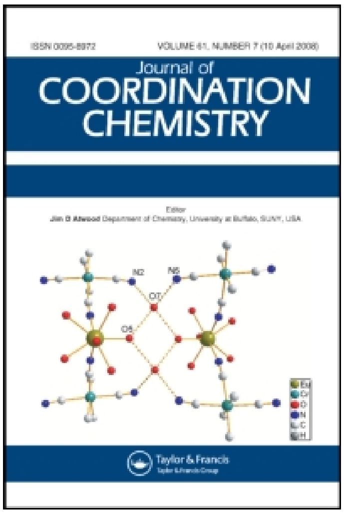

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Comparative Sites for Coordination of Naphthoquinones and its Derivatives: Studies on the Synthesis of a Series of 1,4-Naphthoquinone Derivatives and Their Ni(II) Complexes

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COMPARATIVE SITES FOR COORDINATION OF NAPHTHOQUINONES AND ITS DERIVATIVES: STUDIES ON THE SYNTHESIS OF A SERIES OF 1,4-NAPHTHOQUINONE DERIVATIVES AND THEIR Ni(II) COMPLEXES

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New derivatives (**5–8**) of 5-amino-8-hydroxy-1,4-naphthoquinone (**1**) have been synthesized and characterized by IR, UV–Vis, ^{1}H NMR, mass spectra and CNH. These new ligands and the 5-amino-8-hydroxy-1,4-naphthoquinone (**1**), the 5-amino-6-bromo-8-hydroxy-1,4-naphthoquinone (**2**), the 5-acetylamino-8-hydroxy-1,4-naphthoquinone (**3**) and the 5-dodecanoylamino-8-hydroxy-1,4-naphthoquinone (**4**), were complexed with Ni(II) giving the chelates (**1a–8a**). The structure and site of coordination of these complexes are discussed in relation to their spectroscopic data and thermal analysis.

Keywords: Chelate; naphthoquinone; metal–naphthoquinones complexes

INTRODUCTION

Naphthoquinones are important compounds because of the many applications in organic synthesis,[1] color chemistry,[2] pharmacology,[3] redox processes,[4] polymer chemistry[5] and for liquid crystals,[6] among many others.[7] Some of their significant chemical properties are related to their

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coordination abilities and thus they constitute an interesting class of bidentate ligands.

The orthohydroxyquinones, well described in the literature,[8] behave as bidentate ligands that coordinate to metal atoms through the oxygen atoms of the quinonic and hydroxy groups forming stable five-membered ring complexes. This kind of coordination occurs due to deprotonation that leads to the formation of a monoanionic ligand. However, stable complexes are also observed for aminomercaptomethyl- and diaminonaphthoquinone derivatives where the complexation occurs through the oxygen and nitrogen atoms by deprotonation of the amino group.[9]

In spite of their numerous applications, the study and use of these complexes are restricted by their low solubility in common organic solvents. Usually they are only soluble in DMF or DMSO solvents.

Continuing our interest in the synthesis of aminohydroxynaphthoquinone derivatives[10] and their complexation with transition metals[11] we synthesized new derivatives to improve their solubility. In this paper we report the study of the Ni(II) complexes (**1a–8a**) formed with 5-amino-8-hydroxy-1,4-naphthoquinone[10a] (**1**), 5-amino-6-bromo-8-hydroxy-1,4-naphthoquinone[10c] (**2**) and a series of its derivatives 5-acetylamino-8-hydroxy-1,4-naphthoquinone[10a] (**3**), 5-dodecanoylamino-8-hydroxy-1,4-naphthoquinone[11] (**4**) and the new compounds 5-octanoylamino-8-hydroxy-1,4-naphthoquinone (**5**), 5-decanoylamino-8-hydroxy-1,4-naphthoquinone (**6**), 5-tetradecanoylamino-8-hydroxy-1,4-naphthoquinone (**7**), 5-hexadecanoylamino-8-hydroxy-1,4-naphthoquinone (**8**).

