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cis-Bis(ethylenediamine)bis(pyridine)-nickel(II) dinitrate

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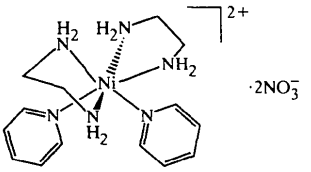
Abstract

The title complex, $[Ni(C_2H_8N_2)_2(C_5H_5N)_2](NO_3)_2$, consists of an Ni^{II} atom in a pseudo-octahedral coordination environment composed of two pyridine donors in a *cis* arrangement and four primary amine donors from two ethylenediamine ligands. The cations pack in layers held together *via* a network of N—H···O hydrogen bonds and close intermolecular interactions with the anions.

Comment

The title complex, $[Ni(en)_2(py)_2](NO_3)_2$ (en is ethylenediamine and py is pyridine), (1), was crystallized during an effort to obtain the nickel(II) complex of a tetradentate bis-Schiff base bis-oxime ligand for studies of the coordination and redox chemistry of nickel(II) with polydentate oxime-containing ligands that leave open coordination positions. Under conditions of pyridine as solvent and in the presence of nickel(II), these ligands are apparently hydrolyzed and the pink–purple compound (1) results. From similar reactions in pyridine, we have also obtained red–orange crystals of the previously reported nickel bis(dione bis-oxime) complex (Williams *et al.*, 1959) that results from hydrolysis of the starting dione mono-oxime or its Schiff base derivative, with transfer of hydroxylamine to form the bis-oxime.



(1)

Compound (1) consists of nickel(II) in a pseudo-octahedral coordination environment composed of two pyridine donors in a *cis* arrangement and four primary amine donors from two ethylenediamine ligands. While unsubstituted pyridines bound to nickel(II) in coordination environments with oxygen, sulfur or halide donors are common, a search of the Cambridge Structural Database (Allen & Kennard, 1993) reveals few nickel complexes with unsubstituted pyridine in an all-nitrogen coordination environment. These structures include isothiocyanate (Valach *et al.*, 1984), porphyrin (Duval *et al.*, 1997; Balch, Noll *et al.*, 1993; Balch, Olmstead & Phillips, 1993), cyanamide (Jager *et al.*, 1992, 1996), azenide (Xuming *et al.*, 1985) or mixed amine/imine (Cobbledick *et al.*, 1986) donor groups in addition to pyridine. Remarkably, only one other nickel structure with all amine and pyridine donors, (2), was found, with a tetraazacyclohexadecine ligand and two *trans* pyridines (Li *et al.*, 1993). The Ni—N_{py} distances in (1) are slightly shorter (average 2.145 Å) than those in (2) (average 2.185 Å), but are within the range for the other Ni–py complexes, while the Ni—N_{amine} distances in (1) are longer (average 2.129 Å) than those in (2) (average 2.041 Å), but about the same as those in $[Ni(en)_3](BPh_4)_2$ (average 2.15 Å; Cramer & Huneke, 1978).

The cations pack in layers, with the anions holding them together *via* a network of N—H···O hydrogen bonds, with N···O distances in the range 2.942 (5)–3.089 (5) Å and H···O separations of less than 2.4 Å, consistent with observations summarized previously by Voet & Rich (1970) and Taylor *et al.* (1984). Additionally, several close intermolecular contacts with N···O distances in the range 3.238 (6)–3.521 (5) Å stabilize the packing in the crystal structure. Much weaker N—H···N and several C—H···O interactions are also observed. These H···N and H···O separations are in the ranges 2.81–3.37 and 2.41–2.57 Å, respectively.

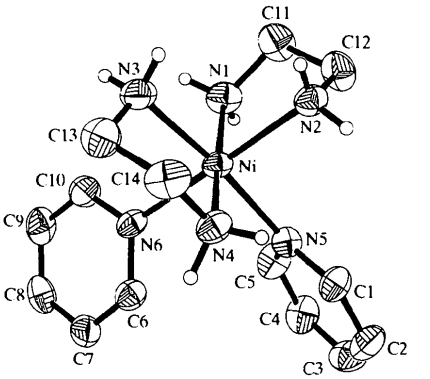


Fig. 1. The structure of the cation of (1) showing 50% probability displacement ellipsoids and the atomic numbering scheme. For clarity, only H atoms on nitrogen are shown.

