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Dinuclear copper(II) complexes of a novel 3-(aminomethyl)naphthoquinone Mannich base: Synthesis, structural, magnetic and electrochemical studies

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ABSTRACT

A novel versatile tridentate 3-(aminomethyl)naphthoquinone proligand, 3-[N-(2-pyridylmethyl)aminobenzyl]-2-hydroxy-1,4-naphthoquinone (HL), was obtained from the Mannich reaction of 2-hydroxy-1,4-naphthoquinone (Lawsone) with 2-aminomethylpyridine (amp) and benzaldehyde. The reactions of HL with $CuCl_2 \cdot 2H_2O$ yielded two novel dinuclear copper(II) complexes, $[Cu(L)(H_2O)(\mu-CI)Cu(L)CI]$ (**1b**), $[CuCl(L)(\mu-Cl)Cu(amp)Cl]$ (**2**) and a polymeric compound, $[Cu(L)Cl)]_n$ (**1a**), whose relative yields were sensitive to temperature, reagents concentration and presence of base. The crystalline structures of 1b and 2 were determined by X-ray diffraction studies. The two copper atoms in complex 1b are connected by a single chloro bridge with a Cu \cdots Cu separation of 4.1342(8) Å and Cu(1)–Cl(1)–Cu(2) angle of $109.31(4)^{\circ}$. In complex **2** the two copper atoms are held together by a chloro and a naphthalen-2-olate bridges $[Cu(1)-Cl(2)-Cu(2) \text{ and } Cu(1)-O(1)-Cu(2) \text{ angles being } 83.31(3) \text{ and } 109.70(9)^\circ$, respectively, and the Cu \cdot Cu separation, 3.3476(9)Å]. As expected, variable-temperature magnetic susceptibility measurements of complex 1b showed weak antiferromagnetic intramolecular coupling between the copper(II) centers, with J = -5.7 cm⁻¹, and evidenced for complex **2** strong antiferromagnetic coupling, with $J \sim -120 \text{ cm}^{-1}$. Furthermore, the magnetic behaviour of compound **1a** suggested an infinite 1D coordination polymeric structure in which the copper(II) centers are connected by Cl-Cu-Cl bridges. Solution data (UV–Vis spectroscopy and cyclic voltammetry) indicated structural changes of 2 and 1a in CH₃CN, and evidenced conversion of polymer 1a into dimer 1b.

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1. Introduction

Quinones are known for their pharmacologic properties [1] and for taking part in many biological processes, such as respiration and photosynthesis [2]. Due to their binding ability, the coordination of these chelating compounds to transition metal ions has also been the subject of growing interest [3]. The main motivations for the synthesis of novel naphthoquinone metal complexes are the study of their biological applications [4,5] and the investigation of their magnetic properties [6–9]. Ligands which contain potentially bridging phenoxo oxygen and nitrogen donor atoms have been widely used in the synthesis of dinuclear copper complexes [10,11].

As the result of our ongoing investigations of biologically active 3-(aminomethyl)naphthoquinone transition metal complexes we described recently the synthesis and antimicrobial activities of novel *Mannich bases* 3-[*N*-(2-phenyl)aminoalkyl]-2-hydroxy-1,4naphthoquinones and of their copper(II) [4] complexes. Interaction with the chelating deprotonated ligands resulted only in formation of mononuclear square planar complexes. Herein we report the synthesis of the aminomethylpyridine derivative, 3-[*N*-(2-pyridylmethyl)aminobenzyl]-2-hydroxy-1,4-naphthoquinone (**HL**), a potentially tridentate ligand, and the analogous complexation reactions, that yielded a polymeric compound and novel copper(II) dimers, whose solid state structures have been established by X-ray diffraction studies. Magnetic studies evidenced antiferromagnetic interaction in all cases, whose strength was found to depend on the type of bridge and the Cu–Cu separation [12]; a possible structure was proposed for the polymer, based on these studies and other spectroscopic data. This is the first report of 3-(aminomethyl)naphthoquinone dinuclear copper(II) complexes.

2. Experimental

2.1. Materials and physical measurements

Solvents (Vetec), 2-hydroxy-1,4-naphthoquinone, CuCl₂·2H₂O (Aldrich) and 2-aminomethylpyridine (Acros) were used as supplied.



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Benzaldehyde (control) was washed with NaOH 1 mol/L and distilled; triethylamine (Tedia Brazil) was distilled prior to use. Microanalyses were performed using a Perkin-Elmer CHN 2400 microanalyser at Central Analítica - Instituto de Química, Universidade Federal de São Paulo, Brazil. Melting points were obtained with use of a Mel-Temp II, Laboratory Devices - USA apparatus and were uncorrected. Conductivity measurements were carried out at 25 °C in acetonitrile using a Schott conductometer. IR spectra (KBr pellets) were recorded on a FT-IR spectrum One (Perkin-Elmer) spectrophotometer. ¹H and ¹³C NMR spectra were recorded with a Varian Unit Plus 300 MHz spectrometer in deuterated CDCl₃; chemical shifts were reported in parts per million (ppm) relative to an internal standard of Me₄Si. The hydrogen signals were attributed through coupling constant values and ${}^{1}H \times {}^{1}H$ – COSY experiments. Electronic spectra were taken on a Carv 50 (Varian) spectrophotometer using spectroscopic grade solvents (Tedia Brazil) in 10^{-3} and 10^{-4} mol/L solutions. Electron paramagnetic resonance (EPR) spectra of the solid samples were obtained at liquid nitrogen temperature (77 K), on a Bruker ESP300E equipment with modulation frequency of 100 kHz, operating at 9.5 GHz (X-band). Variable temperature magnetic susceptibility measurements were carried out using samples of a few mg of compounds 1a, 1b and 2 using a Cryogenic Sx600 SQUID magnetometer operating at temperatures from 1.8 to 300 K. The susceptometer was calibrated with YFeGarnet NIST standard. Cyclic voltammetry experiments were carried out with a BAS Epsilon potentiostat-galvanostat system controlled by software using spectroscopic acetonitrile (Tedia Brazil) in 10⁻³ mol/L solutions. The electrochemical cell was a conventional one with three electrodes: Ag/AgCl was used as reference electrode, a platinum wire as the auxiliary electrode and glassy carbon as the working electrode. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile was used as supporting electrolyte at 0.1 mol/L, and the whole cell was deoxygenated by argon. The ferrocene/ferrocenium (FcH/FcH⁺) couple was used as an internal reference ($E_{1/2}$ 372 mV versus Ag/ Ag⁺; *E*_{1/2} 0.40 V versus NHE) [13].

