762(1)	0.0391(4)	13.1(3)
O9	0.8690(6)	0.502(1)	0.0634(4)	10.1(2)
O10	0.7448(6)	0.6213(9)	0.1092(4)	10.7(2)
OW1	0.0222(6)	0.7198(9)	0.9745(3)	9.3(2)
OW2	0.8696(6)	0.497(1)	0.4726(3)	10.6(2)

RESULTS AND DISCUSSION

A 2 : 1 ligand to metal ratio of pyridine-2-methylcarboxaldoximine and Ni(NO_3)$_2$ produces complexes which are pH dependent. We were able to isolate crystals suitable for X-ray of the predominant complex at low pH (~3) and intermediate pH (~7) but not at the higher pH (~10–12).

The complex formed at pH 3 was salted out with NaBr and gave an octahedral complex with two bromide ions coordinated *cis* to Ni(II). The octahedron is completed by the two pyridine nitrogen atoms *cis* to each other, and each being *trans* to a bromide ion. The two oxime nitrogen atoms are *trans* to each other.

TABLE IV
Table of bond distances in Angstroms and angles in degrees for complex (**1**).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Br1	Ni	2.557(1)	N4	C14	1.32(1)
Br2	Ni	2.592(1)	C1	C2	1.49(1)
Ni	N1	2.036(7)	C2	C3	1.47(1)
Ni	N2	2.101(7)	C3	C4	1.38(1)
Ni	N3	2.051(7)	C4	C5	1.37(2)
Ni	N4	2.082(7)	C5	C6	1.36(2)
O1	N1	1.386(9)	C6	C7	1.36(2)
O2	N3	1.37(1)	C8	C9	1.47(1)
N1	C2	1.27(1)	C9	C10	1.46(1)
N2	C3	1.36(1)	C10	C11	1.39(1)
N2	C7	1.33(1)	C11	C12	1.37(1)
N3	C9	1.29(1)	C12	C13	1.34(1)
N4	C10	1.34(1)	C13	C14	1.40(1)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Br1	Ni	Br2	91.86(5)	Ni	N4	C10	114.2(6)
Br1	Ni	N1	97.9(2)	Ni	N4	C14	125.5(6)
Br1	Ni	N2	93.8(2)	C10	N4	C14	120.1(8)
Br1	Ni	N3	89.6(2)	N1	C2	C1	124.5(9)
Br1	Ni	N4	165.7(2)	N1	C2	C3	113.5(8)
Br2	Ni	N1	88.8(2)	C1	C2	C3	123(1)
Br2	Ni	N2	164.7(2)	N2	C3	C2	115.3(8)
Br2	Ni	N3	100.1(2)	N2	C3	C4	119.9(9)
Br2	Ni	N4	86.7(2)	C2	C3	C4	125(1)
N1	Ni	N2	76.5(3)	C3	C4	C5	120.(1)
N1	Ni	N3	168.2(3)	C4	C5	C6	120.(1)
N1	Ni	N4	96.3(3)	C5	C6	C7	119.(1)
N2	Ni	N3	94.2(3)	N2	C7	C6	123.(1)
N2	Ni	N4	91.4(3)	N3	C9	C8	123.9(9)
N3	Ni	N4	76.7(3)	N3	C9	C10	113.4(8)
Ni	N1	O1	124.3(5)	C8	C9	C10	122.7(9)
Ni	N1	C2	121.0(6)	N4	C10	C9	116.4(8)
O1	N1	C2	114.7(7)	N4	C10	C11	119.7(9)
Ni	N2	C3	113.8(6)	C9	C10	C11	123.9(9)
Ni	N2	C7	127.4(7)	C10	C11	C12	119.2(9)
C3	N2	C7	118.9(8)	C11	C12	C13	121(1)
Ni	N3	O2	125.3(6)	C12	C13	C14	118.(1)
Ni	N3	C9	119.1(6)	N4	C14	C13	122.2(9)
O2	N3	C9	115.3(7)				

Numbers in parentheses are estimated standard deviations.

Both oxime oxygen atoms are protonated and these protons are each weakly and intramolecularly hydrogen bonded to a coordinated bromide. (O···Br = 3.176, 3.118 Å, H···Br = 2.36, 2.50 Å, and O–H···Br = 152, 137°; see orientation in Figure 1). The Ni–Br distances of 2.557(1) and 2.592(1) Å are comparable to those observed (2.511(2) – 2.682(5) Å) in other similar complexes.[11–15] The average Ni–N (oxime) distance (2.043(7) Å) is considerably longer than that (1.866(3) Å) in the square planar aliphatic oxime complexes (e.g., in $[Ni(AO)_2]^+$)[1,2] but is shorter than the average Ni–N (pyr.) distance of 2.091(9) Å. This difference in oxime and amine distance is comparable to that observed in aliphatic amine oxime complexes.[1–5]

