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Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
Disorder in solvent or counterion
 R factor = 0.030
 wR factor = 0.071
Data-to-parameter ratio = 14.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Aqua(pyridine *N*-oxide- κO)[tris(2-hydroxy-aminopropyl)amine- $\kappa^4\text{N}$]nickel(II) dinitrate

The title complex, $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})(\text{C}_9\text{H}_{18}\text{N}_4\text{O}_3)(\text{H}_2\text{O})](\text{NO}_3)_2$, is a six-coordinate pseudo-octahedral nickel(II) complex containing a tripodal amine ligand framework with three oxime donors, as well as pyridine *N*-oxide and aqua ligands. This complex displays crystallographic mirror symmetry and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding between the cation and anion.

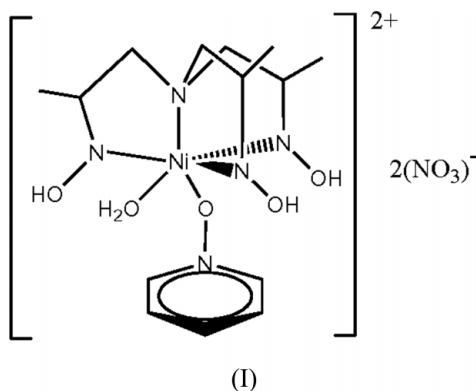
Received 12 November 2004

Accepted 18 November 2004

Online 27 November 2004

Comment

For the past several years, our research has involved the rational design of metal complexes with the overall objective of determining the ligand design factors that dictate the electron stoichiometry in the reactions of a series of oximate-containing Ni^{II} complexes with O_2 . We have reported (Goldcamp, Robinson *et al.*, 2002; Goldcamp *et al.*, 2003) the structural and reactivity studies of various tripodal amine Ni^{II} complexes, including the chloride and nitrate complexes of the tris(oxime) ligand, tris(2-hydroxylaminopropyl)amine (TRISOXH₃; Goldcamp, Krause Bauer, *et al.*, 2002). Additionally, we have undertaken the systematic study of halide substitution effects on the $\text{Ni}(\text{TRISOXH}_3)$ core (Jones *et al.*, 2004). We report here the structural characterization of aqua(pyridine *N*-oxide- κO)[tris(2-hydroxylaminopropyl)amine- $\kappa^4\text{N}$]nickel(II) dinitrate, (I).



The structure of (I) (Fig. 1) is consistent with previously reported structures from our laboratory of Ni^{II} complexes with the TRISOXH₃ ligand. Complex (I) contains a nickel(II) center bound to four ligand N atoms from three oximes and one amine. One water and a pyridine *N*-oxide, bound in a monodentate fashion through the O atom, complete the octahedral coordination. Complex (I) contains molecular and crystallographic mirror symmetry that coincides with atoms Ni, O1, O3, O4, N1, N3, N4, C4, C5, C6, C9, H1 and H9.

Complex (I) is related to $[\text{Ni}(\text{TRISOXH}_3)(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3\cdot\text{H}_2\text{O}$ (Goldcamp, Robinson *et al.*, 2002) which exhibits $\text{Ni}-\text{N}_{\text{amine}}$ and $\text{Ni}-\text{O}_{\text{aqua}}$ distances of 2.085 (2) and

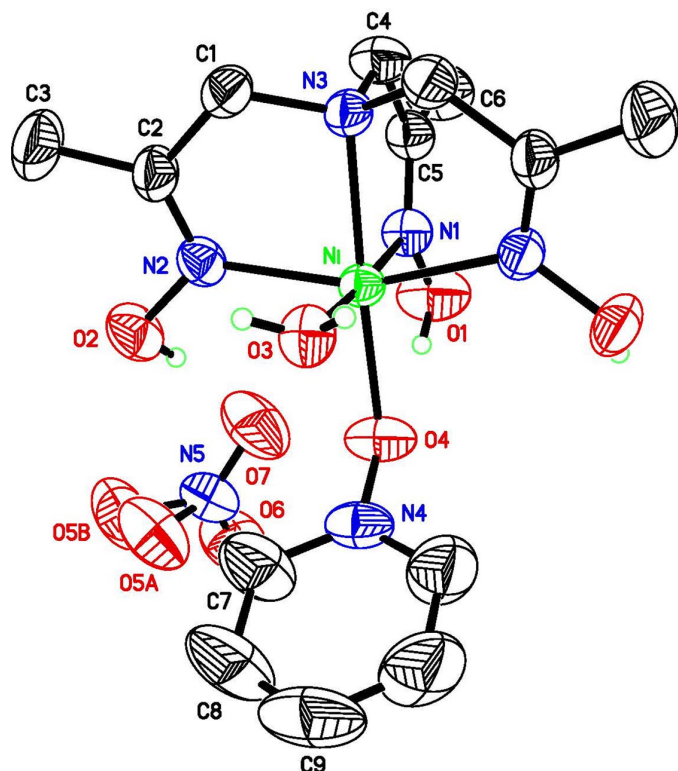


Figure 1
The structure of (I), showing the atomic labelling and 50% probability ellipsoids. For clarity, only hydroxy H atoms are shown.