2.2. X-ray crystallography

Singles crystals were fixed on a glass fiber for the X-ray data collection. Crystal data and structure refinement for complexes **1b** and **2** are show in Table 1.

X-ray diffraction data of complexes were collected from a Bruker KAPPA CCD diffractometer [14], at 295 K and Mo K α monochromatic-graphite radiation. Cell parameters for **1b** and **2** were obtained using PHICHI [15] and refined by DIRAX [16]. The collected reflections were reduced with EVALCCD [17] and corrected by Lorentz polarization and absorption with SADABS [18]. Both molecular structures were solved by SHELXS-97 [19], via Patterson method and refined on F^2 with anisotropic temperature parameters for all non H atoms used SHELXL-97 [20].

For **1b** and **2** the positional parameters of the H atoms bonded to C atoms in the aromatic rings were obtained geometrically, with the C–H distances fixed in 0.93 Å for Csp^2 , and refined as riding on their respective C atoms, with $U_{iso}(H) = -1.2 Ueq(Csp^3)$. H atoms bonded to C atoms in the methylene moiety were obtained geometrically with C–H distances fixed in 0.97 Å for Csp^3 and with $U_{iso}(H) = -1.2 Ueq(Csp^3)$. H atom bonded to C atoms in the methyne moiety were obtained geometrically with C–H distances fixed in 0.98 Å for Csp^3 and with $U_{iso}(H) = -1.2Ueq(Csp^3)$. The positional parameters of H atoms bonded to nitrogen atoms were obtained from a Fourier difference map and refined freely with an isotropic displacement parameter.

For **2** the positional parameters of H1, H3a and H3b atoms bonded to N1 and N3 atoms, respectively, were obtained from a

Table 1

Crystal data and structure refinement for 1b and 2.

	1b	2
Empirical formula	C46H36N4O7Cl2Cu2	C29H25N4O3Cl3Cu2, H2O
Formula weight	954.77	724.98, 18.02
T (K)	295(2)	295(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system, space	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions		
a (Å)	A = 7.5917(15)	A = 13.256(3)
$b(\mathbf{A})$	24.551(5)	10.807(2)
c (Å)	25.041(5)	21.623(4)
B (°)	98.25(3)	94.53(3)
$V(Å^3)$	4618.9(16)	3088.0(11)
Z, calculated density $(\pi \text{ cm}^{-3})$	4, 1.373	4, 1.598
Absorption coefficient (mm ⁻¹)	1.089	1.679
$F(0\ 0\ 0)$	1952	1512
Crystal size (mm)	$0.50 \times 0.20 \times 0.08$	$0.11 \times 0.06 \times 0.06$
Theta range (°)	2.84-25.00	3.01-25.50
Index range	$-9 \leqslant h \leqslant 8$,	$-16 \leq h \leq 16$,
-	$-28 \le k \le 29,$ $-29 \le l \le 29$	$-13 \le k \le 13$, $-26 \le l \le 26$
Reflections collected	68 633	64 394
Independent reflections	8093 [0.0593]	5739 [0.0993]
$[R_{(int)}]$		
Completeness to theta	99.7	99.8
Maximum and minimum transmission	0.9179 and 0.6120	0.9016 and 0.8407
Refinement method	Full-matrix least-	full-matrix least-squares
Data/restraints/	8093/0/574	5739/0/390
narameters	0055/0/574	3733707330
Goodness-of-fit (GOF)	1.017	1.040
Final R indices	$R_{\rm c} = 0.0453$	$R_{\rm c} = 0.0377$
$[I > 2\sigma(I)]$	N1 - 0.0433	N1 - 0.0377
	$wR_2 = 0.0948$	$wR_2 = 0.0678$
R indices (all data)	$R_1 = 0.0746$	$R_1 = 0.0669$
	$wR_2 = 0.1048$	$wR_2 = 0.0745$
Largest difference peak and hole ($e Å^{-3}$)	0.455 and -0.441	0.294 and -0.293

Fourier difference map and refined freely with an isotropic displacement parameter.

The solution and refinement of **1b** revealed the presence of four water molecules as crystallization solvates. The hydrogen atom coordinates corresponding to those water molecules could not be located experimentally in the Fourier map. For this reason, the SQUEEZE procedure contained in the PLATON program [21] was carried out to exclude the electronic density contributions relative to the water molecules. This is valid because the water molecules are not part of the assembly of the organized network. Before the SQUEEZE procedure, these water molecules occupied 707.6 Å³ in the unit cell; after this procedure, which involved the exclusion of 69 electrons per unit cell, this space is void.

2.3. Synthesis of the compounds

2.3.1. Preparation of the ligand 3-[N-(2-pyridylmethyl)aminobenzyl]-2-hydroxy-1,4-naphthoquinone (**HL**)

The Mannich base **HL** was synthesized according to methodology recently described in the literature [4]. To a suspension of 2-hydroxy-1,4-naphthoquinone (Lawsone) (870 mg, 5 mmol) in ethanol (15 mL), kept under stirring at 22 °C, were added the 2aminomethylpyridine (5.6 mL, 5.5 mmol) and, after about 5 min, the benzaldehyde (6.6 mL, 6 mmol). The mixture was stirred at this temperature for 5 h, the bright orange solid was filtered, washed with ethanol and water and dried under vacuum. Yield: 1.253 g (68%); m.p. 133–134 $^{\circ}\text{C}$ (with dec.). ^{1}H NMR (CDCl₃, 300 MHz. ppm): δ (ppm) 8.62 (ddd, I = 4.9, 1.7, 0.9 Hz, 1H, H22); 7.88 (dd, J = 7.7, 1.3 Hz, 1H, H5 or H8); 7.78 (dd, J = 7.7, 1.4 Hz, 1H, H8 or H5); 7.70 (td, J = 7.7, 7.7, 1.7 Hz, 1H, H24); 7.65–7.61 (m, 2H, H25/H23); 7.52 (td, J = 7.7, 7.5, 1.4 Hz, 1H, H6 or H7); 7.40 (td, J = 7.7, 7.5, 1.3 Hz, 1H, H7 or H6); 7.34–7.23 (m, 5H, Ph); 5.73 (s, 1H, H11); 4.48 (d, J = 14.7 Hz, 1H, H19); 4.24 (d, J = 14.7 Hz, 1H, H19'). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm) 185.1, 181.9, 174.2, 151.8, 149.3, 137.1, 137.0, 133.8, 133.5, 131.1, 131.0, 128.8, 128.4, 128.0, 125.9, 125.4, 123.3, 122.7, 113.2, 60.7, 49.7. IR (KBr, v_{max}/cm⁻¹): 3435 (O-H), 3062 (C-H), 2967 (C-H), 1679 (C=O), 1591 (C=N/C=C), 1570 (C=C), 1527 (& N-H), 1476 (C=C), 1278 (C-O/C-N), 1229 (C-O/C-N). UV-Vis $[CHCl_3; \lambda/nm (\log \varepsilon)]$: 267 (4.05), 329 (3.12), 431 (2.96), Anal. Calc. for C₂₃H₁₈N₂O₃.0.5 H₂O: C. 72.74; H. 5.00; N. 7.38. Found C. 72.68; H. 5.07; N. 7.79%.