EXPERIMENTAL

Physical Measurements

Infrared spectra were recorded in the region 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, chemical shifts being reported relative to $SiMe_4$. Molar conductivity was measured with a D20 Digimed conductimeter, using DMSO or DMF as solvents. The mass spectra were recorded on a VG AutoSpec, using PEGNa or alcohol 3-NBA + TFA as matrix. The amount of carbon, hydrogen and nitrogen 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 are uncorrected. Thermal gravimetric analyses were carried out on a Perkin-Elmer System 4. All solvents were of reagent grade and dried when required. The 5-amino-8-hydroxy-1,4-naphthoquinone[10a] **(1)**, 5-amino-6-bromo-8-hydroxy-1,4-naphthoquinone[3] **(2)**, 5-acetylamino-8-hydroxy-1,4-naphthoquinone[10a] **(3)**, 5-laurylamino-8-hydroxy-1,4-naphthoquinone[11] **(4)**, were prepared by following literature procedures. The metal salt $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ was purchased from Merck and used without further purification.

The compounds NQ_{C8} **(5)**, NQ_{C10} **(6)**, NQ_{C14} **(7)** and NQ_{C16} **(8)** were synthesized using the general procedure established for NQ_{C12} **(4)**.[11] The procedure is described for **(6)** as follows.

Synthesis of 5-Decanoylamino-8-hydroxy-1,4-naphthoquinone (NQ_{C10}) (6)

The first step of the procedure was preparation of decanoyl chloride by refluxing 23.54 g (0.13 mol) of decanoic acid with 10 mL (0.13 mol) of thionyl chloride until no more HCl vapor was evolved from the reaction. Afterward, 1.2 mL of the above solution was added to a solution containing 1.00 g (5.29 mmol) of 5-amino-8-hydroxy-1,4-naphthoquinone **(1)** in 75 mL of dioxane. The reaction mixture was refluxed until no starting material was observed on spot TLC. By adding the reaction mixture to water, compound **(1)** was precipitated. The precipitate was rinsed with water and a small amount of cold diethyl ether and dried under vacuum. A pure compound was obtained in 80% of yield by column chromatography, using silica gel and elution with chloroform.

Crystals can be obtained from ethanol solution. M.p. 85–85.5°C. IR main stretching bands (KBr): 3290, 3056, 2948, 2920, 2847, 1683, 1628, 1572, 1260, 1233 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 12.77 s (1H, OH); 12.03 s,br (1H, NH); 9.11 d (1H, HC_6); 7.34 d (1H, HC_7); 6.95 dd (2H, HC_2 and HC_3); 2.49 t (2H, $RC\underline{H}_2-C{=}O$); 1.67 m (2H, $R-C\underline{H}_2-CH_2-C{=}O$); 1.26 m (12H, $(CH_2)_6$); 0.87 t (3H, CH_3). ^{13}C NMR ($CDCl_3$) (190 and 188 (C=Oquin); 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 ($3CH_2$); 14 (CH_3). Elemental analysis ($C_{20}H_{25}NO_4$): found: C, 70.06; H, 7.28; N, 3.97%, calculated: C, 69.93; H, 7.35; N, 4.09%. Mass spectrum (*m/z*): M^+ 343; 231; 189 (100); 133; 41. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{mol}$): 285 (4.00); 510br (3.65); 583sh (3.34).

Characterization of 5-Octanoylamino-8-hydroxy-1,4-naphthoquinone (NQ_{C8}) (5)

M.p. 85°C. IR main stretching bands (KBr): 3290, 3056, 2922, 2846, 1683, 1629, 1257, 1233 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 12.80 s (1H, OH); 12.13 s,br (1H, NH); 9.11 d (1H, HC_6); 7.54 d (1H, HC_7); 6.93 dd (2H, HC_2 and HC_3); 2.51 t (2H, $RC\underline{H}_2$–C=O); 1.87 m (2H, R–$C\underline{H}_2$–CH_2–C=O); 1.26 m (12H, $(CH_2)_6$); 0.93 t (3H, CH_3). Elemental analysis ($C_{18}H_{21}NO_4$): found: C, 69.79; H, 7.00; N, 4.69%, calculated: C, 68.55; H, 6.71; N, 4.44%. Mass spectrum (*m/z*): M^+ 343; 231; 189 (100); 133; 41. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{mol}$): 287 (4.12); 515 (3.79); 575sh (3.44). Molar conductivity (10^{-4} M, DMF, S · cm^2 · mol^{-1}): 2.8.

