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Bis(acetato)bis(pyridine-2-amidoxime-*N*,*N'*)nickel(II)–Ethanol (1/2)

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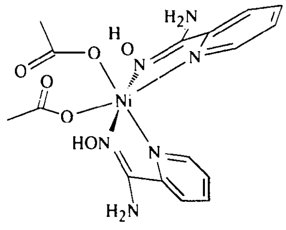
Abstract

The mononuclear complex of the title compound [alternative IUPAC name: bis(acetato-*O*)bis(pyridine-2-carboxamide oxime-*N*,*N'*)nickel(II)–ethanol (1/2)], $[Ni(C_2H_3O_2)_2(C_6H_7N_3O)_2].2C_2H_5OH$, crystallizes from ethanol as a disolvate. The coordination geometry at the Ni atom is distorted octahedral, with crystallographic twofold symmetry. The pyridine-2-carboxamide oxime ligands are coordinated to the metal through the N atoms of the pyridine ring and the oxime group. The acetate ligands are monodentate. The ethanol solvate molecule is linked to the non-coordinated O atom of the acetate ligand *via* a hydrogen bond.

Comment

Amidoximes and their complexes find a wide range of applications in technology, medicine and agriculture (Nicolaides & Varella, 1992). Recent attention has centred on the members of this group which form mono- or polynuclear chelate complexes (Pearse, Raithby & Maughan, 1994; Orama, Saarinen & Korvenranta, 1994). Pyridine-2-amidoxime (py2ao) is known to form stable complexes with various metals (Sanyal, Modak & Mudi, 1983), some of which are exploited in analytical chemistry (Losada del Barrio, Abad & Vicente-Perez, 1986). However, little or no attention has been paid to coordination compounds arising from reactions of py2ao with acetates of the 3*d* metals in organic solvents, despite the fact that the problem could be of interest in view of a possible deprotonation of py2ao in the presence of acetate ions.

The title complex, (I) (Fig. 1), is mononuclear and the central Ni atom is located on a twofold axis ($\frac{1}{2}$, y, $\frac{1}{4}$). The coordination geometry is distorted octahedral, the major distortions being N3—Ni—N3($1-x, y, \frac{1}{2}-z$) 166.2 (2) and N3—Ni—N1 76.18 (11)°. Two mutually *cis* positions are occupied by the O2 atoms of the two monodentate acetato ligands and the two other pairs are occupied by the chelating pyridine N1 and oxime N3 atoms and their symmetry equivalents of the py2ao ligands. The N3 atoms are mutually *trans* and the N1 atoms mutually *cis*.



(I)

Electroneutrality requires that the py2ao ligand is not deprotonated during complex formation, as was confirmed by location of all H atoms. Since pyridine-2-aldoxime loses a proton on complexation to nickel(II) chloride in neutral aqueous solution, we suggest that the NH_2 group of py2ao stabilizes the oxime group

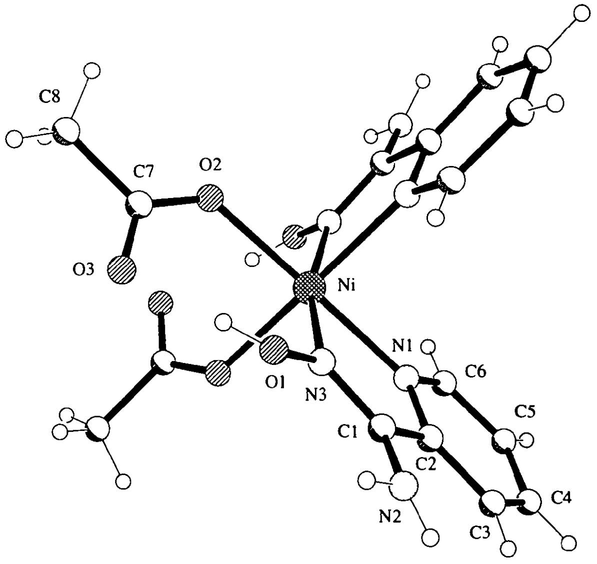


Fig. 1. The title complex in the crystal (solvent omitted). Radii are arbitrary and only the asymmetric unit is numbered.

by delocalization of the lone pair at the N atom. The ensuing reduced electron density at this atom is the probable reason for its low affinity for the metal atom.

In the coordinated state, py2ao forms a five-membered chelate ring with the Ni atom, in which the chelate angle N3—Ni—N1 [76.18 (11)°] is somewhat smaller than comparable angles found in [Ni(H*L*)*L*$_2$].6.5H$_2$O (where H*L* is pyridine-2-aldoxime) (Orama, Saarinen & Korvenranta, 1989). The chelate ring is planar (r.m.s. deviation 0.008 Å). The bond from the Ni atom to the pyridine N atom [Ni—N1 2.116 (3) Å] in the title complex is somewhat longer than that to the oxime N atom [Ni—N3 2.054 (3) Å]. This is consistent with the results of measurements on comparable nickel(II) and copper(II) complexes of py2ao (Pearse, Raithby, Hay & Lewis, 1989; Näsäkkälä, Saarinen, Korvenranta & Orama, 1989).

