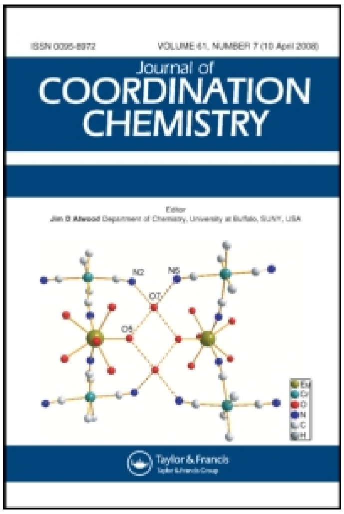

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SYNTHESIS OF 5-DODECANOYLAMINE-8-HYDROXY-1,4-NAPHTHOQUINONE AND STUDY OF SOME OF ITS BIVALENT METAL CHELATES

M. Martinellp[a]; V. Stefanp[a]; A. E. Gerbase[a]; M. Farias[b]
[a] Institute de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil [b] Escola Técnica Federal de Pelotas Praca, Pelotas, RS, Brazil

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SYNTHESIS OF 5-DODECANOYLAMINE-8-HYDROXY-1,4-NAPHTHOQUINONE AND STUDY OF SOME OF ITS BIVALENT METAL CHELATES

M. MARTINELLI[a,*], V. STEFANI[a], A.E. GERBASE[a]
and M. FARIAS[b]

[a]*Instituto de Química, Universidade Federal do Rio Grande do Sul,*
Av. Bento Goncalves, 9500 CEP 91501.970 – Porto Alegre, RS, Brazil;
[b]*Escola Técnica Federal de Pelotas Praca, 20 de Setembro,*
455 CEP 96015.360 Pelotas, RS, Brazil

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Two new naphthoquinone derivatives, 5-dodecanoylamine-8-hydroxy-1,4-naphthoquinone (**1**) and 5-dodecanoylamine-8-acetoxy-1,4-naphthoquinone (**2**), have been prepared and characterized. Their chelating ability with Ni(II) and Co(II) have been studied. Compound (**1**) coordinates to the divalent metal ions as a monoanionic bidentate ligand. The complexes were found to contain two ligands and two molecules of coordinated water. The structure and bonding of the chelates are discussed based on the spectroscopic data.

Keywords: Chelate; naphthoquinone; metal–naphthoquinone complexes;
coordinated compound

INTRODUCTION

Naphthoquinones and their derivatives have been known for a very long time as an important group of natural and synthetic compounds having significant chemical and biological properties.[1–3] Extensive research shows broad application in several areas.[4–7] Their biological activity has been investigated and many of them are efficient antitumor and antimicrobial

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[*] Corresponding author. E-mail: marciam@if.ufrgs.br.

drugs.[1,8–12] On the other hand, the electrochemical behavior and chelating abilities have been investigated because of the role of compounds of this type in redox reactions in several natural processes. These studies are of great value for understanding the mechanism of their chemical and biological properties.[2,11,13–16]

It is generally known that the reactivity and electronic properties of organic ligands can be affected by coordination to the metal ions. Some of the formed complexes, metal–quinone (naphthoquinone and/or derivatives), exhibit marked metallochromic[17,18] properties compared with the organic ligand which finds applications in fields such as diode-laser, optical data storage, laser printers, and many others. Furthermore coordination can enhance chemical or biological properties already shown by the ligand itself.[11,19] In this paper, the syntheses of two new compounds, the 5-dodecanoylamine-8-hydroxy-1,4-naphthoquinone (**1**) and the 5-dodecanoylamine-8-acetoxy-1,4-naphthoquinone (**2**), and their complexation with transition metals such as Ni(II) and Co(II), are reported.