Characterization of 5-Tetradecanoylamino-8-hydroxy-1,4-naphthoquinone (NQ_{C14}) (7)

M.p. 84–85°C. IR main stretching bands (KBr): 3289, 3056, 2919, 2848, 1683, 1630, 1259, 1233 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 12.84 s (1H, OH); 12.12 s,br (1H, NH); 9.14 d (1H, HC_6); 7.35 d (1H, HC_7); 7.00 dd (2H, HC_2 and HC_3); 2.51 t (2H, $RC\underline{H}_2$–C=O); 1.84 m (2H, R–$C\underline{H}_2$–CH_2–C=O); 1.41 m (12H, $(CH_2)_6$); 1.02 t (3H, CH_3). Elemental analysis ($C_{24}H_{33}NO_4$): found: C, 71.74; H, 8.30; N, 3.57%, calculated: C, 72.18; H, 8.27; N, 3.51%. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{mol}$): 287 (3.99); 515 (3.66); 575sh (3.31). Molar conductivity (10^{-4} M, DMF, S · cm^2 · mol^{-1}): 2.0.

Characterization of 5-Hexadecanoylamino-8-hydroxy-1,4-naphthoquinone (NQ_{C16}) (8)

M.p. 84–85°C. IR main stretching bands (KBr): 3289, 3057, 2919, 2848, 1683, 1628, 1256, 1233 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 12.89 s (1H, OH); 12.10 s,br (1H, NH); 9.16 d (1H, HC_6); 7.32 d (1H, HC_7); 7.00 dd (2H, HC_2 and HC_3); 2.51 t (2H, $RC\underline{H}_2$–C=O); 1.84 m (2H, R–$C\underline{H}_2$–CH_2–C=O); 1.41 m (12H, $(CH_2)_6$); 1.01 t (3H, CH_3). Elemental analysis ($C_{26}H_{37}NO_4$): found: C, 73.03; H, 8.48; N, 3.29%, calculated: C, 73.03; H, 8.72; N, 3.27%. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{mol}$): 287 (4.06); 515 (3.73); 575sh (3.40). Molar conductivity (10^{-4} M, DMF, S · cm^2 · mol^{-1}): 2.5.

The Ni(II) complexes were synthesized by the following procedure.

Nickel(II) Complex: $Ni(NQ_{C10})_2 \cdot 2H_2O$ (6a)

An ethanolic solution of compound (6) 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 **(6)** (48.89 mg, 0.27 mmol, in 20 mL of ethanol). The reaction mixture was refluxed for 5 h and was kept at 10°C overnight. The blue precipitate was filtered, washed with water, ethanol and diethyl ether and dried under vacuum. Yield: 54 mg of complex **(6a)** (50%). M.p. > 350°C. IR main stretching bands (KBr): 3300, 2922, 2851, 1699, 1588, 1566, 1266br $\mathrm{cm^{-1}}$. Elemental analysis ($C_{40}H_{52}N_2O_{10}Ni$): found: C, 61.52; H, 6.31; N, 3.56; Ni, 7.25%, calculated: C, 61.64; H, 6.67; N, 3.59; Ni, 7.53%. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{\mathrm{mol}}$): 315 (3.94); 573sh (3.68); 606 (3.78); 659sh (3.66).

Nickel(II) Complex: $Ni(NQ)_2(H_2O)_2$ (1a)

IR main stretching bands of compound **(1a)** in KBr: 3275, 1640br, 1580, 1240br. Elemental analysis $NiL_2(H_2O)_2 = (C_{20}H_{16}N_2O_8Ni)$: found: C, 51.99; H, 2.90; N, 6.11; Ni, 11.88%, calculated: C, 50.99; H, 3.39; N, 5.94; Ni, 12.47%. UV–Vis, 1×10^{-3} M, DMF, nm ($\log \varepsilon_{\mathrm{mol}}$): 306 (3.45); 463 (3.42); 590 (3.43); 632sh (3.43). Yield of 30%. M.p. > 400°C.

Nickel(II) Complex: $Ni(NQ_{Br})_2 \cdot 2H_2O$ (2a)

IR main stretching bands of compound **(2a)** in KBr: 3294, 3056, 1622, 1547, 1280, 1261, 1188, 977 $\mathrm{cm^{-1}}$. Elemental analysis $NiL_2 \cdot 2H_2O = (C_{20}H_{14}N_2O_8Br_2Ni)$: found: C, 38.36; H, 1.74; N, 4.30; Br, 28.04; Ni, 8.94%, calculated: C, 38.40; H, 1.79; N, 4.48; Br, 26.99; Ni, 9.39%. Mass spectrum (*m/z*): M^+ 591.82: found: 591.824 calculated for ($C_{20}H_{10}O_6N_2Br_2Ni$) corresponding to $Ni(NQ_{Br})_2$. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{\mathrm{mol}}$): 317 (3.09); 456 (2.48); 608 (3.16); 655 (3.18). Yield of 70%. M.p. > 400°C.

