

Research Article

Structural and Spectroscopic Properties of Two New Isostructural Complexes of Lapacholate with Cobalt and Copper

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Received 18 November 2011; Revised 24 January 2012; Accepted 24 February 2012

Academic Editor: Peter Baran

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The molecular structures of two isostructural complexes of lapacholate (Lap) anion and dimethylformamide (DMF), $M(\text{Lap})_2(\text{DMF})_2$ with M : Co Cu, were determined by X-ray diffraction methods. The substances crystallize in the triclinic space group $P\bar{1}$ with one molecule per unit cell and cell constants $a = 7.7591(3)$, $b = 10.3560(3)$, $c = 11.2224(4)$ Å, $\alpha = 95.110(2)$, $\beta = 94.310(2)$, and $\gamma = 107.704(2)^\circ$ for the Co complex and $a = 7.9308(2)$, $b = 10.0033(4)$, $c = 10.7508(4)$, $\alpha = 97.387(2)$, $\beta = 93.621(2)$, and $\gamma = 103.980(2)^\circ$ for the Cu complex. The structures were solved from 2933 (Co) and 2888 (Cu) reflections with $I > 2\sigma(I)$ and refined by full matrix least squares to agreement R_1 -factors of 0.041 (Co) and 0.033 (Cu). The metal M(II) ion is sited on a crystallographic inversion center in a MO_6 distorted octahedral environment. This ion is coordinated equatorially to two lapacholate anions through their adjacent carbonyl and phenol oxygen atoms [M–O bond distances of 2.134(1) and 2.008(1) Å (Co) and 2.301(1) and 1.914(1) Å (Cu)] and axially to two DMF molecules through oxygen atoms [M–O bond lengths of 2.143(1) Å (Co) and 2.069(1) Å (Cu)]. The solid state IR transmittance and solution electronic absorption spectra of both Co and Cu compounds are also reported and compared to each other and to the corresponding spectra of other members of the lapacholate metal family of complexes.

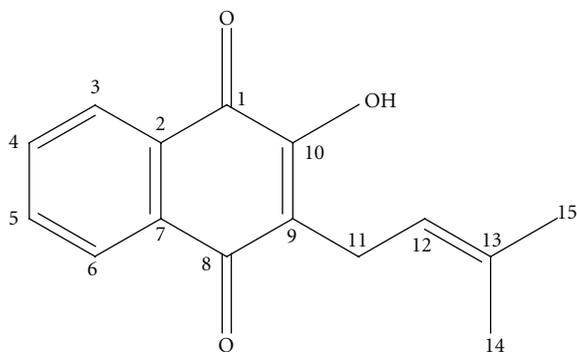
1. Introduction

Lapachol (LapH), [2-hydroxy-3(3-methyl-2-butenyl)-1,4-naphthoquinone] is a yellow pigment present in several plant species, including the Lapacho tree *Tabebuia ipe* (shredded wood) from which it is extracted. This extract is also used as alternative medicine for different illness such as cancer, Chagas, and various skin diseases [1–6]. A tea extract from the inner bark of the Lapacho tree has been used as a folk remedy against many diseases in South America since the time of the Incas [7]. Lapachol presents pharmacological activity similar to acetonaphthonates, flavonates, and hydroxypyronates [8]. Several patents involving pharmaceutical applications of Lapachol have been filed in the last few years; for example, in 2008 alone there were granted 13 related patents [7]. The

quest for improving this activity prompted renewed work during the last 10 years on the synthesis, physicochemical characterization, and pharmacological properties of Lapachol complexes with transition metal ions, including the Zn, Ni, and Mn lapacholates [7, 9, 10].

In alkaline medium, LapH loses a proton. This gives rise to a lapacholate anion (Lap) and turns into a bidentate ligand (Lap) to divalent metal ions through its phenolic and quinonic oxygen atoms located at positions 1 and 2 (see Scheme 1).

We present here the synthesis, characterization and the crystal structure of two new isostructural complexes of Co(II) and Cu(II) with LapH and DMF as ligands of formula $[M(\text{Lap})_2(\text{DMF})_2]$, M : Co, Cu.



