Diaqua{6,6′-dimethoxy-2,2′-[propane-1,3-diylbis(nitrilomethylidyne-*N*)]diphenolato-*O*,*O*′}nickel(II)

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In the title compound, $[Ni(C_{19}H_{20}N_2O_4)(H_2O)_2]$, the Ni atom has a distorted octahedral coordination geometry in which the tetradentate Schiff base ligand acts as a *cis*-N_2O_2 donor defining an equatorial plane, and water molecules occupy the axial positions. The two parts of the molecule are related by a mirror plane that passes through the Ni atom and is perpendicular to the equatorial plane. The angular distortions from normal octahedral geometry are in the range 1–6°, and the equatorial plane, defined by the donor atoms of the Schiff base, is almost square planar. The six-membered ring comprising the Ni, the imine N and the propylene C atoms adopts a half-chair conformation. The Ni—O [2.017 (2) Å] and Ni—N [2.071 (2) Å] distances are within the ranges expected for high-spin octahedral nickel complexes.

Comment

We are currently investigating the preparation and spectro-electrochemical characterization of modified electrodes with electroactive polymers based on nickel(II) and copper(II) complexes with N_2O_2-donor Schiff base ligands, which are obtained by the condensation of salicylaldehyde and ethyl-enediamine derivatives with increasing stereochemical demand (Vilas-Boas *et al.*, 1997, 1998, 2000). The electrochemical characterization of modified electrodes based on nickel complexes with ethylenic bridges has shown that their stability/durability and conductivity in $CH_3CN/TEAP$ (0.1 mol dm^{-3}) increase with the bulkiness of the imine bridge substituents, probably as a consequence of different film compaction imposed by bulky imine bridges (Santos *et al.*, 2000; Vilas-Boas *et al.*, 2000). We are extending this study to polymers based on similar complexes, but with propylene bridges, in order to assess the influence of the longer imine bridge on the electrochemical performance of polymer-modified electrodes. We have prepared the title compound, $[Ni\{(3\text{-MeO})_2salpd\}(H_2O)_2]$, (I), and studied its oxidative polymerization and redox switching in acetonitrile, and have

found that modified electrodes based on {6,6′-dimethoxy-2,2′-[propane-1,3-diylbis(nitrilomethylidyne-*N*)]diphenolato-*O*,*O*′}nickel(II), $[Ni\{(3\text{-MeO})_2salpd\}]$ or L^1, exhibit high electrochemical stability. We report here the molecular structure of the monomer, which is six-coordinate, in contrast with most of the known structures of this type of complex.

(I)
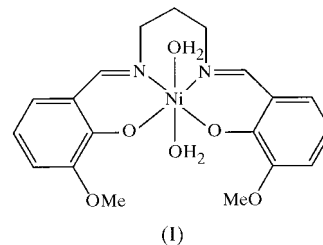
The structure of (I) consists of discrete molecules in which the Ni atom has distorted octahedral coordination geometry, with the tetradentate Schiff ligand acting as a *cis*-N_2O_2 donor and defining the equatorial plane, and with two water molecules occupying the axial positions (Fig. 1). The molecule has crystallographically imposed C_s symmetry, with the Ni atom on a mirror plane which is perpendicular to the general equatorial plane of the molecule. The angular distortions from normal octahedral geometry are in the range 1–6°. The angle subtended at the metal atom in the metallocycle (O1—Ni1—N1) is 88.75 (8)° and that in the propylene bridging moiety (N1—Ni1—N1′) is 96.94 (11)°. The O3—Ni1—O2 angle is 175.20 (10)°.
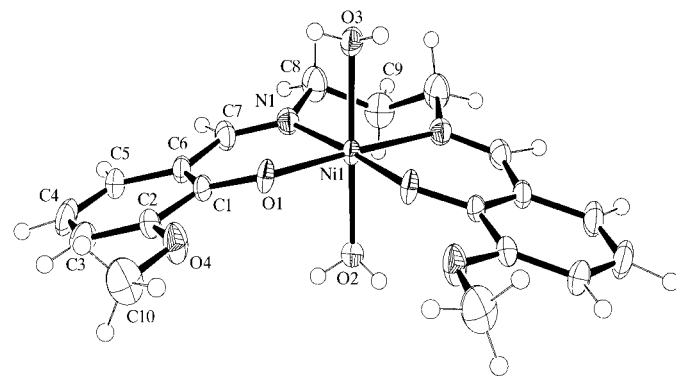