Nickel(II) Complex: $Ni(NQacet)_2(H_2O)_2 \cdot 2H_2O$ (3a)

IR main stretching bands of compound **(3a)** in KBr: 3300br, 1669, 1566, 1590, 1280, 1250 $\mathrm{cm^{-1}}$. Elemental analysis $NiL_2 \cdot 4H_2O = (C_{24}H_{26}N_2O_{13}Ni)$: found: C, 49.47; H, 3.82; N, 4.63; Ni, 10.30%, calculated: C, 48.76; H, 4.06; N, 4.74; Ni, 9.94%. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{\mathrm{mol}}$): 264sh (4.11); 317 (4.27); 560sh (3.95); 607 (4.07); 657 (3.94). Yield of 30%. M.p. > 400°C.

Nickel(II) Complex: $Ni(NQ_{C8})_2(H_2O)_2 \cdot 2H_2O$ (5a)

M.P. above 350°C. IR main stretching bands (KBr): 3360, 2924, 2854, 1666, 1598, 1566, 1265 and 1247 $\mathrm{cm^{-1}}$. Elemental analysis $NiL_2 \cdot 4H_2O = (C_{36}H_{48}N_2O_{12}Ni)$: found: C, 59.05; H, 6.30; N, 3.78; Ni, 8.05%, calculated: C, 59.11; H, 6.61; N, 3.83; Ni, 8.02%. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{mol}$): 319 (4.19); 566 (3.92); 607 (4.03); 660 (3.91).

Nickel(II) Complex: $Ni(NQ_{C14})_2(H_2O)_2 \cdot 2H_2O$ (7a)

Yield of 60%. M.p. > 350°C. IR main stretching bands (KBr): 3339, 3050, 2918, 2849, 1667, 1598, 1559, 1265, 1247 cm^{-1}. Elemental analysis $NiL_2 \cdot 4H_2O = (C_{48}H_{72}N_2O_{12}Ni)$: found: C, 64.04; H, 7.44; N, 3.11; Ni, 6.58%, calculated: C, 62.14; H, 7.82; N, 3.02; Ni, 6.33%. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{mol}$): 290 (3.47), 319sh (3.36), 529sh (3.13), 566sh (3.16), 605 (3.18), 660 (3.07).

Nickel(II) Complex: $Ni(NQ_{C16})_2(H_2O)_2 \cdot 2H_2O$ (8a)

M.p. > 350°C. IR main stretching bands (KBr) 3324, 3051, 1667, 1600, 1561, 1263, 1250 cm^{-1}. Elemental analysis $NiL_2 \cdot 4H_2O = (C_{50}H_{76}N_2O_{12}Ni)$: found: C, 63.89; H, 7.94; N, 2.79; Ni, 6.01%, calculated: C, 63.48; H, 8.19; N, 2.85; Ni, 5.96%. UV–Vis, 1×10^{-4} M, DMF, nm ($\log \varepsilon_{mol}$): 317 (3.76); 569sh (3.51); 610 (3.61); 662 (3.63); 720 (3.59).

RESULTS AND DISCUSSION

The synthetic procedure used to prepare the 5-amino-8-hydroxy-1,4-naphthoquinone **(1)** was reported elsewhere,[10a] together with a series of derivatives including compound **(3)**; the synthesis and characterization of compound **(2)** was reported more recently.[10b] Nevertheless, compound **(1)** is the parent compound for the derivatives presented in this paper. The derivatives **(4)**–**(8)** were prepared by reacting **(1)** with the corresponding acyl chloride under reflux. The red color that appears from the reaction mixture is characteristic of the formation of the acylamino derivatives. All compounds were very soluble in chloroform and in warm ethanol, from which they were recrystallized.