The free py2ao ligand exists as a *Z* isomer in the solid state, with the N atom of the pyridine ring on the same side of the exocyclic C—C bond as the NH$_2$ group (Pearse, Raithby & Lewis, 1989). In the title complex, the ligand also displays a *Z* configuration; however, the pyridine and oxime N atoms are on the same side of the exocyclic C—C bond, thus making the chelate formation described above possible. A comparison of the bond lengths of the title compound and the free ligand shows a slight lengthening of the C2—N1 bond in the complex [1.355 (4) *cf.* 1.336 (3) Å] and a shortening of the N3—O1 bond [1.397 (3) *cf.* 1.419 (2) Å]. Corresponding values in the copper complex (Pearse, Raithby & Lewis, 1989) are 1.352 (4) and 1.414 (3) Å, respectively.

The title structure exhibits a number of hydrogen bonds. Intramolecular contacts are O1—H1···O3 and the possible borderline case of a weak 'chelating' hydrogen bond N2—H2*A*···O1; neighbouring complexes are linked in chains parallel to the *z* axis by N2—H2*B*···O2 contacts from the amine to the acetate and the ethanol molecules are linked to the non-coordinated acetate O atoms (O99—H99···O3; Fig. 2). Weak interactions from the amine to ethanol (N2—H2*A*···O99) are not shown in Fig. 2.

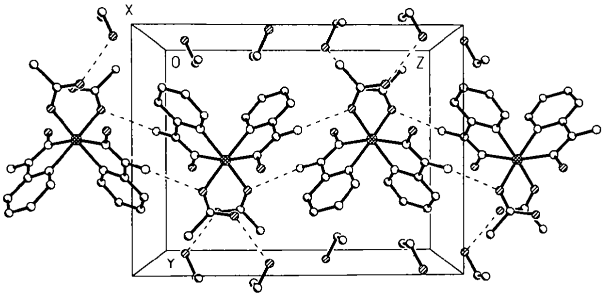


Fig. 2. Packing diagram of the title compound viewed parallel to the *x* axis. H atoms are omitted and hydrogen bonds are shown as dashed lines. There are two such systems per cell, related by the C-centring vector; only one is shown here. (Not all hydrogen bonds of Table 3 are shown.)

Experimental

Pyridine-2-amidoxime was prepared from 2-cyanopyridine and hydroxylamine hydrochloride (Pearse, 1979). Solutions of 1.37 g (0.01 mol) pyridine-2-amidoxime in 30 ml of ethanol and 1.24 g (0.005 mol) nickel(II) acetate–water (1/4) in 30 ml of ethanol were mixed and allowed to stand for 12 h at room temperature. The blue crystals that separated were washed with ethanol and dried in a vacuum. The product was recrystallized from ethanol. The crystals lost solvent readily when exposed to the air. Yield: 1.75 g (64.71%). Elemental analysis: found Ni 10.59, C 44.11, H 5.78, N 15.34%; calculated for [Ni(C$_2$H$_3$O$_2$)$_2$(C$_6$H$_7$N$_3$O)$_2$].2C$_2$H$_5$OH Ni 10.80, C 44.22, H 5.94, N 15.47%.

Crystal data

[Ni(C$_2$H$_3$O$_2$)$_2$(C$_6$H$_7$N$_3$O)$_2$].-
2C$_2$H$_5$OH
M_r = 543.23
Monoclinic
$C2/c$
a = 15.915 (2) Å
b = 10.777 (2) Å
c = 14.387 (2) Å
β = 92.681 (12)°
V = 2464.9 (7) Å^3
Z = 4
D_x = 1.464 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 73 reflections
θ = 3–12.5°
μ = 0.843 mm^{-1}
T = 173 (2) K
Tablet
0.40 × 0.25 × 0.12 mm
Blue

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2444 measured reflections
2167 independent reflections
1690 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0605

$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 18$
$k = -12 \rightarrow 1$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 247 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0454
$wR(F^2)$ = 0.1002
S = 1.042
2167 reflections
169 parameters
H atoms: NH$_2$ with distance restraints, OH rigid, others riding

$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 6.4461P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.461 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.665 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Ni	1/2	0.54687 (6)	1/4	0.0162 (2)
C1	0.5708 (2)	0.4430 (3)	0.4237 (2)	0.0174 (7)
C2	0.4896 (2)	0.3756 (3)	0.4101 (2)	0.0173 (7)
C3	0.4617 (2)	0.2877 (3)	0.4712 (2)	0.0233 (8)
C4	0.3864 (2)	0.2280 (4)	0.4504 (3)	0.0283 (9)