2.3.2. Preparation of the complexes $[Cu(L)Cl]_n$ (1a) and $[Cu(L)(H_2O)(\mu-Cl)Cu(L)Cl]$ (1b)

To a suspension of HL (92 mg; 0.25 mmol) in methanol (15 mL) was added a solution of CuCl₂·2H₂O (43 mg; 0.25 mmol) in 2 mL of methanol at 30 °C, resulting in a clear dark green solution. A few minutes after the addition of Et₃N (0.035 mL; 0.25 mmol) precipitation of a green solid was observed. This compound was filtered off, washed with cold methanol and dried under vacuum. Elemental analysis suggested the following composition: [Cu(L)Cl)].2H₂O **1a.** Yield: 71 mg (57%). m.p. (with dec.) 207 °C. IR (KBr, v_{max} / cm⁻¹): 3445 (O-H), 3154 (N-H), 2941 (C-H), 1677 (C=O), 1611 (C=N), 1591 (C=C), 1547 (& N-H), 1487 (C=C), 1479 (C=C), 1277 (C-O/C-N). UV-Vis [CHCl₃; λ/nm (log ε)]: 265 (4.77), 314 (4.00), 426 (3.59), 667 (2.47). UV–Vis [CH₃CN; λ /nm (log ε)]: 265 (4.70), 319 (3.91), 423 (3.65), 655 (2.54). Anal. Calc. for C23H17ClCuN2O3.2-H₂O: C, 54.76; H, 4.20; N, 5.55. Found: C, 54.00; H, 4.18; N, 5.44%. When the reaction mixture was left stirring under the same conditions for over 5 h darkening was observed. Elemental analysis of the dark green solid 1b isolated after 24 h as described above suggested the following composition: [Cu(L)Cl]·0.5H₂O. Yield: 65 mg (55%). m.p. 194 °C (with dec). IR (KBr, v_{max}/cm⁻¹): 3453 (O–H), 3135 (N-H), 2904 (C-H), 1674 (C=O), 1617 (C=N), 1588 (C=C), 1543 (δ N–H), 1273 (C–O/C–N). UV–Vis [CHCl₃; λ /nm (log ε)]: 269 (4.79), 313 (4.07), 431 (3.73), 651 (2.52). UV-Vis [CH₃CN; λ/ nm (log ɛ)]: 265 (4.70), 319 (3.91), 423 (3.61), 655 (2.53). Anal. Calc. for C₂₃H₁₇ClCuN₂O₃·0.5H₂O: C, 57.86; H, 3.80; N, 5.87. Found: C, 58.65; H, 3.94; N, 6.03%. Best yields of compound 1b were obtained when the reaction is scaled up and carried out under more concentrated conditions: HL (740 mg; 2 mmol) and 45 mL total volume of methanol (yield: 713 mg, 75%). Recrystallization of 1a and 1b from methanol gave identical dark green prismatic crystals of same composition as **1b**. m.p. 181 °C (with dec.). IR (KBr, v_{max} / cm⁻¹): 3428 (O–H), 3309 (N–H), 3170 (N–H), 2908 (C–H), 1666 (C=O), 1615 (C=N), 1589 (C=C), 1550 (& N-H), 1481 (C=C), 1280 (C-O/C-N), 1226 (C-O/C-N). UV-Vis $[CHCl_3; \lambda/nm (\log \varepsilon)]$: 272 (4.75), 312 (4.03), 431 (3.69), 655 (2.49). UV-Vis [CH₃CN; λ/nm (log ε)]: 265 (4.75), 319 (3.95), 423 (3.67), 655 (2.49). Anal. Calc. for C₄₆H₃₆Cl₂Cu₂N₄O₇: C, 57.86; H, 3.80; N, 5.87. Found: C, 58.00; H, 3.77; N, 5.76%.

2.3.3. Preparation of the complex $[CuCl(L)(\mu-Cl)Cu(amp)Cl]$ (2)

To a solution of $CuCl_2 \cdot 2H_2O$ (0.2 mmol; 34 mg) and 2-aminomethylpyridine (0.2 mmol; 0.02 mL) in 5 mL of methanol was added a suspension of complex **1b** (0.05 mmol; 48 mg) in 10 mL of methanol. After stirring for 16 h at 30 °C, the green precipitate was filtered and washed with methanol. Crystals of complex **2** were obtained by slow evaporation of solution of the precipitate in methanol. Furthermore, replacing **1b** with **1a** also gave complex 2 in similar yields. Yield 48 mg (67%). m.p. 150 °C (with dec.). IR (KBr, v_{max}/cm^{-1}): 3448 (O–H), 3152 (N–H), 3034 (C–H), 1677 (C=O), 1662 (C=O), 1610 (C=N), 1591 (C=C), 1553 (& N-H), 1277 (C–O/C–N), 1221 (C–O/C–N). UV–Vis [CHCl₃; λ /nm (log ε)]: 279 (4.33), 322 (3.81), 428 (3.52), 654 (2.38). UV-Vis [CH₃CN; λ/ nm (log ɛ)]: 263 (4.64), 316 (3.78), 411 (3.46), 687 (2.40). Anal. Calc. for C₂₉H₂₅N₄O₃Cl₃Cu₂.CH₃OH: C, 48.49; H, 3.93; N, 7.54. Found: C, 48.45; H, 3.91; N, 7.58%. Complex 2 could also be obtained from decomposition of HL: to a suspension of HL (0.25 mmol; 92 mg) in methanol (15 mL) was added a solution of CuCl₂·2H₂O (0.25 mmol; 43 mg) in 2 mL of methanol, resulting in a clear dark green solution. The solution was left stirring at 30 °C for 1 h. The green **1a** precipitate was filtered off (yield 30 mg, 24%). Slow evaporation of the solvent yielded green hexagonal crystals of complex 2 which were adequate for X-ray analysis (Yield: 10 mg, 6%).