EXPERIMENTAL

Physical Measurements

Infrared spectra were recorded in the region of 4000–200 cm^{-1} on a Mattson GL 3020, Galaxy Series FTIR 3000 spectrophotometer using KBr discs. Electronic spectra were obtained on a Shimadzu UVX–X160 Spectrophotometer, using freshly prepared solutions in DMSO. NMR spectra were recorded on a Varian VXR 200 Spectrometer in $CDCl_3$ solutions, with the chemical shifts being reported relative to $SiMe_4$. Molar electrical conductivities were measured with a D20 Digimed conductimeter, using DMSO or DMF as solvents. The amount of carbon, hydrogen and nitrogen, CHN, was determined using a Perkin–Elmer 2400 Elemental Analyzer. The metal analyses were performed on a Hitachi Z8230 Atomic Absorption Spectrophotometer. Melting points were measured on an Electrothermal IA 9000 Series and were not corrected. Thermal gravimetric analyses, TGA, were performed on a Perkin–Elmer System 4, TGS. All solvents were of reagent grade and were used after drying under appropriate drying agent whenever required. The 5-amino-8-hydroxy-1,4-naphthoquinone (**3**) was prepared following the literature procedure.[15] The metal salts $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ and $Co(C_2H_3O_2)_2 \cdot 4H_2O$ used were purchased from Merck and used without purification.

Synthesis of 5-dodecanoylamine-8-hydroxy-1,4-naphthoquinone (NQ_{C12}) (1)

The first step of the procedure was preparation of dodecanoyl chloride by refluxing 27.46 g (0.13 mol) of lauric acid with 10 mL (16.34 g, 0.13 mol) of thionyl chloride for about three hours or until no more HCl vapor was evolved from the reaction. Afterward, 1.2 mL (1.13 g, 5.29 mmol) of the above solution was added to a solution containing 1.00 g (5.29 mmol) of 5-amino-8-hydroxy-1,4-naphthoquinone (**3**) in 75 mL of dioxane. The reaction mixture was refluxed for about two hours or until no starting material was observed on spot TLC. Compound (**1**) was precipitated by adding the reaction mixture to water. The precipitate was rinsed with water and a small amount of cold diethyl ether and dried under vacuum. A pure compound was obtained in 87% yield by column chromatography, using silica gel and eluting with chloroform. Crystals can be obtained from an ethanol solution.

M.P. 92–92.5°C. IR main stretching bands (KBr): 3289, 3056, 2919, 2849, 1685, 1627, 1259 and 1234 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 12.8 s (1H, OH); 12.1 s,br (1H, NH); 9.1 d (1H, HC_6); 7.3 d (1H, HC_7); 7.10 and 6.9 dd (2H, HC_2 and HC_3); 2.5 t (2H $RC\underline{H}_2$–C=O); 1.8 m (2H, R–$C\underline{H}_2$–CH_2–C=O); 1.4 m (16H, $(CH_2)_8$); 1.0 t (3H, CH_3). ^{13}C NMR ($CDCl_3$) (190 and 188 ($C{=}O_{quin}$); 174 (HN–C=O); 159 (C–OH); 142 and 138 (C_2 and/or C_3); 136 (C_5); 132 and 128 (C_6 and/or C_7); 114 and 113 (C_9 and/or C_{10}); 39 ($CH_2C{=}O$); 32; 30; 26 and 23 (3 CH_2); 14 (CH_3). Anal. Calc. (found) for $C_{22}H_{29}NO_4$(%): C, 71.16 (71.13); H, 7.82 (7.84); N, 3.77 (3.72). The molecular ion was observed for the complex at *m*/*z* M^+ 371; 231; 189(100); 162; 43. UV–Vis, 1×10^{-4} M, nm($mol \cdot L^{-1} cm^{-1}$): 285(15500); 515(5500).

Synthesis of 5-dodecanoylamine-8-acetoxy-1,4-naphthoquinone ($NQ_{C12,acet}$) (2)

A solution of 100 mg (0.269 mmol) of (**1**) and 100 mg (1.219 mmol) of anhydrous sodium acetate in 10 mL of acetic anhydride, was prepared and left under reflux for two hours or until a color change from red to yellow was observed. This solution was cooled and added to water. The precipitate was filtered and washed with water and cold diethyl ether and dried under vacuum, yielding 49 mg (44%) of (**2**).

