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Dimethanolbis(*N*-nitroso-*N*-phenylhydroxylaminato-*O*,*O*′)nickel(II)

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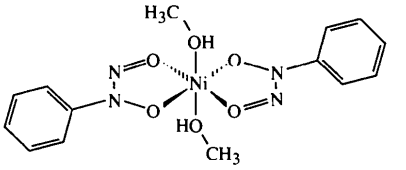
Abstract

The title compound, $[Ni(C_6H_5N_2O_2)_2(CH_3OH)_2]$, contains an Ni atom in a six-coordinate state. The Ni atom displays distorted octahedral coordination. The *N*-nitroso-*N*-phenylhydroxylaminato anions lie in a *trans* position to each other, forming the equatorial plane, and the methanol ligands occupy the axial positions.

Comment

Many metal complexes of *N*-nitroso-*N*-phenylhydroxylamine have been investigated in solution for analytical purposes, but their composition, properties and reactions have not yet been elucidated, except for a few X-ray crystallographic studies on the iron(III), copper(II) and copper(I) complexes (van der Helm, Merrit & Degeilh, 1965; Charalambous, Haines, Harris, Hendrick & Taylor, 1984). It is important to determine the crystal structures of metal complexes of *N*-nitroso-*N*-phenylhydroxylamine, not only from the analytical standpoint, but also from the biophysical one because *N*-nitroso compounds such as dimethylnitrosoamine or nitrosourea have serious cytotoxity as carcinogens (Nishimura *et al.*, 1985; Iishi, Tatsuta, Baba, Uehara & Nakazumi, 1994). In the present study, the crystal structure of the Ni^{II} complex of *N*-nitroso-*N*-phenylhydroxylamine prepared in methanol solution, dimethanolbis(*N*-nitroso-*N*-phenylhydroxylaminato)nickel(II), (I), was determined in order to clarify the binding mode of the nitroso group to the nickel(II).



(I)

The Ni coordination environment is slightly distorted octahedral. Each of the two *N*-nitroso-*N*-phenylhydroxylaminato anions is bound to the Ni atom through the O atoms of the *N*-nitroso and hydroxy groups (the latter being deprotonated), which lie in the same equatorial plane in a *trans* position to each other. Two methanol molecules at the axial sites complete the distorted octahedral arrangement around the Ni atom. The molecular packing (Fig. 2) is stabilized by

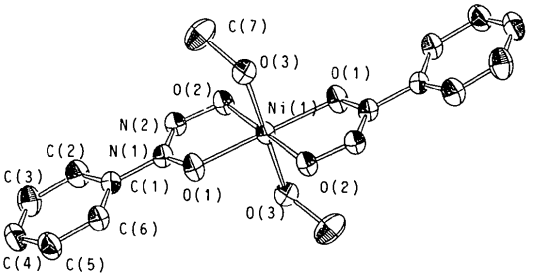


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme, viewed along the *b* axis. Ellipsoids correspond to 50% probability.

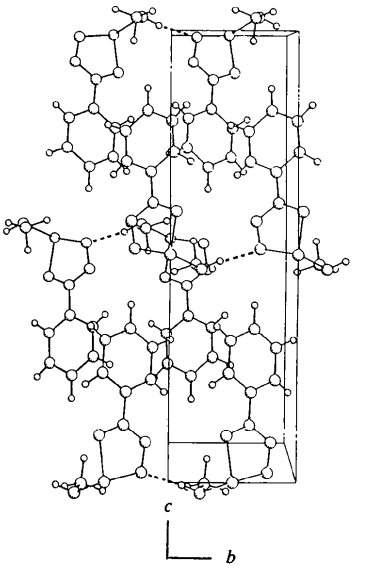


Fig. 2. Packing diagram of the title compound viewed along the *a* axis of the unit cell. Intermolecular hydrogen bonds are represented by dashed lines. The origin of the cell is in the rear left bottom corner.

intermolecular hydrogen bonding between the methanol and the nitroso group: O(3)—H(3)···O(2)(x, 1 + y, z) 2.731 (2) Å.

Experimental

A light green thin needle crystal was obtained by the slow evaporation of an aqueous solution of a mixture of *N*-nitroso-*N*-phenylhydroxylamine ammonium salt (cupferron) and $NiSO_4.6H_2O$ in the molar ratio 1:3 at room temperature. Then the thin needle crystal was dissolved in methanol and a single prismatic crystal was obtained by slow evaporation of the solvent.