Experimental

For the synthesis of the ligand, two equivalents of 1-phenyl-1,2-butanedione 2-oxime and one equivalent of ethylenediamine were reacted in refluxing ethanol for several hours until the ligand precipitated as a white powder. The ligand and $Ni(NO_3)_2$ were combined in a 1:1 ratio in pyridine (6 m*M*). A half volume of toluene was added and the solution was allowed to evaporate until pink–purple needles of (1) formed

in the red–orange solution [m.p. (decomposition, turning from pink–purple to black) 507–513 K]. IR (KBr pellet): 3292 (*m*), 2947 (*m*), 1585 (*m*), 1385 (*s*), 1031 (*s*), 676 (*m*), 518 (*m*) cm^{-1}.

Crystal data

$[Ni(C_2H_8N_2)_2(C_5H_5N)_2](NO_3)_2$
M_r = 461.14
Monoclinic
$P2_1/c$
a = 8.889 (1) Å
b = 8.107 (1) Å
c = 28.715 (1) Å
β = 94.68 (1)°
V = 2062.4 (4) $Å^3$
Z = 4
D_x = 1.485 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 4613 reflections
θ = 3.57–25.37°
μ = 0.989 mm^{-1}
T = 223 (2) K
Needle
0.50 × 0.10 × 0.10 mm
Pink–purple

Data collection

SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.740, T_{max} = 0.928
11 984 measured reflections
4170 independent reflections

2718 reflections with $I > 2\sigma(I)$
R_{int} = 0.085
θ_{max} = 26.37°
$h = -11 \rightarrow 10$
$k = -8 \rightarrow 10$
$l = -33 \rightarrow 35$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.118
S = 1.018
4170 reflections
294 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 2.1385P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.52 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.42 e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni—N3	2.107 (4)	Ni—N1	2.145 (3)
Ni—N2	2.120 (4)	Ni—N5	2.157 (3)
Ni—N6	2.134 (3)	N1—C11	1.480 (6)
Ni—N4	2.142 (3)		
N3—Ni—N2	93.06 (17)	N6—Ni—N1	93.37 (13)
N3—Ni—N6	90.00 (14)	N4—Ni—N1	171.40 (15)
N2—Ni—N6	174.17 (13)	N3—Ni—N5	172.69 (13)
N3—Ni—N4	81.40 (14)	N2—Ni—N5	90.68 (15)
N2—Ni—N4	91.81 (15)	N6—Ni—N5	86.83 (12)
N6—Ni—N4	93.55 (14)	N4—Ni—N5	92.22 (13)
N3—Ni—N1	93.50 (17)	N1—Ni—N5	93.26 (15)
N2—Ni—N1	81.51 (14)		

Table 2. *Hydrogen-bonding geometry and close intermolecular contacts (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O5^{i}	0.85 (5)	2.50 (5)	3.179 (5)	137 (4)
N1—H1*B*···O5^{ii}	0.87 (5)	2.53 (5)	3.401 (6)	179 (4)
N2—H2*A*···O1^{ii}	0.81 (4)	2.51 (4)	3.238 (6)	151 (3)
N3—H3*A*···O3^{ii}	0.81 (4)	2.37 (5)	3.089 (5)	149 (4)
N3—H3*B*···O4^{ii}	0.88 (5)	2.08 (5)	2.942 (5)	166 (4)
N2—H2*B*···O3	0.88 (4)	2.18 (5)	3.019 (5)	161 (4)
N4—H4*B*···O2	0.86 (4)	2.68 (4)	3.521 (5)	168 (3)
N4—H4*A*···O2^{iii}	0.95 (4)	2.23 (4)	3.073 (5)	148 (3)

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

H atoms bound to nitrogen were located directly from the difference map, and both positional and U_{iso} parameters were refined. The remaining H atoms were either located directly or calculated based on geometric criteria. The nitrate O3 atom exhibits a large displacement parameter indicative of some disorder, however a disorder model was not addressed. The other O atoms of the nitrate counter-ions appear normal.

Data collection: *SMART* (Bruker, 1997). Cell refinement: *SMART*. Data reduction: *SAINT* (Bruker, 1997). Program(s) used to solve structure: *SHELXTL* (Version 5.03; Bruker, 1997). Program(s) used to refine structure: *SHELXTL* (Version 5.1; Bruker, 1997). Molecular graphics: *SHELXTL* (Version 5.03). Software used to prepare material for publication: *SHELXTL* (Version 5.03).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1089). Services for accessing these data are described at the back of the journal.

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