M.P. 87.5–88.5°C. IR main stretching bands (KBr): 3247, 2918, 2845, 1765, 1700, 1646 and 1201 cm^{-1}. ^1H NMR ($CDCl_3$) (δ): 12.1 s (1H, NH); 9.3 d (1H, HC_6); 7.4 d (1H, HC_7); 7.1 and 6.9 dd (2H, HC_2 and HC_3); 2.6 s (3H, CH_3COO); 2.5 t (2H, RCH_2–C=O); 1.8 m (2H, R–$C\underline{H}_2$–CH_2–C=O); 1.4 m (16H, $(CH_2)_8$); 1.0 t (3H, CH_3). Mass spectrum (*m*/*z*): M^+ 371; 231;

189(100); 162; 43. Anal. Calc. (found) for $C_{24}H_{31}NO_5$(%): C, 69.73 (69.64); H, 7.51 (7.35); N, 3.39 (3.14). UV–Vis, 1×10^{-4} M, nm(mol·$L^{-1}cm^{-1}$). 272(12950); 432(3320).

Nickel(II) Complex: $Ni(NQ_{C12})_2(H_2O)_2$ (4)

An ethanolic solution of compound (**1**) and of the metal salt were prepared separately. The metal salt solution (33.57 mg, 0.135 mmol, in 10 mL of ethanol) was slowly added to the solution of compound (**1**) (100 mg, 0.27 mmol, in 20 mL of ethanol). The reaction mixture was refluxed for five hours and kept at 10°C overnight. The blue precipitate was filtered, washed with water, ethanol and diethyl ether and dried under vacuum, yielding 70.9 mg, 63%.

IR main stretching bands (KBr). 3338, 2919, 2849, 1667, 1598, 1559, 1249 cm^{-1}. Anal. Calc. (found) $C_{44}H_{60}N_2O_{10}Ni$(%): C, 63.26 (62.23); H, 7.19 (6.99); N, 3.25 (3.33), Ni, 7.03 (7.54). UV–Vis, approximately 1×10^{-4} M in DMF, nm: 285, 530 and 655.

Cobalt(II) Complex: $Co(NQ_{C12})_2(H_2O)_2$ (5)

Initially the potassium salt of compound (**1**) was prepared by adding an excess of K_2CO_3 to a warm solution of 20 mL ethanol containing 100 mg (0.27 mmol) of (**1**). The reaction was left to proceed until a color change from red to blue was observed. Afterward, a solution of the metal salt (32 mg, 0.15 mmol) in 10 mL of ethanol was added to the solution and the reaction mixture was left under reflux for five hours. The blue precipitate was filtered and washed with water, ethanol and diethyl ether and dried under vacuum. The yield obtained was 60 mg, 56%.

IR main stretching bands (KBr): 3273, 2919, 2849, 1666, 1598, 1560, 1246 cm^{-1}. Anal. Calc. (found) for $C_{44}H_{60}N_2O_{10}Co$(%): found: C, 63.24 (63.58); H, 7.19 (7.53); N, 3.35 (3.32), Co, 7.00 (7.05). UV–Vis, approximately 1×10^{-4} M in DMF, nm: 288, 527.

