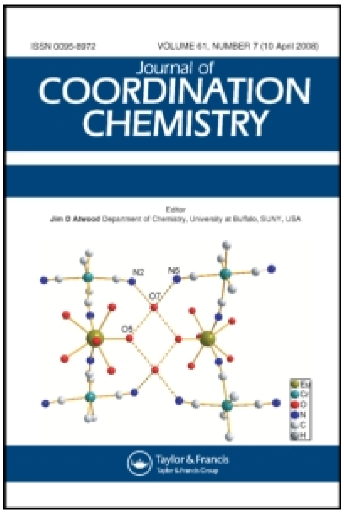

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Synthesis and crystal structure of a new lapacholate complex with nickel(II), $[Ni(Lap)_2(DMF)(H_2O)]$

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Synthesis and crystal structure of a new lapacholate complex with nickel(II), $[Ni(Lap)_2(DMF)(H_2O)]$

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The crystal and molecular structure of dilapacholateaqua(dimethylformamide)nickel(II) was determined by X-ray diffraction. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.8671(9)$ Å, $b = 10.654(1)$ Å, $c = 15.289(2)$ Å, $\alpha = 86.98(1)^\circ$, $\beta = 79.32(1)^\circ$, $\gamma = 87.031(8)^\circ$, and $Z =$ two molecules per unit cell. The structure was solved from 5094 reflections with $I > 2\sigma(I)$ and refined by full matrix least-square to an agreement R_1-factor of 0.0564. The nickel(II) is in a NiO_6 octahedral environment, *cis* coordinated to two lapacholate anions through their adjacent carbonyl [Ni–O distances of 2.075(2) and 2.066(2) Å], and phenyl oxygens [Ni–O lengths of 2.011(2) and 2.021(2) Å], and to a water [d(Ni–Ow) = 2.073(2) Å] and a DMF [d(Ni–O) = 2.076(2) Å] at axial positions. Some physicochemical and spectroscopic properties of the complex are also reported.

Keywords: Lapacholate; Ni(II) complex; Crystal structure; Spectroscopic properties

1. Introduction

Lapachol (LapH), a natural product that can be extracted from the wood of a lapacho tree (gendre *Tabebuia ipé*), and its derivatives are employed as anti-tumor, antibiotic, anti-malarial, and anti-ulcer agents [1, 2]. LapH is also considered a probable anti-cancer agent [3] with a potential to fight the *Tripanosoma cruzi*, the protozoan causing Chagas' disease [4].

LapH, a naphthoquinone with an unsaturated pendant chain at the C3-position and an oxydryl group at the C2-position, is described as [2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone] [4]. In alkaline medium, LapH loses a proton and turns into

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a potential bidentate ligand (Lap) to divalent metal ions. Because of the reactivity derived from its 1,4-quinonic-like structure combined with a keto–enol function, LapH presents pharmacological activity similar to acetonaphthonates, flavonates, and hydroxypyronates [2, 5–7]. The quest for improving this activity prompted a renewed work during the last 10 years on the synthesis, physicochemical characterization, and pharmacological properties of LapH complexes with transition metal ions, including Co(II), Zn(II), and Cu(II) [8, 9].

We present here the synthesis and structural characterization by X-ray diffraction and spectroscopic methods of a complex of LapH with Ni(II), $Ni(Lap)_2(DMF)(H_2O)$.

2. Experimental

2.1. *Preparation*

LapH was extracted with chloroform from the sawdust of a lapacho tree. The solid was purified by recrystallization and characterized employing IR spectroscopy. The complex was prepared by mixing stoichiometric aqueous solutions of nickel(II) nitrate and sodium acetate. A LapH solution (0.06 M) of absolute alcohol was added to the resulting product (nickel(II) acetate 0.03 M), then heated to 60°C and stirred for an hour. A magenta-colored solid precipitated was filtered out and dissolved in dimethylformamide (DMF). Dark red single crystals adequate for structural X-ray diffraction studies were obtained by the slow evaporation of the solvent.

2.2. *Chemical analysis*

The LapH content in the complex was determined following the procedure [7] by measuring the ligand electronic absorption maxima at 330 and 390 nm ($\varepsilon_{330} = 2.8 \times 10^3\,\mathrm{cm^{-1}\,M^{-1}}$ and $\varepsilon_{390} = 1.4 \times 10^3\,\mathrm{cm^{-1}\,M^{-1}}$) [9]. Nickel was assessed by atomic absorption with a GBC 904 spectrophotometer.