The IR and ^{1}H NMR characterizations of **(5)**–**(8)** are typical of this family of derivatives similar to the results obtained for compound **(4)**.[11] The main IR bands of **(4)** are at 3289, 3056, 1685, 1627, 1259, 1234 cm^{-1} corresponding to the stretching frequencies of the νNH, νOH, νNC=O, both νC=O quinonic and the two band for C–O–H group, respectively (Table I). The ^{1}H NMR spectrum is also similar to **(4)**. The most important features of these compounds are the deshielding of the proton on C_6 of *ca.* 2 ppm

TABLE I The most important IR bands of the free ligands and the complexes in KBr

Compounds	$\nu(N-H_2)$	$\nu(N-H)$	$\nu(O-H)$	$\nu(C=O)_1$	$\nu(C=O)_4$	$\nu(NC=O)$	$\nu(CO-H)$	$\nu(CO-M)$
(1)	3346w 3259m		3154w	1606vs			1242s	
(1a)		3275m		1640m	1580vs		1240br,vs	
(2)	3409m 3256w		3063w	1610vs			1280m 1234s	
(2a)		3294m	3056w	1622s	1547vs		1280s 1261vs	
(3)		3208w	3081w	1623vs		1697s	1269vs 1220vs	
(3a)	Broad		Broad	1566vs	1590vs	1669m		1280s 1250sh,s
(4)		3289m	3056w	1627vs		1685vs	1259s 1234vs	
(4a)	Broad		Broad	1559vs	1598vs	1667m		1259s 1249sh,s
(5)		3290m	3056w	1629vs		1683s	1257vs 1233vs	
(5a)	Broad		Broad	1566vs	1598vs	1666m		1265s 1247s
(6)		3290m	3056w	1628vs		1683s	1260vs 1233vs	
(6a)	Broad		Broad	1566vs	1588vs	1699m		1266br,vs
(7)		3289m	3056w	1630vs		1683s	1259s 1233vs	
(7a)	Broad		Broad	1559vs	1598vs	1667m		1265vs 1247s
(8)		3289m	3057w	1628vs		1683m	1256s 1233vs	
(8a)	Broad		Broad	1561vs	1600vs	1667m		1263vs 1250s

from the ring current of the NC=O group and the singlet observed at 12 ppm assigned to the NH proton.

The mass spectra and elemental analyses are also in agreement with the proposed formulation for compounds **(5)**–**(8)**.

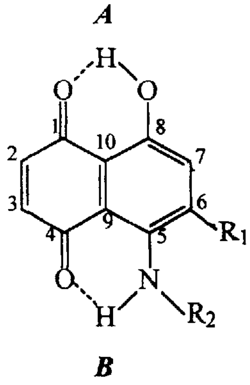
The UV–Vis spectra of the derivatives **(3)**–**(8)** show a blue shift (of *ca.* 63 nm for the main band) due to the effect of substitution on the parent naphthoquinone **(1)** as can be seen in Table II. However, on comparing the spectra among themselves, there is little difference as far as the shape of the bands is concerned.

We can identify three different groups among the ligands, the parent naphthoquinone **(1)**, the bromo derivative **(2)** and the acyl derivatives **(3)**–**(8)**. All of them, despite their chemical differences, seem to present a common feature which is the strong hydrogen bond between the OH phenolic and $(C=O)_1$ and the NH group and $(C=O)_4$, at sites A and B, as can be seen in Figure 1.

TABLE II Electronic spectral data of the naphthoquinonic derivative compounds and its Ni(II) complexes[a]

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	*d–d*
(1)[10a]	306(3.94)	542sh(3.80), 578(3.97), 623sh(3.91)	
(2)[10b]	309(3.77)	576(3.91), 619sh(3.80)	
(3)[10a]	285(3.69)	503(3.44)	
(4)[11]	285(4.19)	515(3.74), 575sh(3.39)	
(5)	287(4.12)	515(3.79), 575sh(3.44)	
(6)	285(4.00)	510(3.65), 583sh(3.34)	
(7)	287(3.99)	515(3.66), 575sh(3.31)	
(8)	287(4.06)	515(3.73), 575sh(3.40)	
(1a)	306(3.45)	590(3.43), 632sh(3.43)	463(3.42)
(2a)[13]	317(3.09)	608(3.16), 655(3.18)	456(2.48)
(3a)	264sh(4.11), 317(4.27)	560sh(3.95), 607(4.07)	657sh(3.94)
(4a)[11]	317(3.94)	573(3.68), 606(3.78)	659(3.66)
(5a)	319(4.19)	566(3.92), 607(4.03)	660(3.91)
(6a)	315(3.94)	573sh(3.68), 606(3.78)	659sh(3.66)
(7a)	290(3.47), 319sh(3.36)	529sh(3.13), 566sh(3.16)	605(3.18), 660(3.07)
(8a)	317(3.76)	569sh(3.51), 610(3.61)	662(3.63), 720(3.59)

[a] λ_{max} value in nm and log ε_{mol} in parentheses.