TABLE V

Table of bond distances in Angstroms and angles in degrees for complex (2).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ni	O3	2.073(2)	C10	C11	1.361(4)
Ni	O4	2.064(2)	C11	C12	1.371(5)
Ni	N1	2.031(2)	C12	C13	1.360(5)
Ni	N2	2.104(2)	C13	C14	1.371(5)
Ni	N3	2.042(2)	N5	O5	1.184(7)
Ni	N4	2.113(2)	N5	O6	1.212(6)
O1	N1	1.362(3)	N5	O7	1.247(6)
O2	N3	1.381(3)	N5	O8	1.198(8)
N1	C2	1.279(4)	N5	O9	1.258(8)
N2	C3	1.351(4)	N5	O10	1.176(7)
N2	C7	1.328(4)	O5	O6	2.091(8)
N3	C9	1.261(4)	O5	O7	2.095(8)
N4	C10	1.343(4)	O5	O8	1.21(1)
N4	C14	1.330(4)	O5	O9	1.20(1)
C1	C2	1.495(4)	O6	O9	1.29(1)
C2	C3	1.473(4)	O6	O10	1.140(9)
C3	C4	1.371(4)	O7	O8	1.19(1)
C4	C5	1.368(5)	O7	O10	1.29(1)
C5	C6	1.357(5)	O8	O9	2.11(1)
C6	C7	1.369(5)	O8	O10	2.07(1)
C8	C9	1.483(5)	O9	O10	2.102(9)
C9	C10	1.490(4)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O3	Ni	O4	175.85(8)	N1	C2	C1	123.6(3)
O3	Ni	N1	93.67(7)	N1	C2	C3	114.3(2)
O3	Ni	N2	89.44(8)	C1	C2	C3	122.1(3)
O3	Ni	N3	88.47(8)	N2	C3	C2	116.5(2)
O3	Ni	N4	88.14(8)	N2	C3	C4	120.5(3)
O4	Ni	N1	90.47(8)	C2	C3	C4	123.0(3)
O4	Ni	N2	91.4(1)	C3	C4	C5	120.2(3)
O4	Ni	N3	91.28(9)	C4	C5	C6	119.4(3)
O4	Ni	N4	87.78(9)	C5	C6	C7	118.4(3)
N1	Ni	N2	78.13(9)	N2	C7	C6	123.4(3)
N1	Ni	N3	94.48(9)	N3	C9	C8	124.4(3)
N1	Ni	N4	171.14(9)	N3	C9	C10	114.2(3)
N2	Ni	N3	172.18(8)	C8	C9	C10	121.5(3)
N2	Ni	N4	110.58(9)	N4	C10	C9	115.4(2)
N3	Ni	N4	76.88(9)	N4	C10	C11	122.4(3)
Ni	N1	O1	122.0(2)	C9	C10	C11	122.2(3)
Ni	N1	C2	118.5(2)	C10	C11	C12	119.5(3)
O1	N1	C2	119.1(2)	C11	C12	C13	119.1(3)
Ni	N2	C3	112.2(2)	C12	C13	C14	118.1(3)

TABLE V continued

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
NI	N2	C7	129.3(2)	N4	C14	C13	124.1(3)
C3	N2	C7	118.4(3)	O5	N5	O6	121.5(6)
Ni	N3	O2	123.5(2)	O5	N5	O7	118.9(6)
Ni	N3	C9	120.0(2)	O6	N5	O7	119.6(5)
O2	N3	C9	116.5(2)	O8	N5	O9	118.5(9)
NI	N4	C10	113.5(2)	P8	N5	O10	121.8(9)
NI	N4	C14	129.7(2)	O9	N5	O10	119.5(8)
C10	N4	C14	116.8(2)				

Numbers in parentheses are estimated standard deviations.

Most of the distortion from 90° bond angles around the nickel can be attributed to the limited bite of the bidentate ligand. As can be seen in Figure 1, the ligands are very planar (maximum deviation from least-squares planes was less than 0.1 Å). Ligand bond distances and angles are normal.

In complex (**2**), the octahedral nickel(II) coordination is completed by two planar bidentate amine oxime ligands with *cis* oxime groups and two *trans* water molecules above and below this plane. In this complex, isolated at near neutral pH, the two oximes have lost one proton to give the usual short hydrogen bond between oxime oxygens (O···O = 2.524(3), O1–H = 1.52 and O2–H = 1.07 Å). The average Ni–N (oxime) bonds (2.037(6) Å) and Ni–N (pyr.) bonds (2.108(4) Å) are comparable to those in complex (**1**), and the latter are similar to those (2.116(4)–2.117(6) Å) in related complexes.[16,17] The *trans* water oxygens (average Ni–O = 2.069(5) Å) are bonded in rather normal fashion (*e.g.*, 2.076(5) and 2.101(5) Å in diaquo-2,9-bis(1-methylhydrazino)-1,10-phenanthroline-(2,6-diacetylpyridine)nickel(II)[17]). The nitrate counter ion of complex (**2**) has two sets of oxygen atom positions with equal occupancy, each of which produces a rather normal nitrate geometry. In addition there are two partially occupied lattice water positions (OW1, 0.6 and OW2, 0.6). The occupancies were obtained from least-squares refinement and may actually be 0.5 rather than 0.6. Hydrogen atoms could not be clearly located on the water oxygen atoms. The alternate water locations probably give rise to hydrogen bonding with the nitrate oxygen atoms.

It should be noted that the complex (**2**) obtained at pH 6–7 has the two bidentate ligands coplanar, in contrast to complex (**1**). This undoubtedly results in some repulsion between pyridine rings, as clearly evidenced by the twist of the pyridine rings to opposite sides of the coordination plane of the four nitrogen atoms despite the opening of the N2–Ni–N4 angle to 110.58(9)°; undoubtedly this steric strain is balanced by the formation of the strong O···O intramolecular hydrogen bond.

The above nickel complexes should be compared with the Pt(II) complex, which is square-planar and diamagnetic. Thus the ligand appears to be of intermediate field strength, weaker than the aliphatic amine oxime (AO) which gives square-planar complexes with both Ni(II)[1] and Pt(II).[8]

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