3. Results and discussion

3.1. Synthesis

The Mannich base **HL** is synthesized by the one-pot Mannich condensation between 2-hydroxy-1,4-naphthoquinone (Lawsone), 2-aminomethylpyridine and benzaldehyde (**HL**, 68%) (Scheme 1). The resulting bright orange powder is soluble in CHCl₃, CH₂Cl₂, DMSO and slightly soluble in alcohols. **HL** undergoes decomposition in solution, but is stable is the solid state. Rapid recrystallization from ethanol gave analytically pure samples which were characterized by elemental analysis, IR, UV–Vis, ¹H NMR, and ¹³C NMR spectroscopy.

The reaction of 3-[N-(2-pyridylmethyl)aminobenzyl]-2-hydroxy-1,4-naphthoquinone**HL**with CuCl₂·2H₂O and Et₃N (1:1:1), inmethanol (0.017 mol/L final concentrations of**HL**and Cu²⁺) at30 °C results in the immediate precipitation of a light green solid**1a**(57%) which analyses as [Cu(L)Cl)].2H₂O. If the reaction mixtureis left stirring for a further 5 h darkening is observed and the darkgreen solid**1b**isolated by filtration (55%) analyses as [Cu(L)Cl]-0.5H₂O. Compound**1b**is obtained in up to 75% yield when the reaction is carried out under higher concentration of the reagents(0.044 mol/L). Recrystallization of**1a**and**1b**from methanol givesidentical dark green prismatic crystals of same composition as**1b**.X-ray diffraction analysis, revealed a di-copper(II) compound, $[Cu(L)(H₂O)(<math>\mu$ -Cl)Cu(L)Cl] **1b** (Scheme 2).

When the reaction of **HL** with $CuCl_2 \cdot 2H_2O$ is carried out under dilute conditions (0.017 mol/L), and in the absence of Et₃N, at 30 °C, precipitation of some green **1a** (24%) is observed after about an hour. Slow evaporation of the mother liquor yields hexagonal shaped light green crystals of compound **2** and a greenish yellow solution. X-ray diffraction analysis showed that complex [CuCl(L)(μ -Cl)Cu(amp)Cl] (**2**), obtained in 6% yield, is a di-copper species stabilized by one L⁻ and one aminomethylpyridine (**amp**) ligands. The latter ligand is formed as the result of hydrolysis of **HL**, possibly catalyzed by Cu²⁺. Attempts at isolating the expected hydrolysis product by column chromatography of the greenish yellow mother liquor on silica gel, with ethyl acetate as eluent, gave a mixture of products, according to NMR spectroscopy. Under the



Scheme 1. Synthesis of proligand HL.



Scheme 2. Formation of complexes 1a and 1b.

same conditions but in the absence of Cu^{2+} **HL** also undergoes decomposition to unidentified products. Best yield (30%) of complex **2** is obtained when the reaction is carried out at 20 °C.

Complex **2** is best synthesized by addition of **1b** to a solution of **amp** and CuCl₂·2H₂O in methanol, the yields depending on the temperature, concentration and proportion of the reagents. At 30 °C, with **1b**:aminomethylpyridine:CuCl₂·2H₂O = 1:2:2, compound **2** is obtained in 40% yield. With a twofold excess of **amp** and CuCl₂·2H₂O, however, the product is isolated in 67%. Furthermore, replacing **1b** with **1a** also gives complex **2** in similar yields. These reactions are summarized in Scheme 3.

3.2. Crystal structures of $[Cu(L)(H_2O)(\mu-Cl)Cu(L)Cl]$ (1b) and $[CuCl(L)(\mu-Cl)Cu(amp)Cl]$ (2)

Complexes **1b** and **2** were studied by X-ray diffraction. Compound **1b** crystallizes from methanol as bright-green prisms. The molecular structure of **1b** is shown in Fig. 1 together with the



Fig. 1. View of the ORTEP-3 [24] projection of $[Cu(L)(H_2O)(\mu-Cl)Cu(L)Cl]$ (**1b**) showing the π stacking of the naphthoquinone rings. Displacement ellipsoids at the 50% level.

labelling scheme used. Selected bond distances and angles with estimated standard deviations are listed in Table 2 and hydrogen bond parameters are reported in Table S1 (Supporting information).

The structure of compound **1b** reveals two copper(II) centers bridged by a chloro ligand and bonded to two chelating L^- via the naphthalen-2-olate oxygen, a pyridine and an amine nitrogens.

Both metal centers exhibit approximate square-pyramidal (spy) geometry, with the apical positions occupied by Cl(1). The value of the trigonality index τ [22] (τ = zero corresponds to a spy geometry and τ = one, to a trigonal bipyramidal (tbp) structure) is 0.033 for Cu(1) [where β represents the angle N(1)–Cu(1)–O(1) and α ,



Scheme 3. Synthesis of complex 2 from 1b (A) and hydrolysis of HL with formation of complex 2 (B).

Table 2	
Selected bond lengths (Å) and angles (°) for complex	1b.