(1) $R_1 = H, R_2 = H$
(2) $R_1 = Br, R_2 = H$
(3) $R_1 = H, R_2 = \text{-(C=O)CH}_3$
(4-8) $R_1 = H, R_2 = \text{-(C=O)(CH}_2)_n\text{CH}_3$; n=10, 6, 8, 12, 14

FIGURE 1 The coordination sites A and B of the naphthoquinones.

On reacting the ligands and metal salts in ethanol under reflux, a dark precipitate was obtained. These products were washed extensively with chloroform, water, ethanol and ether and dried under vacuum.

In spite of the attempt to use naphthoquinones derivatives with a long hydrophobic substituent **(4–8)** in order to increase the solubility of the complexes **(1a–8a)**, all of them are insoluble in common organic solvents and only slightly soluble in DMSO. The result of the elemental analyses, for all complexes supported a metal to ligand ratio of 1 : 2 and the presence of some water molecules. For complex **(1a)** the formula $ML_2(H_2O)_2$ is proposed since its TGA shows the loss of mass at 150°C corresponding to two molecules of water coordinated to the metal. However, for complex **(2a)** the water shown by elemental analysis is the lattice water rather than water coordinated to the metal ion since the curve of mass lost in the TGA shows a continuous decay until 60°C. For all the other complexes the analysis shows the presence of four water molecules, two molecules coordinated to the metal and two molecules in the lattice according to their TGA and elemental analysis. Some deviation of the CHN data was sometimes observed for the complexes despite the efforts in purifying the products since they are quite insoluble. The presence of these impurities is better observed in the MS/FAB spectra of **(4a)** and **(2a)**. Nevertheless, the molecular ion peaks of 591 for **(2a)** and 798 for **(4a)** are well recognized and confirmed by mass spectra simulation. Therefore, the formula correspondent to all the complexes is $ML_2(H_2O)_2 \cdot 2H_2O$ except complex **(2a)** which is $ML_2 \cdot 2H_2O$. The molar conductivity measurements of all complexes agree with this formulation since they behave as non-electrolytes and their melting points were not reached until 350°C.

Aminonaphthoquinones have two possible sites that can coordinate to a metal atom, shown in Figure 1. We observe that, depending on the nature and size of the groups bonded to the parent naphthoquinone, different coordination is present. From the spectroscopic data we are able to assign which of these sites are coordinating to the metal ion.

The most important IR absorption frequencies of the ligand and their complexes are given in Table I. Upon coordination, the IR spectra of the complexes compared with the ligands show significant changes in the wide region between 4000 and 200 cm^{-1}. These rich IR data are the basis for the discussion of the coordination site of the ligands since compounds **(1)**–**(8)** have both hydroxy and amino group free for coordination.

Because of the quality of the data obtained for complex **(2a)** we will begin the discussion with it. The IR data of complex **(2a)** compared with ligand **(2)** show drastic modification in the region of 4000–3000 cm^{-1}. The set of bands relative to NH_2 at 3409 and 3256 cm^{-1} in spectrum of **(2)** disappear giving place to a new single band at 3294 cm^{-1} assigned to the N–H of the imide group present in the spectrum of **(2a)**. These data suggest that the metal is coordinated to the nitrogen atom by the deprotonation of NH_2 group. In the C=O region it is possible to observe that the broad band, at 1610 cm^{-1}, attributed to both C=O quinonic groups in the ligand splits in two bands, at 1622 and at 1547 cm^{-1}. They were assigned to the non-coordinated $(C{=}O)_1$ group and the coordinated $(C{=}O)_4$, respectively. The region relative to C–OH stretching frequency also shows some changes, the bands at 1280 and 1234 cm^{-1} shift to 1280 and 1261 cm^{-1}. Although these shifts in a simple system are an indication of coordination, we observed that in the naphthoquinone systems any addition of an R group or coordination to a metal center causes an electronic delocalization which is reflected in a shift of almost all bands of the spectrum.