2.3. *X-ray diffraction data*

Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with EXPRESS [9] and reduced with XCAD4 [10]. The data were corrected numerically for absorption with PLATON [11]. The structure was solved by direct methods with SHELXS [12] and the molecular model was refined by full-matrix least-squares procedure on F^2 with SHELXL [13]. All hydrogens but on water were positioned stereo-chemically and refined with the riding model. The hydrogens of DMF were refined as rigid groups allowed to rotate around the corresponding N–C bonds. The water H-atoms were located in a difference Fourier map and refined isotropically at their found positions. Crystal data, data collection procedure, and refinement results are summarized in table 1.

2.4. *Spectra*

Infrared absorption spectra from 4000 to 400 $\mathrm{cm^{-1}}$ were collected at a resolution of 4 $\mathrm{cm^{-1}}$ on KBr-sandwiched samples with a Perkin-Elmer GX FT-IR instrument.

Table 1. Crystal data and refinement results for $Ni(Lap)_2(DMF)(H_2O)$.

Empirical formula	$C_{33}H_{35}NNiO_8$
Formula weight	632.33
Wavelength (Å)	1.54184
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)[a]	
a	9.8671(9)
b	10.654(1)
c	15.289(2)
α	86.98(1)
β	79.32(1)
γ	87.031(8)
Volume (Å^3), Z	1575.8(3), 2
Calculated density (mg m^{-3})	1.333
Absorption coefficient (mm^{-1})	1.314
$F(000)$	664
Crystal size (mm^3)	$0.32 \times 0.28 \times 0.16$
Crystal color/shape	Dark red/prism
θ range for data collection (°)	2.94–68.93
Limiting indices	$-11 \leq h \leq 11$, $0 \leq k \leq 12$, $-18 \leq l \leq 18$
Reflections collected	6078
Independent reflection	5766 [$R_{\mathrm{int}} = 0.0750$]
Completeness to $\theta = 68.93$	99%
Observed reflections [$I > 2\sigma(I)$]	5094
Max. and min. transmission	0.8216 and 0.7061
Data/restraints/parameters	5766/0/396
Goodness-of-fit on F^2	1.063
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0564$, $wR_2 = 0.1659$
R indices (all data)	$R_1 = 0.0630$, $wR_2 = 0.1759$
Largest difference peak and hole (e Å^{-3})	1.022 and −0.586

Corrections: Lorentz, polarization and absorption. Neutral scattering factors and anomalous dispersion corrections. Structure solved by direct and Fourier methods. The final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms. R indices defined as: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [a]Least-squares refinement of the angular settings for 25 reflections in the $14.37 < \theta < 34.36°$ range.

The electronic spectra (UV-Vis and Diffuse Reflectance) of both the solid state and solution (mixture of water and DMF) samples were run on a double-beam GBC 918 spectrophotometer equipped with a diffuse reflectance sphere.

3. Results

3.1. *Physical properties*

The solid is dark red, stable in air, and soluble in DMF, methanol, anhydrous ethanol, ether, and acetone. It is less soluble in benzene and carbon tetrachloride and insoluble in water.

3.2. *Analytical results*

Elemental analyses: Found (average of several determinations in %) for Ni: 9.18(8); LapH: 76.9(4). Anal. Calcd (%) for Ni: 9.28; LapH: 76.32.

Table 2. Bond lengths (Å) and angles (°) around the nickel(II) in $Ni(Lap)_2(DMF)(H_2O)$.

Bond distances		Bond angles	
O–Ni	2.076(2)	O(12)–Ni–O(22)	102.76(7)
O(1W)–Ni	2.073(2)	O(12)–Ni–O(21)	175.20(8)
O(11)–Ni	2.075(2)	O(22)–Ni–O(21)	80.16(7)
O(12)–Ni	2.011(2)	O(12)–Ni–O(11)	80.61(7)
O(21)–Ni	2.066(2)	O(21)–Ni–O(11)	96.60(7)
O(22)–Ni	2.021(2)	O(12)–Ni–O	87.69(8)
–	–	O(22)–Ni–O	91.57(9)
–	–	O(21)–Ni–O	88.43(8)
–	–	O(11)–Ni–O	90.29(8)
–	–	O(12)–Ni–O(1W)	93.65(8)
–	–	O(22)–Ni–O(1W)	92.26(9)
–	–	O(21)–Ni–O(1W)	90.01(8)
–	–	O(11)–Ni–O(1W)	85.76(8)
–	–	O–Ni–O(1W)	175.56(9)