Cu(1)-O(1)	1.950(2)	N(2)-Cu(1)-O(1W)	162.61(12)
Cu(1)-N(2)	1.997(3)	O(1)-Cu(1)-N(1)	164.61(9)
Cu(1)–N(1)	2.005(3)	N(2)-Cu(1)-N(1)	83.04(11)
Cu(1)-O(1W)	2.016(2)	O(1)-Cu(1)-N(2)	88.12(10)
Cu(1)-Cl(1)	2.4982(10)	N(4)-Cu(2)-N(3)	83.24(12)
Cu(2)-O(4)	1.988(2)	O(4)-Cu(2)-N(4)	85.86(9)
Cu(2)-N(4)	2.018(3)	O(4)-Cu(2)-N(3)	161.87(10)
Cu(2)-N(3)	2.031(3)	N(4)-Cu(2)-Cl(2)	165.05(9)
Cu(2)-Cl(2)	2.2782(11)	Cu(1)-Cl(1)-Cu(2)	109.31(4)
Cu(2)-Cl(1)	2.5698(10)		
$Cu(1) \cdots Cu(2)$	4.1342(8)		

N(2)–Cu(1)–O(1W)] and 0.053, for Cu(2) [where β represents the angle Cl(2)–Cu(2)–N(4) and α , O(4)–Cu(2)–N(3)]. The coordination spheres of Cu(1) and Cu(2) are completed with a water molecule and a chlorine atom, respectively. The Cu(1) and Cu(2) centers deviate from their mean equatorial planes O(1)/N(2)/N(1)/O(1w) and O(4)/N(4)/N(3)/Cl(2) by 0.0323 and 0.0006 Å, respectively, and the dihedral angle between the two equatorial planes is 70.01(8)°. To our knowledge this is the first dinuclear copper (II) structure with this structural motif, although an analogous di- μ -chloro-di- μ -imidazolato-tetracopper(II) complex has been described in the literature [23].

The packing contains molecules connected by classical and non classical hydrogen bonds, building an infinite 3D network *via* intermolecular weak directional forces along the [100], [010] and [001] crystallography directions, see Fig. S2 and Table S1 (Supporting information).

Compound **2** crystallizes from methanol as dark-green hexagons. The molecular structure of **2** is presented in Fig. 2 together with the labelling scheme used. Selected bond distances and angles with estimated standard deviations are presented in Table 3 and hydrogen bond parameters, in Table S2 (Supporting information).

The molecular structure of compound **2** contains two copper(II) atoms bridged asymmetrically by a chloride and by the L^- naph-thalen-2-olate oxygen. The Cu–Cl distance values are similar to those found in other pentacoordinate copper(II) complexes that contain bridging phenoxy oxygen atoms [11,25,26]. The two copper(II) centers are separated by 3.3476(9) Å.



Fig. 2. View of an ORTEP-3 [24] projection of [CuCl(L)(µ-Cl)Cu(amp)Cl] (2) evidencing the asymmetrically bridged chloride and the chelate coordination. Displacement ellipsoids at the 50% level.

 Table 3
 Selected bond lengths (Å) and angles (°) for complex 2.

		· · · · ·	
Cu(1)-N(2)	2.009(2)	N(4)-Cu(2)-O(1)	167.70(9)
Cu(1) - N(1)	2.012(2)	N(3)-Cu(2)-Cl(1)	173.53(8)
Cu(1) - O(1)	2.0308(19)	O(1)-Cu(2)-Cl(2)	76.78(6)
Cu(1)-Cl(2)	2.2820(10)	N(2)-Cu(1)-O(1)	160.76(9)
Cu(1)-Cl(3)	2.5402(10)	N(1)-Cu(1)-Cl(2)	173.46(8)
Cu(2)-N(3)	2.009(3)	O(1)-Cu(1)-Cl(2)	88.76(6)
Cu(2) - N(4)	2.018(3)	Cu(1)-Cl(2)-Cu(2)	83.31(3)
Cu(2) - O(1)	2.063(2)	Cu(1)-O(1)-Cu(2)	109.70(9)
Cu(2)-Cl(1)	2.2684(10)		
Cu(2)-Cl(2)	2.7295(9)		
Cu(2) - O(2)	2.470(2)		
Cu(1)-Cu(2)	3.3476(9)		
$Cu(1) \cdot \cdot Cu(2)$	3.3476(9)		

The structural motif exhibited in this complex is uncommon, although there are four other structurally characterized copper(II) complexes of nitrogen donor-based ligands containing both a bridging phenolate anion and a chloride anion in which similar Cu(II)–Cu(II) distances were encountered [27]. Both metal centers exhibit approximate square-pyramidal geometry, with τ , for Cu(1) of 0.045 [where β represents the N(1)–Cu(1)–Cl(2) angle and α , N(2)–Cu(1)–O(1)] and of 0.097, for Cu(2) [where β represents the Cl(1)–Cu(2)–N(3) angle and α , O(1)–Cu(2)–N(4)].

 L^{-} interacts further with Cu(1) via the pyridine and amine nitrogens forming a five membered chelate ring N(2)/C(19)/C(18)/N(1)/Cu(1) that deviates from the plane of fitted atoms (r.m.s) by 0.0807 Å. All amine-Cu(II) and pyridine-Cu(II) bond distances are within the normal range observed in other copper(II) complexes of aminomethylpyridine and analogous ligands. The coordination sphere of Cu(1) is completed by Cl(3) located in the apical position of the square based pyramid. Cu(2) also contains a chloride in the apical position and is bonded to an aminomethylpyridine ligand, the chelate ring N(4)/C(28)/C(29)/N(3)/Cu(2) deviating from the plane of fitted atoms by 0.1351 Å. Finally, Cu(2) also interacts weakly with the carbonyl oxygen of L^{-} [Cu(2)–O(2) 2.470(2)Å]; this interaction does not lead to lengthening of the carbonyl bond [O(2)-C(2) 1.229(3)Å], compared with that of the carbonyl in the para position [O(3)-C(9) 1.231(4) Å]. The Cu(1) and Cu(2) centers deviate from their mean equatorial planes (O(1)/Cl(2)/N(2)/N(1))and (Cl(1)/N(4)/N(3)/O(1)) by 0.1000 and 0.1234 Å, respectively, and the dihedral angle between the two equatorial planes is 89.56(6)°.

The crystal structure contains molecules related by the axial c-glide plane and 2_1 screw axis, building an infinite 2D network *via* intermolecular weak directional forces along of (001) plane (Fig. S3 Supporting information).

3.3. Conductivity measurements

The molar conductivity values for complexes **1a**, **1b** and **2** in acetonitrile are 31.3, 10.7 and $17.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively, indicative of neutral complexes, according to the literature [28].