Figure 1
The molecular structure of $[Ni\{(3\text{-MeO})_2salpd\}(H_2O)_2]$ with the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The equatorial plane, defined by the donor atoms of the Schiff base ligand, is essentially planar, and the maximum deviation of the Ni atom from the least-squares equatorial plane is −0.005 (1) Å. The ligand-chelate-ring atoms N1—C7—C6—C1—O1 define a plane that makes an angle of 14.58 (3)° with the equatorial plane, and is almost coplanar with the plane defined by the atoms of the benzene ring. The two salicylaldehyde moieties are bent in an umbrella configuration and form, obviously, an angle of 29.16 (5)°. The six-membered ring comprising the Ni, the imine N and the propylene C atoms adopts a half-chair conformation; the imine C8 and C9 atoms are 0.288 (4) and −0.361 (5) Å, respectively, from the equatorial coordination plane.

The Ni—O(Schiff base) distance [2.017 (2) Å] is shorter than the Ni—N distance [2.071 (2) Å], as observed in other metal complexes with similar ligands having the same propylene–imine bridge (Akhtar & Drew, 1982; Drew *et al.*, 1985; Elerman *et al.*, 1993). This situation can be contrasted with what is normally found in similar simple complexes with unsubstituted ethylene–imine bridges, for which the Ni—N distances are shorter than the Ni—O distances (Manfredotti & Gusatini, 1983; Akhtar, 1981; Blake *et al.*, 1995), and has been attributed to the steric hindrance of the bulkier trimethylene group between the N atoms. As a consequence, ligands with a longer aliphatic chain will cause weaker ligand fields. The Ni—O(water) distance is only slightly longer than the Ni—O(Schiff base) distance, and this observation shows conclusively that the two water molecules are bound axially. The ease of axial coordination in complexes with propylene bridges is a result of the weak ligand field produced by the Schiff base.

Axial coordination influences the Ni—O and Ni—N bond distances of the Schiff base. The values range from 1.84 to 1.90 Å in four-coordinate low-spin Ni complexes with similar Schiff bases having a propylene–imine bridge (Akhtar & Drew, 1982; Drew *et al.*, 1985), and from 1.85 to 1.88 Å in the adduct of L^1 with SnPh$_3$Cl·H$_2$O (Clarke *et al.*, 1994). In the high-spin five-coordinate Ni complex with a similar Schiff base, but which lacks the methoxy groups, and one axially bound water molecule, the values are 2.034 and 2.034 Å (Elerman *et al.*, 1993), and in the L^1·H$_2$O adduct with SnPh$_3$Cl·H$_2$O, the bond distances range from 1.99 to 2.06 Å (Clarke *et al.*, 1994). In the six-coordinate complex of L^1, these distances are always longer than 2 Å. These observations suggest that the axial binding of one or two water molecules weakens the equatorial field (the equatorial bond distances are about 0.1 Å longer) and changes the spin state of the nickel to high spin. The high-spin state of the complex is confirmed by the diffuse reflectance electronic spectrum, which exhibits in the near IR/visible region the three *d–d* transitions typical of high-spin octahedral nickel complexes.