RESULTS AND DISCUSSION

Reaction of the parent naphthoquinone (**3**) with dodecanoyl chloride leads to the new compound 5-dodecanoylamine-8-hydroxy-1,4-naphthoquinone (**1**). This reaction is easily monitored by color change from deep blue to the characteristic dark red of compound (**1**). The mass spectrum of the isolated compound shows molecular ions at *m/z* 371, 231, 189(100), 162, 43, corresponding to the addition of the chain on the parent compound (**3**). The peak at 189 results from transposition of the hydrogen from the CH_2 group adjacent to the carbonyl group to the nitrogen atom and, consequently, the elimination of a ketene species containing twelve carbons (*m/z* 182 = $CH_3(CH_2)_9CH{=}O$), thus regenerating the starting material, (**3**). The peak at 231(*m/z*) is referred to as the McLafferty transposition with formation of the naphthoquinone moiety with a H–N–C(OH)=CH2 group. The ^1H NMR spectrum of (**1**) is similar to (**3**) showing additional signals for the added chain and some important chemical shifts compared with the starting material. The new signals are the triplet at 2.5 ppm due to the vicinal protons to the carbonyl group, $RC\underline{H}_2C{=}O$; the multiplet at 1.8 ppm for the protons on the $RC\underline{H}_2CH_2C{=}O$, C_β of the chain; the multiplet at 1.4 ppm for 8 units of CH_2 and finally the triplet at 1.0 ppm relative to the CH_3 group. It is also possible to observe significant shifts from 7.4 to 9.1 ppm, for the proton on C_6, belonging to the aromatic protons forming an AB system. The proton on the nitrogen also shows a very large shift from 8.4 to 12.1 ppm. The above data strongly support the idea that the amino group was deprotonated and the dodecanoyl group is bonded to the nitrogen atom. This configuration justifies the large shift, *ca.* 4 ppm, observed for the proton on the imino group and the large shift *ca.* 2 ppm, assigned to the proton on C_6 due to the ring current effect induced by the carbonyl group of the imide group. The IR spectrum of (**1**) compared with (**3**) shows that the two bands at 3346 and 3258 cm^{-1} due to the asymmetric and symmetric stretching of the NH_2 group observed in (**3**) disappear giving a single band at 3289 cm^{-1} corresponding to a NH stretching mode in (**1**). The stretching frequency of the OH group shifts from 3154 to 3056 cm^{-1} while two new bands relative to symmetric and asymmetric stretching of the C–H from the long chain appear at 2849 and 2919 cm^{-1}. There is also a new band at 1685 cm^{-1} due to the carbonyl on the NHC=O and a shift of the $C{=}O_{quin}$ from 1590 to 1627 cm^{-1}. Another important change in the IR spectra was the splitting of the band at 1241 cm^{-1} related to the C–OH vibration to bands at 1259 and 1234 cm^{-1} which has already been observed in similar systems.[15]

The new compound (**2**) made from acetylation of (**1**) showed an IR spectrum with bands at 3247 and 1765 cm^{-1} assigned to the N–H stretching and to the carbonyl of the acetyl group, respectively. In compound (**2**) only one band at 1201 cm^{-1} characteristic of $-O(C{=}O)CH_3$ group is observed. Its ^1H NMR spectrum shows an additional singlet at 2.6 ppm for the CH_3 and the disappearance of the –OH signal related to compound (**1**). From these

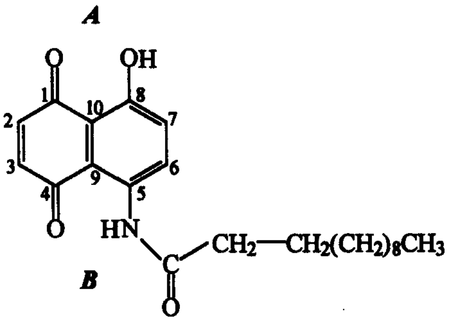

FIGURE 1 Structure of compound (1), showing the potential coordination sites A and B.

data it is possible to conclude that the acetylation has occurred on the oxygen atom bonded to C_8. The mass spectrum of (**2**) showed the same molecular weight as (**1**), common result for this kind of compound due to the lability of the acetyl group. The NMR and elemental analysis however, clearly showed addition of the acetyl group.

The ability of these naphthoquinones as chelating agents can be seen in Figure 1 where two potential sites, A and B, for coordinating a metal ion are shown. Site A refers to bonding through both oxygens of the $(C{=}O)_1$ and C–OH groups, while site B bonds through the oxygen of $(C{=}O)_4$ and the nitrogen of the NHR group.