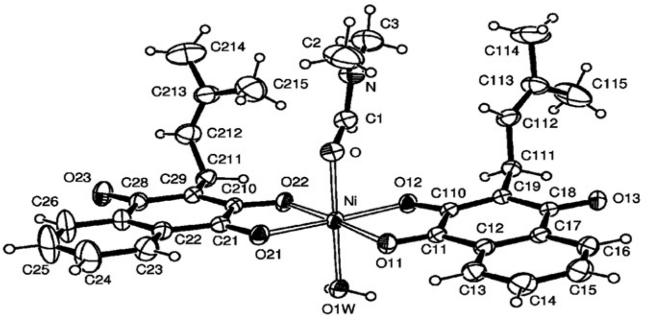

Figure 1. Molecular structure of $Ni(Lap)_2(DMF)(H_2O)$ showing the labeling of the non-H atoms and their displacement ellipsoids at the 50% probability level. Nickel(II)–ligand bonds are indicated by open lines.

3.3. *Structural results*

Bond distances and angles around nickel are given in table 2. An ORTEP [14] drawing of the complex is shown in figure 1 and a PLATON [11] diagram of the crystal packing is shown in figure 2.

4. Discussion

4.1. *Crystal structure*

The Ni(II) is in a slightly distorted octahedron (figure 1), equatorially *cis*-coordinated to two lapacholate anions (Lap), bidentate through their adjacent carbonyl and phenol oxygens [Ni–O bond distances of 2.075(2) and 2.011(2) Å for ligand 1 and 2.066(2) and 2.021(2) Å for ligand 2]. Axial positions are occupied by the oxygen of water [d(Ni–Ow) = 2.073(2) Å] and DMF [d(Ni–O) = 2.076(2) Å]. *Trans* O–Ni–O angles range from 175.20(8)° to 176.21(7)° and *cis* O–Ni–O angles are within 80.16(7)° to 96.60(7)°.

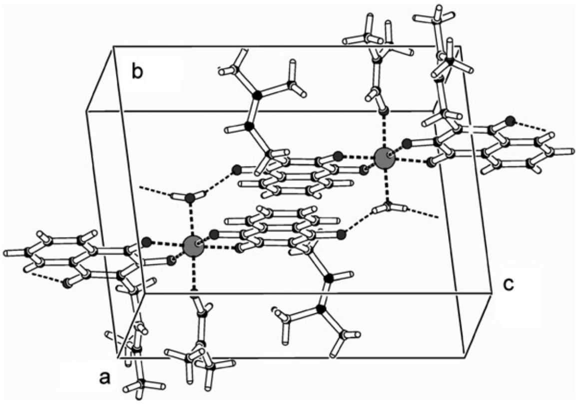

Figure 2. Crystal packing of $Ni(Lap)_2(DMF)(H_2O)$. Thick dashed lines indicate Ni-ligand bonds while H-bonds are shown by thin dashed lines.

Both Lap ligands are planar (rms deviation of fitted atoms from the least-squares plane is 0.063 Å for Lap 1 and 0.015 Å for Lap 2) and nearly co-planar to each other [9.50(2)°] with Ni(II) lying at the planes intersection [at less than 0.07 Å].

The nickel complex is isomeric to the related $M(Lap)_2(DMF)(H_2O)$, M: Co(II), Zn(II) isomorphous complexes [7, 15] where M(II) is also in a distorted octahedral environment, but coordinated by two nearly orthogonal (*cis*) Lap anions with the water and DMF molecules completing the octahedral coordination at *cis*-positions. The equatorial bonding of Lap to Ni(II) is similar to that reported for distorted octahedral $Zn(Lap)_2(EtOH)_2$, but here the Zn(II) atom is sited on a crystallographic inversion center and therefore the pair of chelating anions bind the metal in a *trans* conformation [7].