Crystal data

$[Ni(C_6H_5N_2O_2)_2(CH_4O)_2]$	Mo $K\alpha$ radiation
M_r = 397.02	λ = 0.71069 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/c$	θ = 24.8–25.0°
a = 8.052 (2) Å	μ = 1.182 mm^{-1}
b = 5.488 (2) Å	T = 296 K
c = 19.308 (2) Å	Prism
β = 95.39 (1)°	0.4 × 0.4 × 0.4 mm
V = 849.5 (3) Å^3	Light green
Z = 2	
D_x = 1.552 Mg m^{-3}	

Data collection

Rigaku AFC-5*R* diffractometer	R_{int} = 0.040
ω–2θ scans	θ_{max} = 27.50°
Absorption correction: none	h = 0 → 10
2298 measured reflections	k = 0 → 7
2153 independent reflections	l = −24 → 24
1696 observed reflections [$I > 2\sigma(I)$]	3 standard reflections monitored every 150 reflections
	intensity decay: 0.30%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.006
R = 0.033	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
wR = 0.049	$\Delta\rho_{min}$ = −0.43 e Å^{-3}
S = 2.31	Extinction correction: none
1696 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
115 parameters	
H atoms not refined	
$w = 4F_o^2/\sigma^2(F_o^2)$	

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

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Ni(1)	0	0	1/2	2.19 (2)
O(1)	−0.0720 (2)	0.0454 (3)	0.5955 (1)	2.87 (7)
O(2)	−0.1589 (2)	−0.2834 (3)	0.50645 (8)	2.58 (6)
O(3)	−0.1865 (2)	0.2484 (3)	0.45882 (9)	2.72 (7)
N(1)	−0.1628 (2)	−0.1405 (3)	0.6113 (1)	2.20 (7)
N(2)	−0.2105 (2)	−0.3137 (4)	0.5689 (1)	2.51 (8)
C(1)	−0.2089 (3)	−0.1562 (4)	0.6818 (1)	2.27 (8)
C(2)	−0.3003 (3)	−0.3537 (5)	0.7028 (1)	3.2 (1)
C(3)	−0.3371 (4)	−0.3643 (5)	0.7712 (1)	3.7 (1)
C(4)	−0.2812 (3)	−0.1839 (5)	0.8179 (1)	3.5 (1)
C(5)	−0.1907 (4)	0.0122 (5)	0.7962 (1)	3.5 (1)
C(6)	−0.1531 (3)	0.0266 (4)	0.7276 (1)	2.9 (1)
C(7)	−0.3599 (4)	0.2082 (5)	0.4625 (2)	4.4 (1)

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

Ni(1)—O(1)	2.000 (2)	N(1)—N(2)	1.290 (3)
Ni(1)—O(1^i)	2.000 (2)	N(1)—C(1)	1.445 (3)
Ni(1)—O(2)	2.025 (2)	C(1)—C(2)	1.392 (3)
Ni(1)—O(2^i)	2.025 (2)	C(1)—C(6)	1.385 (3)
Ni(1)—O(3)	2.126 (2)	C(2)—C(3)	1.383 (4)
Ni(1)—O(3^i)	2.126 (2)	C(3)—C(4)	1.386 (4)
O(1)—N(1)	1.308 (2)	C(4)—C(5)	1.387 (4)
O(2)—N(2)	1.322 (2)	C(5)—C(6)	1.388 (4)
O(3)—C(7)	1.422 (3)		
O(1)—Ni(1)—O(1^i)	180.00	O(1)—N(1)—N(2)	124.4 (2)
O(1)—Ni(1)—O(2)	78.43 (6)	O(1)—N(1)—C(1)	117.7 (2)
O(1)—Ni(1)—O(2^i)	101.57 (6)	N(2)—N(1)—C(1)	117.8 (2)
O(1)—Ni(1)—O(3)	90.52 (7)	O(2)—N(2)—N(1)	112.8 (2)
O(1)—Ni(1)—O(3^i)	89.48 (7)	N(1)—C(1)—C(2)	120.7 (2)
O(2)—Ni(1)—O(2^i)	180.00	N(1)—C(1)—C(6)	117.5 (2)
O(2)—Ni(1)—O(3)	95.01 (7)	C(2)—C(1)—C(6)	121.8 (2)
O(2)—Ni(1)—O(3^i)	84.99 (7)	C(1)—C(2)—C(3)	118.6 (2)
O(3)—Ni(1)—O(3^i)	180.00	C(2)—C(3)—C(4)	120.4 (2)
Ni(1)—O(1)—N(1)	109.6 (1)	C(3)—C(4)—C(5)	120.4 (2)
Ni(1)—O(2)—N(2)	114.0 (1)	C(4)—C(5)—C(6)	120.0 (2)
Ni(1)—O(3)—C(7)	123.0 (2)	C(1)—C(6)—C(5)	118.8 (2)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELX86* (Sheldrick, 1985), *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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