The reactions of (**1**) with Ni(II) and Co(II) salts were carried out using ethanol as solvent. In all cases the metal complexes were isolated as a fine precipitate, stable in air. Their melting points were not reached until 350°C.

The high insolubility,[1] insoluable in common organic solvents and water, and slightly soluble in DMSO and DMF, is a remarkable characteristic of the complexes. This insolubility may indicate the presence of strong intermolecular associations in the solid state.[13] The molar electrical conductivity measurements in DMSO and DMF of the complexes reveal nonelectrolyte behavior. All attempts to grow single crystals suitable for X-ray diffraction were unsuccessful.

Despite the lack of a crystal structure, the formula $ML_2(H_2O)_2$ can be proposed based on the CHN data for Ni(II) (**4**) and Co(II) (**5**) complexes, and confirmed by the thermal gravimetric analysis. The latter analysis shows a mass loss equivalent to two water molecules at 153°C, which means that the water molecules are coordinated to the metal. The slight slope of the decomposition curve, from 153°C to 680°C, suggests that loss of the coordinated water molecules does not lead to a breakdown of the chelate structure.

The reaction of (**1**) with Fe(II), Cu(II), Cr(III) and Pd(II) salts can lead to formation of the complexes if (**1**) is treated with K_2CO_3 and the reaction is kept under reflux for five hours. The products obtained were extensively washed with ethanol, chloroform and diethyl ether. However, this procedure was not enough to purify the products. Therefore, despite the IR spectra being very similar to those for complexes (**4**) and (**5**), the elemental analyses are not conclusive.

The coordination site proposed for the new chelates as well as the bonding properties of the ligands are discussed on the basis of spectroscopic analysis.

IR spectroscopy is an important tool to determine the site of coordination. The IR spectra of the ligands as well as the IR spectra of the complexes were recorded between 4000 and 200 cm^{-1} and the most relevant bands are shown in Table I.

The changes in the infrared spectra of (**1**) compared with (**3**) are the two bands at 3289 and 3056 cm^{-1} corresponding to the stretching frequencies of the NH and OH group. Similar to what was observed on the previous work done on compound (**3**), a low frequency for the OH vibration, 3154 cm^{-1}, is also observed and attributed to strong intramolecular hydrogen bridging.[15] On complexation and taking the Ni(II) complex (**4**) as a reference, a broad band of the coordinated water covers this region making assignment impossible. In the carbonyl region, the spectrum of complex (**4**) shows a shift of the carbonyl of the NHC=O group from 1685 to 1667 cm^{-1} while the band of the C=O quinonic splits in two bands at 1598 and 1559 cm^{-1}. The band at 1559 cm^{-1} shows a downward shift of *ca.* 32 cm^{-1} compared with the parent ligand, evidence of the coordination. The C–O–H deformation mode observed at 1232 cm^{-1} in the ligand is found to undergo an upward shift to 1249 cm^{-1}, *ca.* 15 cm^{-1}. This indicates an increase in the bond order normally observed upon metal coordination due to deprotonation of the OH group.[21,22] The M–O stretching frequencies are observed at 459 and 268 cm^{-1}.

On the basis of the IR data we propose that compound (**1**) coordinates to the metal through site A. In this reaction deprotonation of the ligand induces formation of a semiquinone[27] and complexation of two ligands to one metal atom leads to the formation of nonelectrolyte complexes, in agreement with the observed behavior for all analogous complexes.[1,22,28]

The UV–Vis data are essential relate the electronic structures with the molecular geometry. For the organic compounds the electronic spectrum of the laurilated derivatives (**1**) and (**2**) compared with (**3**) shows a hypsochromic shift of the bands as reported in Table II. Modification in band