SCHEME 1: Molecular structure of Lapachol with carbon labeling as in the X-ray study.

2. Experimental

2.1. Preparation

Co Complex. This compound was prepared at room temperature, by mixing 0.99 g of Lapachol in 50 mL of dimethylformamide (DMF), solution of concentration 0.08 M, with 0.74 g of cobalt(II) acetate tetrahydrate in 100 mL of water (0.03 M). The precipitate, with a yield of 78.6%, was separated by filtration, washed with water, dried, and redissolved in dimethylformamide. Single crystals adequate for structural X-ray diffraction were obtained by slow evaporation of the solvent.

Cu Complex. 0.54 g of Lapachol in 20 mL of DMF (0.1 M) was added to a hot (60°C) solution of 0.56 g of copper(II) acetate in 50 mL of water (0.06 M). The resulting solution was stirred and kept at 60°C during few minutes and then left at room temperature. The precipitate obtained, with a yield of 64.9%, was filtered out from the solution which was then allowed to evaporate until the appearance of single crystals. These were separated by filtration, washed with water, and then dried.

Lapachol was extracted with chloroform from the sawdust of "Lapacho" (*Tabebuia ipé*) and purified with absolute alcohol.

2.2. Chemical Analysis. The Lapachol content in both complexes was determined following the procedure described in [9] by measuring the ligand electronic absorption maxima at 330 and 390 nm ($\epsilon_{330} = 2.8 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ and $\epsilon_{390} = 1.4 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$) [8]. Cobalt and copper content were determined by atomic absorption with a GBC 904 spectrophotometer.

2.3. X-ray Diffraction Data. The X-ray measurements were performed on an Enraf-Nonius Kappa-CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Diffraction data were collected (φ and ω scans with κ -offsets) with COLLECT [11]. Integration, scaling, and reduction of the diffraction intensities were performed with HKL DENZO-SCALEPACK [12] suite of programs. The data

for the Co complex were corrected numerically for absorption effects with PLATON [13]. No absorption correction was applied to the Cu complex as the linear absorption coefficient times the largest crystal size was 0.116. The unit cell parameters were obtained by least-squares refinement based on the angular settings for all collected reflections using HKL SCALEPACK [12]. The structures were solved by direct methods with SHELXS-97 [14] and the molecular model refined by full-matrix least-squares procedure on F^2 with SHELXL-97 [15]. The H-atoms were positioned stereochemically and refined with the riding model. The locations of methyl hydrogen atoms were optimized during the refinement procedure by treating them as rigid bodies which were allowed to rotate around the corresponding C–C bond. Crystal data and refinement results are summarized in Table 1. Full crystal structure data have been deposited at the Cambridge Crystallographic Data Centre under reference codes CCDC 846042 (Co complex) and CCDC 846043 (Cu complex). Enquiries for data can be directed to: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK, CB2 1EZ or (e-mail) deposit@ccdc.cam.ac.uk or (fax) +44 (0) 1223 336033.

2.4. Spectra. Infrared transmittance spectra from 4000 to 400 cm^{-1} region were collected at a resolution of 4 cm^{-1} on KBr-sandwiched samples with a Perkin Elmer GX FT-IR instrument. The electronic spectra (UV-Vis) of both solutions of DMF samples were run on a double-beam GBC 918 spectrophotometer.

2.5. Thermogravimetric Analysis. TGA was performed under flowing oxygen (50 mL/min) with a Shimadzu TGA-50 instrument at a heating rate of $5^\circ\text{C}/\text{min}$ from room temperature to 500°C .

3. Results

3.1. Physical Properties. The dark red crystals of both complexes were stable in ambient conditions. They are soluble in DMF, ethanol, and ether, less soluble in benzene, and insoluble in water.

3.2. Analytical Results. Elemental analyses: for the Co complex, Anal Calcd (%). Co: 8.59; LapH: 70.35. Found (%) Co: 8.52 ± 0.3 ; LapH: 70.66. For the Cu complex, anal Calcd (%) Cu: 9.20; LapH: 70.19. Found (%) Cu: 9.14 ± 0.08 ; LapH: 69.86.