The packing view down the *a* axis (Fig. 2) shows that the molecules are arranged in chains along a twofold screw axis at $y + \frac{1}{4}$, $z + \frac{1}{4}$. The chains are formed by parallel stacking of benzene moieties (3.7 Å), with the imine bridges alternating along the axis. Extensive hydrogen bonding is observed between coordinated water molecules: both H2*A* and H3*A* (and their symmetry equivalents) appear to be strongly involved in hydrogen bonding to O1 in neighbouring molecules, which progagates a total of eight hydrogen bonds for each molecule in the lattice. Notwithstanding their importance in the packing of these molecules in the crystal, the presence of interactions between the benzene moieties suggests that the crystal packing is also controlled by π–π* interactions between these moieties. This packing is somewhat reminiscent of that found in the similar four-coordinate Ni complex with 2,2′-[propane-1,3-diylbis(nitrilomethylidyne-*N*)]dinaphthol (Akhtar & Drew, 1982), in which the umbrella-shaped molecules stack parallel to the *c* axis, with each Ni atom almost directly above the other. In the six-coordinate complexes of L^1, the axially bound water molecules prevent such an arrangement and to preserve the stacking of the aromatic moieties, the water–nickel–water fragments are not collinear, but are almost parallel and alternate along the *a* axis.
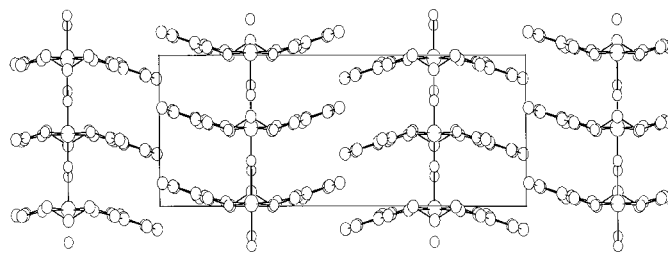

Figure 2
The crystal packing of [Ni{(3-MeO)$_2$salpd}(H$_2$O)$_2$] viewed down the *a* axis.

Experimental

The title nickel(II) complex was prepared by refluxing an ethanol/water solution of nickel acetate monohydrate with an equimolar amount of the ligand (obtained by Schiff condensation in ethanol of *o*-vaniline with 1,3-propanediamine). Upon cooling, a green solid was obtained which was recrystallized from acetonitrile. Crystals of diffractometric quality were obtained by slow evaporation of a dimethylformamide solution.

Crystal data

[Ni(C$_{19}$H$_{20}$N$_2$O$_4$)(H$_2$O)$_2$]	Mo $K\alpha$ radiation
$M_r = 435.12$	Cell parameters from 2000
Orthorhombic, *Pnma*	reflections
$a = 7.4077 (11)$ Å	$\theta = 4.8–28.2°$
$b = 22.064 (3)$ Å	$\mu = 1.064$ mm^{-1}
$c = 11.585 (2)$ Å	$T = 293 (2)$ K
$V = 1893.5 (5)$ Å^3	Needle, light green
$Z = 4$	$0.4 \times 0.1 \times 0.1$ mm
$D_x = 1.526$ Mg m^{-3}	

Data collection

Stoe Image Plate Detector System	$R_{int} = 0.096$
Area-detector scans	$\theta_{max} = 26.13°$
Absorption correction: numerical	$h = -9 \rightarrow 9$
($IPDS\ FACEIT$; Stoe & Cie,	$k = -27 \rightarrow 23$
1996)	$l = -14 \rightarrow 14$
$T_{min} = 0.458$, $T_{max} = 0.930$	3 standard reflections
9095 measured reflections	frequency: 90 min
1898 independent reflections	intensity decay: none
1583 reflections with $I > 2\sigma(I)$	

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.017 (2)	Ni1—O2	2.090 (2)
Ni1—N1	2.071 (2)	Ni1—O3	2.100 (2)
O1^i—Ni1—O1	85.55 (9)	N1—Ni1—O2	88.70 (6)
O1^i—Ni1—N1	174.30 (7)	O1—Ni1—O3	91.82 (7)
O1—Ni1—N1	88.75 (8)	N1—Ni1—O3	88.11 (6)
N1—Ni1—N1^i	96.94 (11)	O2—Ni1—O3	175.20 (10)
O1—Ni1—O2	91.70 (6)		

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

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = -0.002$
1847 reflections	$\Delta\rho_{max} = 0.86$ e Å^{-3}
183 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A$\cdots$O1^i	0.72 (3)	2.15 (3)	2.810 (3)	152 (4)
O3—H3A$\cdots$O1^{ii}	0.76 (3)	2.41 (3)	3.107 (3)	152 (4)

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

All H atoms were refined [C—H 0.86 (3)–1.05 (3) Å].

Data collection: *IPDS EXPOSE* (Stoe & Cie, 1996); cell refinement: *IPDS CELL* (Stoe & Cie, 1996); data reduction: *IPDS INTEGRATE* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*III *for Windows* (Johnson & Burnett, 1998); software used to prepare material for publication: *SHELXL*93.

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