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Key indicators

Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.036
 wR factor = 0.097
Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

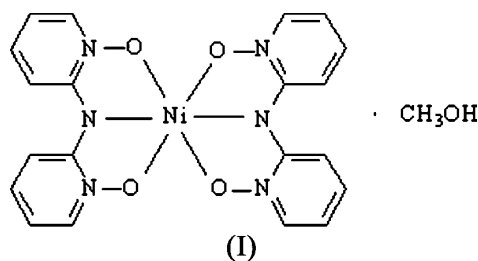
Bis[bis(1-oxo-2-pyridyl)aminato]nickel(II) methanol solvate

The title complex, $[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2)_2] \cdot \text{CH}_3\text{OH}$, is a mononuclear nickel(II) compound containing two di-2-pyridylamine N,N' -dioxide (dpa dioxide) ligands that are nearly perpendicular to each other. The Ni^{II} ion of the complex has a distorted octahedral environment with the equatorial plane formed by an N atom from each amine group and two O atoms of one ligand, while the axial positions are occupied by two O atoms of the second ligand. In the solid state, hydrogen-bonding interactions are dominant, with solvent molecules also participating in hydrogen bonding.

Received 22 March 2006
Accepted 20 April 2006

Comment

Transition metal complexes with polypyridylamine ligands, possessing diverse structures and special optical and electromagnetic properties (Xu *et al.*, 2004), have aroused great interest among researchers. Multi-pyridyldiamine ligands usually exhibit donor as well as acceptor properties and can be used as popular chelating ligands (Jing *et al.*, 2000). Recently, we have described a number of transition metal complexes using multidentate N -donor groups as ligands (Shieh *et al.*, 1997; Wang *et al.*, 1998; Chang *et al.*, 1999; Peng *et al.*, 2000) where we showed that it was difficult for such ligands to coordinate to some metals, such as rare earth metals. Hence, we have developed the derivative of the polypyridylamine ligand, polypyridylamine-oxide (Zeng *et al.*, 2003), in which N -oxides offer functional group manipulation and structural modification possibilities that are not usually accessible by other methods (Cope & Ciganek, 1963). In this paper, we report the synthesis and crystal structure of the title complex by reaction of Ni^{2+} with the di-2-pyridylamine dioxide ligand. To the best of our knowledge, this species represents the first example of a complex with this ligand.



The structure of the title compound, (I), shown in Fig. 1, has a distorted octahedral coordination geometry in which the central Ni ion is six-coordinated by four O atoms and two N atoms. The equatorial plane is formed by atoms N2 and N5 of different ligands and O3 and O4 of one ligand, while the axial

positions are occupied by atoms O1 and O2 of the other ligand (Table 1). The four atoms of the equatorial plane are nearly coplanar, with mean deviation 0.0142 (5) Å. However, the O1–Ni1–O2 angle (Table 1) indicates that the octahedral geometry is distorted.

The two pyridine rings in each ligand in the title complex are not coplanar, forming dihedral angles of 26.6 (5) and 7.4 (3)° for C11–C20-dpa and C1–C10-dpa, respectively. The two dpa dioxide ligands lie nearly perpendicular to each other, with a dihedral angle between the two least-squares planes through C1–C10 and C11–C20 of 75.0 (2)°.

The solvent molecule is found to undergo hydrogen bonding through the methanol atom O5 to O4 of one of the ligands.

Experimental

Dpa dioxide (0.1 g) was dissolved in methanol (20.0 ml) and Ni(ClO₄)₂·6H₂O (0.03 g) was added. The resulting solution was stirred for 5 h in air at room temperature. The mixture was filtered and the filtrate was crystallized by diffusion of diethyl ether at room temperature. After several days, green single crystals of (I) were obtained.

Crystal data

[Ni(C ₁₀ H ₈ N ₃ O ₂) ₂]·CH ₄ O	Z = 8
<i>M_r</i> = 495.14	<i>D_x</i> = 1.578 Mg m ⁻³
Orthorhombic, <i>Pbca</i>	Mo Kα radiation
<i>a</i> = 11.3969 (17) Å	<i>μ</i> = 0.98 mm ⁻¹
<i>b</i> = 12.911 (2) Å	<i>T</i> = 273 (2) K
<i>c</i> = 28.337 (4) Å	Block, green
<i>V</i> = 4169.5 (11) Å ³	0.30 × 0.22 × 0.20 mm

Data collection

Bruker APEX-II area-detector diffractometer	25649 measured reflections
<i>φ</i> and <i>ω</i> scans	5108 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2004)	3665 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.77, <i>T_{max}</i> = 0.82	<i>R_{int}</i> = 0.040
	<i>θ_{max}</i> = 28.2°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 1.9608P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	(Δ/σ) _{max} = 0.002
<i>S</i> = 1.01	$\Delta\rho_{max} = 0.33 \text{ e } \text{Å}^{-3}$
5108 reflections	$\Delta\rho_{min} = -0.38 \text{ e } \text{Å}^{-3}$
299 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ni1–N5	2.0036 (16)	Ni1–O4	2.0705 (15)
Ni1–N2	2.0113 (16)	Ni1–O3	2.0720 (15)
Ni1–O1	2.0659 (16)	Ni1–O2	2.1074 (15)
N5–Ni1–N2	177.40 (7)	O4–Ni1–O3	157.72 (6)
N5–Ni1–O1	78.47 (7)	O1–Ni1–O2	155.64 (6)
O1–Ni1–O4	90.31 (7)	O3–Ni1–O2	95.11 (6)

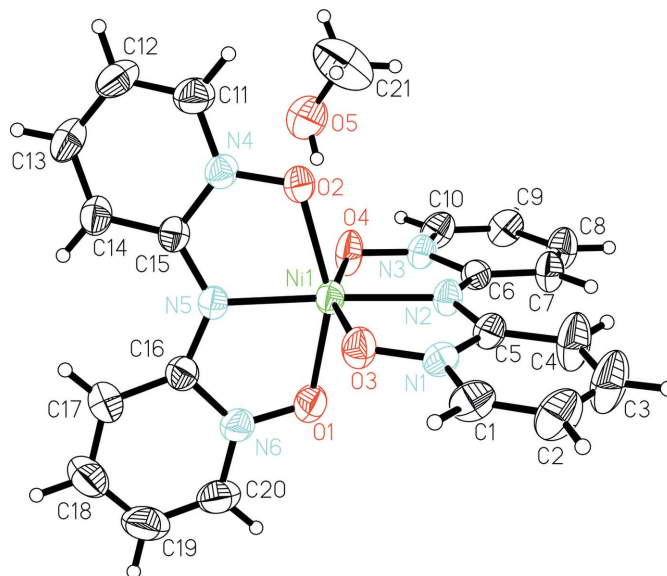


Figure 1

The asymmetric unit of (I), showing 50% probability displacement ellipsoids.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O5–H5···O4	0.83	1.89	2.719 (3)	174

The H atoms were positioned geometrically and treated as riding on their parent atoms, with *X*–H distances of 0.93 Å (pyridine ring), 0.83 Å (OH group) and 0.96 Å (methyl), and with *U*_{iso}(H) = 1.2*U*_{eq}(C_{pyridine}) and 1.5*U*_{eq}(C_{methyl},O).

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *APEX2*; software used to prepare material for publication: *APEX2*.

The authors are grateful for the support of this work by the Natural Science Foundation of Jiangxi Province (grants 0520036 and 0620029).

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