4. Discussion

4.1. Structural Results. An ORTEP [16] drawing of the copper complex is shown in Figure 1, and corresponding bond distances and angles around the metal ion for both complexes are in Table 2. The metal ions are sited on a crystallographic inversion center in a distorted octahedral environment, equatorially coordinated to two symmetry-related lapacholate anions acting as bidentate ligands through their

TABLE 1: Crystal data and structure solution methods and refinement results for $M(\text{Lap})_2(\text{DMF})_2$ (M: Co, Cu) complexes.

	$\text{Co}(\text{Lap})_2(\text{DMF})_2$	$\text{Cu}(\text{Lap})_2(\text{DMF})_2$
Empirical formula	$\text{C}_{36}\text{H}_{40}\text{CoN}_2\text{O}_8$	$\text{C}_{36}\text{H}_{40}\text{CuN}_2\text{O}_8$
Formula weight	687.63	692.24
Temperature ($^\circ\text{K}$)	296(2)	120(2)
Wavelength (\AA)	0.71	0.73
Crystal system, space group	Triclinic, $P-1$ (#2)	
Unit cell dimensions		
a (\AA)	7.7591(3)	7.9308(2)
b (\AA)	10.3560(3)	10.0033(4)
c (\AA)	11.2224(4)	10.7508(4)
α ($^\circ$)	95.110(2)	97.387(2)
β ($^\circ$)	94.310(2)	93.621(2)
γ ($^\circ$)	107.704(2)	103.980(2)
Volume (\AA^3)	850.65(5)	816.83(5)
Z , calculated density (Mg/m^3)	1, 1.342	1, 1.407
Absorption coefficient (mm^{-1})	0.558	0.725
$F(000)$	361	363
Crystal size (mm)	$0.32 \times 0.19 \times 0.10$	$0.16 \times 0.12 \times 0.06$
Crystal color/shape	dark red/prism	dark red/fragment
θ -range for data collection ($^\circ$)	2.60 to 26.00	2.64 to 26.00
Index ranges	$-9 \leq h \leq 9,$ $-12 \leq k \leq 12,$ $-13 \leq l \leq 13$	$-9 \leq h \leq 9,$ $-12 \leq k \leq 12,$ $-13 \leq l \leq 13$
Reflections collected/unique	11610/3342 [$R(\text{int})$ = 0.0656]	14328/3210 [$R(\text{int})$ = 0.0482]
Completeness to $\theta = 26.00^\circ$	99.6(%)	99.8%
Observed reflections [$I > 2\sigma(I)$]	2933	2888
Max. and min. transmission	0.9447 and 0.8429	0.9578 and 0.8929
Data/restraints/ parameters	3342/0/218	3210/0/218
Goodness of fit on F^2	1.043	1.053
Final R indices ^a [$I >$ $2\sigma(I)$]	$R_1 = 0.0411,$ $wR_2 = 0.1028$	$R_1 = 0.0330,$ $wR_2 = 0.0784$
R indices (all data)	$R_1 = 0.0517,$ $wR_2 = 0.1077$	$R_1 = 0.0396,$ $wR_2 = 0.0820$
Largest peak and hole	0.503 and $-0.427 e \cdot \text{\AA}^{-3}$	0.286 and -0.607

^a R indices defined as: $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}$.

sample and therefore it will not be further discussed. In the $2800\text{--}3000\text{ cm}^{-1}$ spectral range there appear bands due

TABLE 2: Bond lengths [\AA] and angles [$^\circ$] around the metal ions in $M(\text{Lap})_2(\text{DMF})_2$, M: Co, Cu.

Bond distances			
CO–O(2)	2.008(1)	Cu–O(2)	1.914(1)
CO–O(1)	2.134(1)	Cu–O(1)	2.301(1)
CO–O	2.143(1)	Cu–O	2.069(1)
Bond angles			
O(2)–CO–O(1')	100.62(5)	O(2)–Cu–O(1')	101.44(5)
O(2)–CO–O(1)	79.38(5)	O(2)–Cu–O(1)	78.56(5)
O(2)–CO–O'	91.18(6)	O(2)–Cu–O'	90.03(5)
O(1)–CO–O'	88.24(5)	O(1)–Cu–O'	90.71(5)
O(2)–CO–O	88.82(6)	O(2)–Cu–O	89.97(5)
O(1)–CO–O	91.76(6)	O(1)–Cu–O	89.29(5)

Primed atoms are related to unprimed ones through the inversion symmetry operation: $-x, -y, -z$.