3.4. Electronic spectra

The UV–Vis spectra for complexes **1a**, **1b** and **2**, in chloroform and acetonitrile solutions at 10^{-4} mol/L (Figs. S5–S7 Supporting information) exhibit three absorptions around 270, 310 and 430 nm. The intense band at 270 nm is assigned to ligand $\pi \rightarrow \pi^*$ transitions. The other two bands between 310 and 430 nm are typical of ligand-to-metal charge transfer (LMCT) of the naphthoquinonate moiety to the metal ion. The d–d transition band can be visualized in concentrated chloroform solutions at 10^{-3} mol/L, around 650 nm, for the dinuclear complexes **1b** and **2** and at 667 for **1a**. These absorptions are consistent with a square-pyramidal geometry of the Cu(II) centres in these complexes [25,29,30]. When the spectrum of **1a** is recorded in acetonitrile the d–d transition band appears at 655 nm *i.e.* the spectrum is identical to that of **1b** thus indicating conversion of **1a** into **1b** in this solvent. In the case of complex **2**, the slight shift of the maximum of 655 nm in CHCl₃ to 687 nm in acetonitrile may suggest distortion of the geometry of the Cu(II) centers possibly by coordination of the solvent to the metal ions and cleavage of the bridges.

3.5. Electrochemical studies

The redox behaviour of complexes **1a**, **1b** and **2** and of Mannich base **HL** was evaluated by cyclic voltammetry (CV), at room temperature, in acetonitrile/Bu₄NPF₆. The CVs, depicted in Fig. 3 (and Figs. S8–S10 Supporting information), were obtained versus ferrocene/ferrocenium (FcH/FcH⁺).

The CV of *Mannich base* **HL** (Fig. S8, Supporting information) in acetonitrile shows four *quasi*-reversible processes attributed to the quinone groups of **HL** and of its deprotonated form \mathbf{L}^{1-} ($E_{1/2(1)} = -0.385$, $E_{1/2(2)} = -1.07$, $E_{1/2(3)} = -1.01$, $E_{1/2(4)} = -1.74$ V). The irreversible waves at the positive range of the voltammogram can be assigned to the self-protonation processes of the species in solution as described in the literature [31]. The data obtained for complexes **1a**, **1b** and **2** are summarized in Table 4.

The voltammograms of the three complexes show only one characteristic wave for the quinone portion of \mathbf{L}^- ($E_{\mathrm{p1/2(3)}}$ around -1.60 V), thus confirming, in solution, interaction *via* the naphthalen-2-olate oxygen in the three cases. In the voltammograms of complexes **1b** and **2** (Fig. S9, Supporting information and Fig. 3, respectively) two irreversible peaks are observed and assigned to the Cu^{II},Cu^{II} \rightarrow Cu^{II},Cu^I and Cu^{II},Cu^I \rightarrow Cu^I,Cu^I processes, respec-



Fig. 3. Cyclic voltammogram of **2** in 0.1 mol/L Bu_4NPF_6/CH_3CN obtained at 0.1 V/s with a glassy carbon electrode, the potentials being referred to the ferrocene/ ferrocenium (FcH/FcH⁺) pair internal standard.

Table 4

Electrochemical data for **1b**, **1a** and **2**, determined by cyclic voltammetry in acetonitrile at a glassy carbon electrode; scan rate 0.1 V/s; E vs. ferrocene/ferrocenium (FcH/FcH⁺) pair internal standard.

Compound	$E_{p1c}(V)$	$E_{p2c}(V)$	$E_{{ m p1/2(3)}}\left({ m V} ight)$
1a	-0.67	-1.13	-1.55
1b	-0.63	-1.09	-1.54
2	-0.83	-1.21	-1.60

tively, indicating that in both cases, in solution the two copper ions exhibit different coordination environments, like in the solid state. In addition, an extra sharp anodic peak around = -0.68 V versus FcH/FcH⁺ is seen on the CV curve of complexes **1b** and **2** which is characteristic of a redissolution process of copper(0) on the electrode surface [32]. The CV of complex **1a** (Fig. S10, Supporting information) is similar to that of **1b** thus confirming the conversion of **1a** into **1b** in acetonitrile solution, as observed in the electronic spectra.

3.6. Magnetic susceptibility studies and EPR

The magnetization properties of all compounds have been studied to evaluate the magnetic interactions between the two copper ions in **1b** and **2** and specially the existence of Cu–Cu interactions in compound **1a** whose structure is unknown.

Variable temperature magnetic susceptibility measurements in the 1.8–300 K temperature range, under a constant magnetic field of 1 kOe were carried out and the results are presented in Figs. 4 and 5 and Fig. S13 Supporting information in the form of $\chi_m T$ versus *T* plots where χ_m is the molar susceptibility. Data were corrected for



Fig. 4. Plot of $\chi_m T$ vs. *T* per mol of crystalline sample of $[Cu(L)(H_2O)(\mu-Cl)Cu(L)Cl]$ (**1b**). Full line is the best fit with Bleaney Bowers equation and 17% paramagnetic contribution, from which *J* = -5.7 cm⁻¹.



Fig. 5. Plot of χ vs. *T* per mol of crystalline sample of [CuCl(L)(μ -Cl)Cu(amp)Cl] (**2**). Inset: $\chi_m T$ vs. *T* plot, with a maximum at 105 K.

gelatine capsule sample holder as well as for diamagnetic and temperature independent paramagnetism contributions.

The data for a crystalline sample of **1b** from which a crystal was selected for the X-ray diffraction study show that $\gamma_m T$ remains constant over most of the temperature range, at its 300 K value of 0.83 cm³ K mol⁻¹, consistent with two magnetically isolated Cu^{II} $(S = \frac{1}{2})$ centers in the molecule (Fig. 4). Below 50 K, the $\chi_m T$ product decreases to reach a value of 0.2 cm³ K mol⁻¹ at 2 K. This behaviour is typical of an antiferromagnetically weakly coupled copper pair. The coupling constant, $J = -5.7 \text{ cm}^{-1}$, was estimated from a fit of $\chi \times T$ data with the Bleaney Bowers equation and a monomer or impurity term (see Supporting information). The data obtained for a sample of **1b** before recrystallization is identical to that described above for the crystalline sample of 1b. To our knowledge, there is no report in the literature of a dinuclear copper complex linked by only one chloro bridge. Dinuclear complexes containing two chloro bridges have been described [25,33] and in all cases magnetic couplings were found weaker than for the analogous complexes containing phenolate bridges, as the result of weaker overlap between the copper(II) orbitals.