C5	0.3413 (2)	0.2587 (4)	0.3698 (3)	0.0283 (9)
C6	0.3718 (2)	0.3500 (4)	0.3129 (2)	0.0253 (8)
C7	0.6132 (2)	0.7735 (3)	0.2056 (2)	0.0214 (8)
C8	0.6327 (3)	0.8728 (4)	0.1356 (3)	0.0379 (10)
N1	0.4450 (2)	0.4077 (3)	0.3312 (2)	0.0182 (6)
N2	0.6250 (2)	0.4148 (3)	0.4960 (2)	0.0225 (7)
N3	0.5849 (2)	0.5240 (3)	0.3606 (2)	0.0180 (6)
O1	0.66296 (14)	0.5815 (2)	0.3755 (2)	0.0238 (6)
O2	0.56704 (15)	0.6838 (2)	0.1782 (2)	0.0211 (6)
O3	0.6439 (2)	0.7865 (2)	0.2869 (2)	0.0327 (7)
C98	0.4145 (3)	0.0859 (5)	0.1514 (4)	0.0597 (15)
C99	0.3214 (3)	0.0937 (4)	0.1358 (3)	0.0431 (11)
O99	0.2869 (2)	−0.0152 (3)	0.0956 (2)	0.0394 (7)

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

Ni—N3	2.054 (3)	C4—C5	1.375 (5)
Ni—N1	2.116 (3)	C5—C6	1.383 (5)
Ni—O2	2.118 (2)	C6—N1	1.335 (4)
C1—N3	1.287 (4)	C7—O3	1.255 (4)
C1—N2	1.354 (4)	C7—O2	1.265 (4)
C1—C2	1.487 (5)	C7—C8	1.511 (5)
C2—N1	1.355 (4)	N3—O1	1.397 (3)
C2—C3	1.380 (5)	C98—C99	1.491 (7)
C3—C4	1.381 (5)	C99—O99	1.408 (5)
N3^{i}—Ni—N3	166.2 (2)	C2—C3—C4	118.9 (3)
N3^{i}—Ni—N1	93.92 (11)	C5—C4—C3	118.9 (3)
N3—Ni—N1	76.18 (11)	C4—C5—C6	119.2 (3)
N1—Ni—N1^{i}	89.7 (2)	N1—C6—C5	122.8 (3)
N3—Ni—O2^{i}	91.95 (10)	O3—C7—O2	124.7 (3)
N1—Ni—O2^{i}	89.64 (9)	O3—C7—C8	117.3 (3)
N3—Ni—O2	97.68 (10)	O2—C7—C8	117.9 (3)
N1—Ni—O2	173.76 (10)	C6—N1—C2	117.7 (3)
O2^{i}—Ni—O2	91.67 (13)	C6—N1—Ni	126.9 (2)
N3—C1—N2	124.6 (3)	C2—N1—Ni	115.4 (2)
N3—C1—C2	114.6 (3)	C1—N3—O1	112.1 (3)
N2—C1—C2	120.7 (3)	C1—N3—Ni	119.9 (2)
N1—C2—C3	122.5 (3)	O1—N3—Ni	127.8 (2)
N1—C2—C1	113.9 (3)	C7—O2—Ni	132.8 (2)
C3—C2—C1	123.6 (3)	O99—C99—C98	112.4 (4)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O99—H99$\cdots$O3^{i}	0.84	2.08	2.909 (4)	172
O1—H1$\cdots$O3	0.84	1.73	2.561 (3)	170
N2—H2$A\cdots$O1	0.83	2.23	2.589 (4)	106
N2—H2$A\cdots$O99^{ii}	0.83	2.36	3.086 (4)	146
N2—H2$B\cdots$O2^{iii}	0.83	2.20	3.012 (4)	168

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

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data, have been deposited with the IUCr (Reference: FG1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-(Benzenethiolato)bis(*tert*-butyl isocyanide)carbonyl(cyclopentadienyl)molybdenum(II), $[Mo(C_6H_5S)(C_5H_9N)_2(C_5H_5)(CO)]$

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Abstract

In $[CpMo(SPh)(CO)(CN^tBu)_2]$, Cp = η^5-C_5H_5, the Mo atom adopts conventional four-legged piano-stool coordination geometry; a pair of *cis* CN^{t}Bu ligands, together with carbonyl and benzenethiolato groups, make up the base. The Mo—CN^{t}Bu bond lengths [2.053 (4) Å *trans* to S, 2.086 (4) Å *trans* to CO] show a small but significant difference.

Comment

While investigating the reactivity of the binuclear complex $[Cp_2Mo_2(\mu\text{-}H)(\mu\text{-}SPh)(CO)_4]$ (Schollhammer *et*