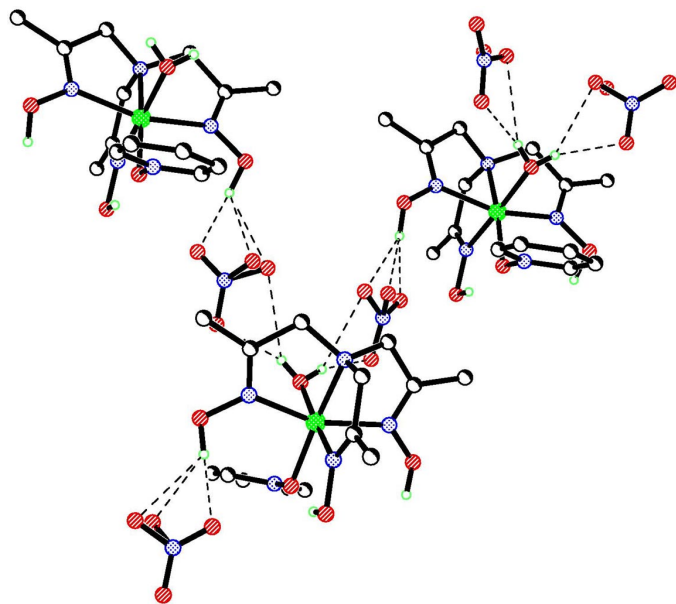


Figure 2
Hydrogen-bonding interactions (dashed lines) of (I) with the nitrate anion. For clarity, only hydroxy H atoms are shown.

2.076 (2) Å, respectively. The related distances in (I) are Ni—N3 = 2.089 (3) Å and Ni—O3 = 2.099 (3) Å.

The Ni—O(pyridine *N*-oxide) angle in (I) is comparable to other Ni^{II} complexes possessing both a tripodal amine and, for example, a 2-formylpyridine *N*-oxide ligand as in [1-[ethoxy-(2-pyridyl *N*-oxide)methyl]-3-(8-quinolylmethyl)-5-[(2-pyridyl

N-oxide)methylene]-3-azapentane-1,5-diamine}nickel(II) diperchlorate [(II); He *et al.*, 1999] and 2,2'-[5-(2-aminoethyl)-1-hydroxy-2,5,8-triazanon-8-ene-1,9-diyl]bis-(pyridine *N*-oxide)nickel(II) hexafluorophosphate [(III); Gou *et al.*, 1991]. However, the distance between the Ni atom and the pyridine *N*-oxide O atom in (I) [2.002 (3) Å] is shorter than reported values for (II) and (III) of 2.070 (3) and 2.110 (3)/2.029(4) Å, respectively. This suggests a stronger bonding interaction in (I), due to the ability of the oxime groups to act as π -acceptors more efficiently than the amine groups on the other complexes. In addition, nickel complexes with monodentate-bound pyridine *N*-oxide ligands, such as [Ni(pyridine *N*-oxide)₆](BrO₃)₂ (Paduan-Filho *et al.*, 1981 and [Ni(pyridine *N*-oxide)₆](BF₄)₂ (van Ingen Schenau *et al.*, 1974) exhibit Ni—O distances of 2.062 (3) and 2.060 (1) Å, while for Ni(2,4-pentanedionato)₂(pyridine *N*-oxide)₂ (Horrocks *et al.*, 1968), the distances are 2.105 (5) and 2.088 (5) Å.

The pyridine *N*-oxide ligand in (I) is bound to the Ni atom in what can be described as sp^2 hybridization about the O atom [O4—N4 = 1.333 (4) Å and Ni—O4—N4 = 119.1 (2)°]. This type of bonding appears to be typical for pyridine *N*-oxide (average O—N = 1.343 Å) (van Ingen Schenau *et al.*, 1974; Paduan-Filho *et al.*, 1981), whether bound to a metal or free as in PyNO·HCl (Tsoucaris, 1961) and PyNO (Ülkü *et al.*, 1971). Unlike Ni(2,4-pentanedionato)₂(pyridine *N*-oxide)₂ (Horrocks *et al.*, 1968), where the pyridine *N*-oxide is tilted with respect to the Ni—O—N bond (dihedral angles are 67.5 and 48.4°), no such ring tilt is present in (I) as the crystallographic mirror symmetry requires the dihedral angle to be exactly 90°.