As expected the $\chi_m T$ versus T curve obtained for complex **2** indicates strong antiferromagnetic coupling between the copper ions and exhibits a maximum of γ around 105 K (Fig. 4). Below 10 K a Curie tail is observed which is frequently ascribed to paramagnetic impurity [34]. A rough estimate of the coupling constant was obtained from the maximum of $\chi \times T$, $J \sim -120$ cm⁻¹, which is much larger than for complex 1b, due to the presence of both naphthalen-2-olate and chloride bridges which maintain the two copper ions at closer proximity $[3.3476(9) \times 4.1342(8) \text{ Å}]$. Studies have shown that short Cu-O bonds and large Cu-O-Cu angles in square-pyramidal phenolate-bridged Cu dimers result in strong overlap of $d_{x^2-v^2}$ orbitals and thus produce strong antiferromagnetic couplings [25,29,35]. Copper(II) dimers with both halide and phenolate bridges have been shown to exhibit strong antiferromagnetic coupling constants around -100 cm^{-1} [34]. The short Cu–O bonds relative to the long Cu–X bonds point at a dominant coupling through the phenolate bridge [34] which explains the stronger coupling constant observed for complex 2 as compared to **1b** that contains only one chloro bridge.

The $\gamma_m T$ versus T curve obtained for compound **1a** (the precursor of dimer 1b), illustrated in Fig. S11 Supporting information, shows a $\gamma_m T$ of 0.44 cm³ K mol⁻¹ around room temperature, which increases as T is lowered, indicating ferromagnetic interaction. A good fit to the Bleaney Bowers equations with $I/k_{\rm B}$ = 10.5 K could be obtained above the maximum at 5 K. Below this maximum, $\chi_m T$ starts to decrease, suggesting weaker antiferromagnetic interdimer interactions. Such behaviour could be explained by two different models. Either this compound exhibits an infinite 1D coordination polymeric structure in which the copper(II) centers are connected by Cl-Cu-Cl bridges, similar to those found for *N*-(2-pyridylmethyl)-L-glycine (Hpgly) and *N*-(2-pyridylmethyl)-Lalanine (Hpala) copper(II) complexes, namely [Cu(pgly)Cl]·H₂O and [Cu(pala)Cl]·H₂O, respectively, for which no magnetic data have been reported [36]. The Cl-Cu-··Cl-chain would present predominant ferromagnetic interactions increasing the effective moment, and a weak antiferromagnetic interaction forming an alternating linear chain. The other possibility is the presence of antiferromagnetic interchain interactions between ferromagnetic chains which would be responsible for the decrease of $\chi_m T$ below 4 K. Unfortunately, crystals of **1a** suitable for an X-ray diffraction study could not be obtained to prove either model, since this compound rearranges into 1b in solution.

Powder X-Band (9.5 GHz) EPR spectra of powdered samples of **1a**, **1b** and **2** were collected at 77 K. Table 5 presents the EPR parameters for the three complexes.

Table 5						
EPR parameters	for	complexes	1a,	1b	and	2

Complex	$A_{\perp} (\times 10^{-4} {\rm cm}^{-1})$	$A_{//} (\times 10^{-4} \mathrm{cm}^{-1})$	g_{\perp}	<i>g</i> //
1a 1b 2	25	65	2.0635 2.0700 2.0450	2.1880 2.1250 2.2050

Values for g_{\perp} larger than those observed for $g_{||}$ are consistent with a tetragonally elongated square-pyramidal geometry around the copper(II) ions in the three complexes, in agreement with the X-ray structures of **1b** and **2** [25,29,37]. The very low parallel component of the hyperfine coupling constant (not resolved in the spectra of the **1a** and **2**) has been explained by considering a mixture of the d_{z^2} and $d_{x^2-y^2}$ orbitals as the ground state [38].

4. Conclusions

Three novel copper(II) complexes of the Mannich base 3-[N-(2pyridylmethyl)aminobenzyl]-2-hydroxy-1,4-naphthoquinone HL were synthesized and fully characterized both in the solid state and in solution. The complexation reactions were found to depend on the reaction conditions, in part because of the facile decomposition of HL upon standing in solution. Marked differences in products solubility were also responsible for drastic changes in product distribution and yields upon varying the reagents concentration. In spite of the lability of this proligand, the monoanion L^{-} acted as a versatile tridentate donor allowing formation of interesting complexes with different structural arrangements. By careful choice and monitoring of the reaction conditions reasonable yields of each of the products could be obtained. The X-ray diffraction studies revealed two dinuclear copper(II) complexes 1b and 2 with approximate square-pyramidal geometries around the metal ions, complex **1b** presenting an uncommon structural motif with a single chloro- bridge. Both complexes 1b and 2 presented antiferromagnetic interactions, but as expected on the basis of their solid state structures, significant differences in coupling constants, J were observed. As for other systems, both the nature of the bridge and the Cu...Cu distance in these dimers exert significant influence on the J values. Based on the magnetic susceptibility data a possible structural arrangement consisting of a polymeric structure connected by Cu-Cl-Cu bridges was proposed for complex 1a.

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Appendix A. Supplementary data

CCDC 726553 and 726554 contain the supplementary crystallographic data for **2** and **1b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.07.011.