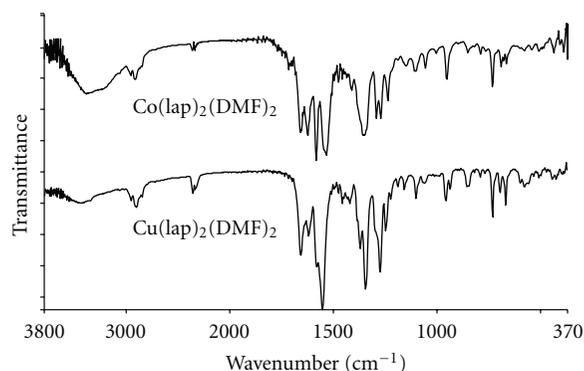


FIGURE 2

to CH stretching of the CH–CH, CH₂, and CH₃ groups. The stretching mode of noncoordinated to metal C8–O3 group appears at 1585 cm^{-1} (Co) and 1582 cm^{-1} (Cu), and stretching mode of the quinonic CO group (C1–O1) coordinated to the metal appears at 1630 cm^{-1} (Co) and 1621 cm^{-1} (Cu). These bands are red-shifted with respect to the corresponding bands of uncomplexed lapachol [19] at 1660 and 1640 cm^{-1} , upon coordination to the metal and the resonance between the para- and orthonaphthoquinone forms that involves those carbonyl groups and the non-coordinated, C8–O3, hydrogen bonded (shifts from 1640 to 1585 and 1582 cm^{-1} , resp.). In the region between 1620 and 1660 cm^{-1} , overlapping bands appear that can be assigned to CO and DMF stretching modes [20]. The bands located at 1542 and 1545 cm^{-1} correspond to the quinone ring C–C stretching mode [18].

Medium intensity bands between 1339 and 1370 cm^{-1} can be assigned to the DMF CN stretching, overlapping with the CH absorption of lapachol side chain [21]. Bands in the $1276\text{--}1275\text{ cm}^{-1}$ range are attributed by Sawhney and Matta [22] to lapachol C10–O2 (single bond, phenol) stretching modes, but it is not possible to make definitive assignments as there may also appear overlapping in-plane CC and CH coupled vibrations [22, 23].

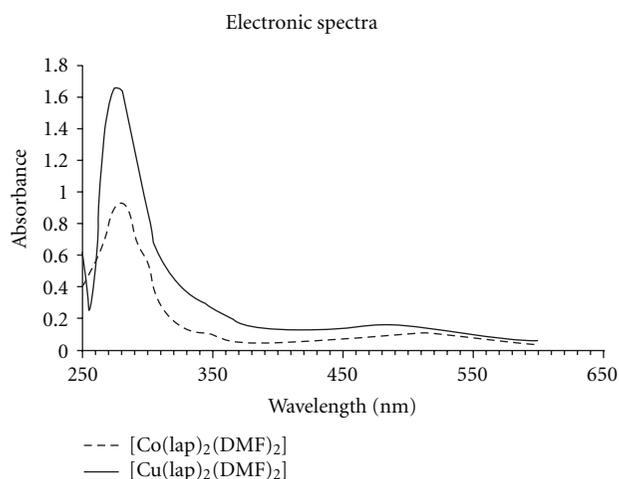


FIGURE 3

The M–O stretching modes are expected in the region from 500 to 200 cm^{-1} , as in acetylacetonates of Cu^{2+} and Ni^{2+} where IR bands are reported at 455 and 291 cm^{-1} , and 438 and 271 cm^{-1} , respectively [24, 25]. Being out of the useful range of our instrument, they will not be discussed any further.