Hydrogen bonding (Fig. 2 and Table 2) is observed between the nitrate anions and both an oxime O atom and the aqua ligand. Intramolecular hydrogen bonding is also observed between an oxime H atom and the O atom on the pyridine *N*-oxide. Similar hydrogen-bonding patterns are observed for other Ni^{II}(TRISOXH₃)XY complexes, where X and Y are halides and/or solvent molecules (Goldcamp, Robinson *et al.*, 2002; Goldcamp *et al.*, 2003; Jones *et al.*, 2004).

Experimental

Equimolar amounts of Ni(TRISOXH₃)(NO₃)₂ (Goldcamp, Robinson *et al.*, 2002), and pyridine-*N*-oxide were combined in acetonitrile. Vapor diffusion of diethyl ether into an acetonitrile solution yielded crystals suitable for analysis.

Crystal data

[Ni(C₅H₅NO)(C₉H₁₈N₄O₃)-
(H₂O)](NO₃)₂
*M*_r = 526.12
Orthorhombic, *Cmc*2₁
a = 11.0671 (10) Å
b = 14.0481 (10) Å
c = 14.8625 (12) Å
V = 2310.7 (3) Å³
Z = 4

*D*_x = 1.512 Mg m⁻³
Mo K α radiation
Cell parameters from 5192
reflections
 θ = 2.7–29.4°
 μ = 0.91 mm⁻¹
T = 294 (2) K
Block, purple
0.54 × 0.45 × 0.30 mm

Data collection

Bruker SMART 1K CCD diffractometer	2547 independent reflections
ω scans	2427 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.634$, $T_{\text{max}} = 0.765$	$\theta_{\text{max}} = 29.4^\circ$
7484 measured reflections	$h = -14 \rightarrow 15$
	$k = -17 \rightarrow 19$
	$l = -20 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 1.1661P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{\text{max}} = 0.007$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{\AA}^{-3}$
2547 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{\AA}^{-3}$
176 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1636 Friedel pairs
	Flack parameter = 0.065 (16)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ni—O4	2.002 (3)	Ni—O3	2.099 (3)
Ni—N1	2.024 (3)	O1—N1	1.395 (4)
Ni—N2	2.0521 (19)	O2—N2	1.400 (3)
Ni—N3	2.089 (3)	O4—N4	1.333 (4)
O4—Ni—N1	90.98 (11)	O4—Ni—O3	92.59 (11)
O4—Ni—N2	100.07 (6)	N1—Ni—O3	176.43 (13)
N1—Ni—N2	90.51 (5)	N2—Ni—O3	88.87 (6)
N2—Ni—N2	159.82 (11)	N3—Ni—O3	95.23 (11)
O4—Ni—N3	172.19 (11)	N4—O4—Ni	119.1 (2)
N1—Ni—N3	81.20 (13)	O1—N1—Ni	125.6 (2)
N2—Ni—N3	80.12 (5)	O2—N2—Ni	128.80 (15)

Symmetry code: (i) $1 - x, y, z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 \cdots O4	0.88	2.14	2.999 (4)	164
O2—H2 \cdots O7	0.99	1.88	2.856 (4)	168
O2—H2 \cdots O5A	0.99	2.47	3.080 (17)	119
O2—H2 \cdots O5B	0.99	2.53	3.146 (16)	120
O3—H3 \cdots O6 ⁱⁱ	0.79	2.08	2.826 (3)	158
O3—H3 \cdots O5B ⁱⁱ	0.79	2.57	3.260 (15)	148

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

The hydroxy H atoms were located directly and held fixed at those locations. The remaining methylene, methyl and aromatic H atoms

were either located or included in calculated positions (C—H = 0.97, 0.96 and 0.93 \AA , respectively) and were treated with a riding model in subsequent refinements. The isotropic displacement parameters for the H atoms were set as aU_{eq} of the adjacent atom ($a = 1.5$ for OH and CH₃, and 1.2 for all other H atoms). Some disorder is present, as indicated by the enlarged anisotropic displacement parameters of the benzene ring and the anion. Only atom O5 of the nitrate anion was resolved into two alternate positions (occupancy set at 0.5).

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Crystallographic data were collected through the Ohio Crystallography Consortium located at the University of Toledo, Toledo, Ohio 43606 (Ohio Board of Regents 1995 Investment Fund CAP-075).

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