- References
- R.H. Thompson, Naturally Occurring Quinones IV: Recent Advances, Champman & Hall, London, 1997.
- [2] T.W. Goodwin, E.I. Mercer, Introduction to Plant Biochemistry, Pergamon Press, New York, 1972.
- [3] (a) C.G. Pierpont, Coord. Chem. Rev. 216–217 (2001) 99;
- (b) K. Yamada, H. Tanaka, S. Yagishita, K. Adachi, T. Uemura, S. Kitagawa, S. Kawata, Inorg. Chem. Commun. 45 (2006) 4322.
- [4] A.P. Neves, C.C. Barbosa, S.J. Greco, M.D. Vargas, L.C. Visentin, C.B. Pinheiro, A.S. Mangrich, J.P. Barbosa, G.L. da Costa, J. Braz. Chem. Soc. 20 (2009) 712.
- [5] (a) N.H. Gokhale, K. Shirisha, S.B. Padhye, S.L. Croft, H.D. Kendrick, V. Mckee, Bioorg. Med. Chem. Lett. 16 (2006) 430; (b) N.H. Gokhale, K. Shirisha, S.B. Padhye, S.L. Croft, H.D. Kendrick, W. Davies, C.E. Anson, A.K. Powell, J. Inorg. Biochem. 95 (2003) 249; (c) J. Chen, Y. Huang, G. Liu, Z. Afrasiabi, E. Sinn, S. Padhye, Y. Ma, Toxicol. Appl. Pharmacol. 197 (2004) 40; (d) A.I. Francisco, M.D. Vargas, T.P. Fragoso, J.W.M. Carneiro, A. Casellato, F.C. Silva, V.F. Ferreira, J.P. Barbosa, C. Pessoa, L.V. Costa-Lotufo, J.D.B. Marinho Filho, M.O. Moraes, A.S. Mangrich, J. Braz. Chem. Soc. 21 (2010) 1293; (e) A.P. Neves, G.B. Silva, M.D. Vargas, C.B. Pinheiro, L.C. Visentin, J.D.B. Marinho Filho, A.J. Araújo, L.V. Costa-Lotufo, C. Pessoa, M.O. Moraes, Dalton Trans., doi:10.1039/C0DT00572J. [6] S.Y. Salunke-Gawali, V.G. Rane, C. Puranik, Guyard-Duhayon, F. Varret, Polyhedron 23 (2004) 2541. [7] P. Garge, R. Chikate, S. Padhye, J. Savariault, P. de Loth, J. Tuchagues, Inorg. Chem. 29 (1990) 3315. [8] S. Salunke-Gawali, R. Dalvi, K. Ah, S. Rane, J. Therm. Anal. Calorim. 76 (2004) 801.
- [9] (a) S. Rane, S. Gawali, S. Padhye, Indian J. Chem. 42A (2003) 255;
 (b) S.Y. Rane, E.M. Khan, D.R. Thube, S.B. Padhye, S.K. Date, P.P. Bakare, Indian J. Chem. 39A (2000) 1117.
- [10] R. Gupta, S. Mukherjee, R. Mukherjee, J. Chem. Soc., Dalton Trans. (1999) 4025.
- [11] L. Rodríguez, E. Labisbal, A. Sousa-Pedrares, J.A. García-Vázquez, J. Romero, M.L. Durán, J.A. Real, A. Sousa, Inorg. Chem. 45 (2006) 7903.
- [12] (a) V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfield, Inorg. Chem. 15 (1976) 2107;
- (b) A. Asokan, B. Varghese, P.T. Manoharan, Inorg. Chem. 38 (1999) 4393.
- [13] R.R. Gagne, C.A. Koval, G.C. Lisensky, Inorg. Chem. 19 (1980) 2854.
- [14] Nonius, COLLECT, Nonius BV, Delft, The Netherlands, 1998.
- [15] A.J.M. Duisenberg, R.W.W. Hooft, A.M.M. Schreurs, J. Kroon, J. Appl. Crystallogr. 33 (2000) 893.
- [16] A.J.M. Duisenberg, J. Appl. Crystallogr. 25 (1992) 92.

- [17] A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, J. Appl. Crystallogr. 36 (2003) 220.
- [18] G.M. Sheldrick, sADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.
- [19] G.M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [20] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [21] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
- [22] A.W. Addison, T.N. Rao, J. Reedjik, J. Van Rijn, G.C. Vershcoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
- [23] H.-L. Zhu, L.-M. Zheng, D.-G. Fu, P. Huang, W.-M. Bu, W.-X. Tang, Inorg. Chim. Acta 287 (1999) 52.
- [24] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
- [25] X.H. Bu, M. Du, L. Zhang, Z.L. Shang, R.H. Zang, H. Shionoya, J. Chem. Soc., Dalton Trans. (2001) 729.
- [26] (a) M. Vaidyanathan, M. Palaniandavar, R.S. Gopalan, Inorg. Chim. Acta 324 (2001) 241;

(b) D. Kong, J. Mao, A.E. Martell, A. Clearfield, Inorg. Chim. Acta 342 (2003) 260;

- (c) Y. Xie, Q. Liu, H. Jiang, J. Ni, Eur. J. Inorg. Chem. (2003) 4010.
- [27] (a) S.P. Foxon, D. Utz, J. Astner, S. Schindler, F. Thaler, F.W. Heinemann, G. Liehr, J. Mukherjee, V. Balamurugan, D. Ghoshc, R. Mukherjee, Dalton Trans. (2004) 2321;
 - (b) P. Kamaras, M.C. Cajulis, M. Rapta, G. Brewer, G.B. Jameson, J. Am. Chem. Soc. 116 (1994) 10334;

(c) K.D. Karlin, A. Farooq, J.C. Hayes, B.I. Cohen, T.M. Rowe, E. Sinn, J. Zubieta, Inorg. Chem. 26 (1987) 1271;

(d) R.J. Majeste, C.L. Klein, E.D. Stevens, Acta Crystallogr., Sect. C 39 (1983) 52.
 [28] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

- [29] S. Torelli, C. Belle, I. Gautier-Luneau, J.L. Pierre, E. Saint-Aman, J.M. Latour, L.L. Pape, D. Luneau, Inorg. Chem. 39 (2000) 3526.
- [30] S.J. Brudenell, L. Spiccia, E.R.T. Tiekink, Inorg. Chem. 35 (1996) 1974.
- [31] C. Frontana, I. Gonzalez, J. Electroanal. Chem. 603 (2007) 155.
- [32] D. Zurita, C. Scheer, J.L. Pierre, E. Saint-Aman, J. Chem. Soc., Dalton Trans. (1996) 4331.
- [33] M. Rodríguez, A. Llobet, M. Corbella, A.E. Martell, J. Reibenspies, Inorg. Chem. 38 (1999) 2328.
- [34] I.A. Koval, M. Huisman, A.F. Stassen, P. Gamez, O. Roubeau, C. Belle, J.L. Pierre, E. Saint-Aman, M. Lüken, B. Krebs, M. Lutz, A.L. Spek, J. Reedijk, Eur. J. Inorg. Chem. (2004) 4036.
- [35] (a) L. Merz, W. Haase, J. Chem. Soc., Dalton Trans. (1980) 875;
- (b) W.E. Marsh, W.E. Hatfield, D.J. Hodgson, Inorg. Chem. 21 (1982) 2679.
- [36] X. Wang, J.D. Ranford, J.D. Jagadese, J. Vittal, J. Mol. Struct. 796 (2006) 28.
 [37] E. Guimarães, A.S. Mangrich, V.G. Machado, D.G. Traghetta, M.A. Lobo, J. Braz.
- [37] E. Guimaraes, A.S. Mangrich, V.G. Machado, D.G. Iragnetta, M.A. Lobo, J. Braz. Chem. Soc. 12 (2001) 734.
- [38] I.C. Mendes, J.P. Moreira, N.L. Speziali, A.S. Mangrich, J.A. Takahashi, H. Beraldo, J. Braz. Chem. Soc. 17 (2006) 1571.