TABLE I Most important IR bands of the organic compounds and the complexes

Band	ν(N–H)	ν(O–H)	ν(NHC=O)	$\nu(C{=}O)_1$	$\nu(C{-}O)_4$	ν(C–OH)	ν(C–OM)	ν_{ass}(M–O)	ν_{sim}(M–O)
(1)	3289 m	3056 w	1685 s	1627 s	1627 s	1259 s 1232 s			
(2)	3247 m		1700 s*	1646 s, br	1646 s, br		**		
(3)	3346 m 3258 m	3154 w, br		1590 s	1590 s	1241 m			
(4)	3338 m, vbr	3338 m, vbr	1667 w	1559 s	1598 s		1249 s	459 w	268 w
(5)	3273 m, vbr	3273 m, vbr	1666 w	1560 s	1598 s		1246 s	456 w	256 w

* and ** are additional bands of **(2)** at 1765 s for $\nu(OC{=}OCH_2CH_3)$ and at 1201 s for ν(C–O–C), respectively for the acetyl group bonded to the oxygen atom.

TABLE II UV–Vis bands observed for compounds (1), (2) and (3) and complex (4) in nm(log ε)

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	*d–d*
(1)	285(4.19)	515(3.74)	
(2)	272(4.11)	432(3.52)	
(3)	296(3.78)	541(3.71) 572(3.89) 617(3.81)	
(4)	285	530	655

shape is also observed. The band at 296 nm of (3) is shifted to at 285 nm and the set of three bands centered on 541(sh), 572, 617 nm changes to one broad single band at 515 nm. The first band is assigned to the $\pi \rightarrow \pi^*$ naphthoquinone transition and the second one to $n \rightarrow \pi^*$ transition. Even more drastic are the hypsochromic shifts observed for compound (2) compared with (3), where the two sets of bands have shifted to 272 and 432 nm, respectively. This type of shift is well discussed in the literature.[29]

Because of the low solubility of complexes (4) and (5), their UV–Vis spectra can only be analyzed qualitatively. However, the shifts observed for the bands compared with the free ligand indicate complexation. More difficult, however, is to assign the *d–d* transitions and consequently to determine the geometry of the complexes by this technique. The CHN and TGA data, as mentioned earlier, show that there are two ligands and two molecules of coordinated water for each metal atom, corresponding to a *pseudo* octahedral geometry for the Ni(II) (4) and Co(II) (5) complexes.

In the case of Ni(II), d^8 complex (4), in an octahedral geometry and containing a weak field ligand, three transitions were expected.[20] The first transition, ν_1, ${}^3T_{2g} \leftarrow {}^3A_{2g}$ should appear in the range of 7700–10 000 cm^{-1}, the second transition, ν_2, ${}^3T_{1g}$ (F) $\leftarrow {}^3A_{2g}$ at 12 900–1800 cm^{-1} and the third transition, ν_3, ${}^3T_{1g}$ (P) $\leftarrow {}^3A_{2g}$, at 2400–2800. The spectrum of complex (4) exhibits absorption bands at 655, 530 and 285 nm. From this spectrum the band at 655 nm (15267 cm^{-1}) is the only one that can be assigned as a *d–d* transition corresponding to the v_2 transition, ${}^3T_{1g}$ (F) $\leftarrow {}^3A_{2g}$.[20,23–26] The v_1 transition is out of the range of the equipment and the third transition, v_3, is obscured by the bands of the ligand. For the spectrum of Co(II), d^7, complex (5), in an octahedral environment more complex *d–d* transitions are expected.[23–25] However none of them are observed because they are obscured by the strong bands of the ligand (1).

The various attempts reacted between compound (2) with metal salts failed even when more drastic conditions such as higher temperature or stronger bases were used. Compound (**2**) was always recovered unchanged from the reaction mixture. This lack of reactivity of the ligand is due to the blockage of site A by the acetyl group. Although site B is a potential site for coordination, this proton seems to be involved in a strong bridging interaction which does not allow it to react and/or the size of the chain attached to the nitrogen atom promotes its protection.

Preliminary results on the biological activity showed that compound (**3**) has higher bactericide activity against *Staphylococcus aureus* than the ampicilin used as reference.[30] The potential activity of compounds (**1**) and (**2**) and the chelates is under investigation.

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