$Ni(Lap)_2(DMF)(H_2O)$ complexes are arranged in the lattice as a layered structure nearly parallel to the crystal *ac* plane. The water molecules bridge neighboring complexes on a layer (figure 2) through $O \cdots H–Ow–H \cdots O$ bonds [$O \cdots H$ distances of 1.995 and 1.976 Å, $Ow–H \cdots O$ angles of 164.7° and 172.0°], and adjacent layers through $Ni \cdots Ow–H \cdots O$ bonds.

4.2. *IR spectrum*

Up to 668 cm^{-1}, the IR absorption spectrum (Supplementary material) resembles other lapacholate complexes with transition metals [7, 8]. The OH stretching region shows two main features: a well-defined shoulder at 3651 cm^{-1} assigned to free hydroxyls (not H-bonded) and a band centered around 3368 cm^{-1} due to OH involved in H-bonding. Bands observed at 1661 and 1639 cm^{-1} in the spectrum of free LapH have been assigned to carbonyl [8]. In the nickel(II) complex, the red-shifted band at 1625 cm^{-1} can be safely attributed to the same group, as coordination with Ni(II) weakens the carbonyl bonding. Similar behavior is reported in the IR spectrum of the related $[Ni(Lap)_2] \cdot 5H_2O$ complex where a sharp carbonyl band appears at 1655 cm^{-1} [16]. The band at 582 cm^{-1} in $Ni(Lap)_2(DMF)(H_2O)$ is also red-shifted, attributed to the mesomerism of adjacent unsaturated C-atoms on phenolate [17]. The absorption band at 1295–1180 cm^{-1} has been attributed to lapacholate phenol C–O stretching [18]. However, this band also includes coupled in-plane C–C and C–H modes that appear in the same spectral region [17].

The Ni(II)–O stretching modes should be from 500 to 200 cm^{-1}, as M(II)–O stretching modes in Cu(II) and Ni(II) acetyl ketones have been reported to occur in the 455–291 cm^{-1} and 438–271 cm^{-1} regions, respectively [16]. In fact, we found weak absorption bands at 497, 441, 397, and 374 cm^{-1} in the IR spectrum of $Ni(Lap)_2(DMF)(H_2O)$ which can be assigned to the Ni–O bonds.

4.3. *Electronic spectra*

The visible region of the solid state diffuse reflectance spectrum (Supplementary material) displays a broad and strong absorption centered at about 500 nm, responsible for the dark red color of the complex. This band could be assigned to a $\pi \rightarrow \pi^*$ transition involving the quinonic carbonyl groups [19]. Based on the UV-Vis spectroscopy of aromatic rings showing that $\pi \rightarrow \pi^*$ transitions occur at 214, 231 and 340 nm for benzene ring and at 277 nm for quinonic ring [19], we assign the sharp and intense band at 238 nm and the weak shoulders at 271 and 341 nm observed in the solution spectrum.

4.4. *Thermal behavior*

DTG and DTA spectra are shown in the Supplementary material. The first loss of water molecule at 200°C (found weight loss: 3.0%, Anal. Calcd: 2.8%), is followed by DMF at 350°C (found: 9%, Anal. Calcd: 11.5%).

5. Conclusions

Reaction of nickel(II) nitrate and sodium acetate in aqueous solution with LapH in alcohol produces a solid with the characteristic dark red color of lapacholates. Dissolving the solid in DMF gives $Ni(Lap)_2(DMF)(H_2O)$ where eight oxygens coordinate Ni(II) in a slightly distorted NiO_6 octahedron. The Ni(II) is equatorially *cis* coordinated to two bidentate Lap anions. Water and DMF occupy the axial positions. The crystal is further stabilized by a strong H-bonding network involving water as donor and *p*-quinonic oxygen as an acceptor of neighboring complexes. This is confirmed by intense and broad IR absorption in the O–H stretching region.

The strong redish-brown color arises from an intense absorption band centered about 500 nm. This band could be assigned to a mesomeric (*p*-quinone ↔ *o*-quinone) transition of the quinonic ring conjugated system.

The thermal behavior of the solid state complex suggests that lapacholate–Ni(II) binding survives heating beyond 350°C.

Supplementary material

Tables containing complete information on atomic coordinates and equivalent isotropic parameters (table S4), bond distances and angles (table S5), anisotropic thermal parameters (table S6), hydrogen atomic positions (table S7), and H-bond distances and angles (table S8) are available from the authors upon request and have been deposited at the Cambridge Crystallographic Date Centre, under deposition number CCDC 724224.

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