4.3. Electronic Spectra. The electronic spectra of the Co and Cu complexes (Figure 3) show in the UV strong bands at 280 nm (Co) and 284 nm (Cu) and shoulders at 345 and 350 nm, respectively. In the visible region there appear a medium intensity broad band with maximum absorption at 510 nm (Co) and 490 nm (Cu) which give rise to the intense dark red color exhibited by the complexes. These bands may be due to the conjugated system mesomeric: $\text{O2-C10} = \text{C9-C8} = \text{O3} \leftrightarrow \text{O2} = \text{C10-C9} = \text{C8-O3}$ (p-quinone \leftrightarrow o-quinone) [9]. This band could be assigned to a transition ($\pi \rightarrow \pi^*$) of the quinone carbonyls [25].

The electronic absorption bands of aromatic rings assigned to $\pi \rightarrow \pi^*$ transitions are observed at 214 and 231 nm (benzene ring), 277 nm (quinone ring), and 340 nm (benzene ring) [24]. In the electronic spectra of the complexes we observe a sharp and intense band at 238 nm and weak shoulders at 271 and 341 nm that could be attributed to those transitions.

4.4. Thermogravimetric (TGA) Analysis. As expected, the thermogravimetric data for both isostructural complexes are very similar to each other. The TGA recording for $[\text{Co}(\text{Lap})_2(\text{DMF})_2]$ is shown in Figure 4. The first step ends at about 250 $^{\circ}\text{C}$ and has a mass loss of 20.8% and corresponds to the elimination of two molecules of DMF (theoretical value: 21.2%). The second and third steps between 275 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$ correspond to the oxidation reaction of the lapacholate groups. The total mass loss is 88.6% while the expected value for the formation of the Co_2O_3 is 87.9% [18].

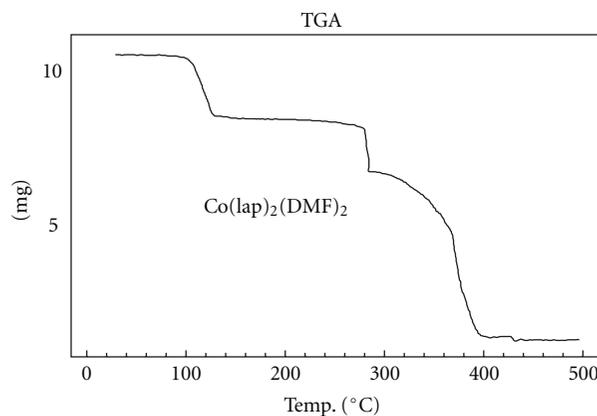


FIGURE 4

5. Conclusions

From the above discussion, we can draw the following main conclusions.

- (i) We confirm here the chelating versatility of lapacholate ligand toward transition metal ions, through their phenol and *ortho* and *para* carbonyl oxygen atoms, by reporting two new isostructural $\text{M}(\text{Lap})_2(\text{DMF})_2$ (M: Co, Cu) members of an ever growing family of lapacholate-metal complexes. We also demonstrate the ability of DMF molecule (along with other polar solvents like water and ethanol) to complete octahedral binding sites around metal in lapacholate complexes.
- (ii) We have determined the vibration structure of the new complexes by assigning most of their modes and characterized common features that relate the isostructural pair to each other and to other members of the lapacholate-metal family of complexes.
- (iii) The dark-red color of the complexes can be traced to a strong and broad electronic absorption band centered at about 510 nm (Co) and 490 nm (Cu) in the UV-visible spectra which can be assigned to p-quinone \leftrightarrow o-quinone mesomerism in the quinonic ring conjugated system. Listings of fractional coordinates and equivalent isotropic displacement parameters of the non-H atoms (Tables S3a, b), full intramolecular bond distances and angles (Tables S4a,b), anisotropic displacement parameters for the non-H atoms (Tables S5a,b), and hydrogen atoms positions (Tables S6a,b) are provided as Supplementary Material available online at doi:10.1155/2012/973238.

Acknowledgments

This work was supported by CONICET of Argentina and FAPESP of Brazil. O. E. Piro is a Research fellow of CONICET. This paper is in memory of Professor P. J. Aymonino.

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