For complex **(1a)**, the IR data show almost the same pattern observed for **(2a)**, coordination on site B, which means a band at 3275 cm^{-1} and the splitting of the C=O band into two other bands at 1640 and 1580 cm^{-1}. No change is observed in the 1300–1200 cm^{-1} region.

The similarity of the results obtained for the complexes **(1a)** and **(2a)** was not expected because of the differences in their chemical behavior related to the acylation reaction of the parent compounds **(1)** and **(2)**, that occurred in opposite sites. In compound **(1)** the acyl group was determined to be bound on the N atom,[12] site B, while in **(2)**, the acyl derivative showed that the bond had occurred on the oxygen of the phenolic group,[13] site A. The reactivity of these acyl derivatives with Ni(II) salts was also different. Recent investigation[13] showed that the acyl derivative of **(2)** which has site A blocked led to isolation of $Ni(QNBracet)_2$ and its spectroscopic data suggested that the coordination had occurred through the N atom and $(C-O)_4$ group, *i.e.* site B. On the other hand, the acyl derivative of **(1)**, compound **(3)**, that has site B blocked, forms a complex with Ni(II), complex **(3a)**, on site A.

By considering these data and the presence of bands of the imide group in the spectra of complex **(2a)** and **(1a)**, we conclude that coordination of the metal is through site B, which means by the N atom and $(C=O)_4$.

In the IR spectrum of chelates **(3a)**–**(8a)** from 3400 to 3000 cm^{-1}, characteristic for the groups NH_2, NH and OH, is hidden by a broad band which is related to the presence of coordinated water making the assignment of the site of coordination more difficult. The presence of two water molecules was confirmed by their elemental and thermogravimetric analyses. As a general rule, upon coordination the broad band *ca.* 1628 cm^{-1} relative to two C=O groups splits into two new bands *ca.* 1595 and 1563 cm^{-1}, assigned to the uncoordinated, $(C=O)_1$, and coordinated, $(C=O)_4$, groups. The two bands characteristic of the vibration of the C–OH group *ca.* 1259 and 1231 cm^{-1} in the ligand suggest a tendency to shift to higher frequencies when the complex is formed. These results show that for the ligands **(3)**–**(8)**, the O–H is deprotonated and coordinates with metal ions through site A involving both oxygen atoms.

Comparing the UV–Vis spectra of free **(1)**–**(8)** ligands and the complexes **(1a)**–**(8a)** shows a shift of the ligand bands suggesting the complexation of the metal ion. The position of the band maxima and of discernible shoulders are given in Table II as well as their ε data. The bands of compounds **(1)** and **(8)** concern transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of the uncomplexed ligands are well characterized in the regions of *ca.* 290 and *ca.* 500 nm, respectively. A bathochromic shift is observed when the ligands are complexed. This effect is better observed for bands in the second region of the spectra which shows that this region is quite sensitive to the presence of the metal ion.

Complexes **(1a)** and **(2a)** showed bands at 463 and 456 nm, respectively, which are absent in the spectra of the free ligand. This band could be assigned either as transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ν_3 for an octahedral geometry or $^1A_{1g} \rightarrow {}^1B_{1g}$, ν_2 for a square planar geometry.[14] The other expected bands seem to be hidden underneath the free ligand bands. Since the spectra were recorded in a coordinating solvent we assume an octahedral geometry rather than square planar. Lack of ^{1}H NMR signals may indicate paramagnetic character, thus confirming the UV–Vis data. On the other hand, the elemental analyses and TGA support the formula $NiL_2(H_2O)_2 \cdot 2H_2O$ for **(1a)** and $NiL_2 \cdot 2H_2O$ for **(2a)** in solid state.

Complexes **(3a)**–**(8a)** showed a different behavior in their UV–Vis spectra compared with complexes **(1a)** and **(2a)**. The red shift was more pronounced, *ca.* 100 nm, but somehow the pattern of the bands was kept. This does not allow us to conclude if the shoulders at 650–720 nm are the *d–d* transition expected for an octahedral geometry or belong to the set of $n \rightarrow \pi^*$ of the parent ligand that had drastically shifted. It is also not possible to establish if the two bands(shoulders) at that region refer to the *d–d* transitions attributed to $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$ belonging to a distorted octahedral geometry.[15]

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