Electrocatalytic reduction of carbon dioxide induced by bis(*N*-R-2-hydroxy-1-naphthaldiminato)-copper(II) (R = *n*-octyl, *n*-dodecyl): Magnetic and theoretical studies and the X-ray structure of bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II)

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Abstract

Copper(II) complexes of *n*-alkyl-2-hydroxy-1-naphthaldimine Schiff bases (with *n*-alkyl: *n*-octyl, and *n*-dodecyl) have been synthesized, to study steric and electronic effects of long alkyl chain substituents on their structure and properties. These complexes have been characterized with FT-IR, UV–Vis, magnetic susceptibility and cyclic voltammetry both in nitrogen and carbon dioxide atmosphere. Metal-ligand coordination is inferred from the shifting of the $\nu_{C=N}$ stretching vibration mode in the 1610–1620 cm^{-1} region when compared to that of the free ligand. The UV–Vis spectra show one band around 640 nm typical for square planar Cu(II) complexes. Results obtained from cyclic voltammetry indicate electrocatalytic reduction of carbon dioxide around −0.90 V (versus Ag/AgCl). Bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II) has been studied with X-ray diffraction. The molecular structure shows the copper atom in a planar environment and the *n*-octyl chains having thermal disorder. The crystal packing shows stacked units intermolecularly separated by 3.33 Å, probably due to π–π interactions between naphthyl groups, and Cu–O and O–O separations of 3.95 and 3.42 Å, respectively. The magnetic susceptibility data between 10 and 300 K are indicative of diluted paramagnetic behavior. Density functional theory calculations of spin density for the *n*-octyl complex shows the unpaired electron localized along the planar CuO_2N_2 moiety. The calculated electrostatic potential show electron rich regions on the oxygen atoms.

Keywords: Copper complexes; Cyclic voltammetry; Crystal structure; Magnetic properties; Theoretical study

1. Introduction

As a means of organizing complex molecules, the Langmuir–Blodgett technique has many potential applications for molecular electronics, nonlinear optics, and conducting thin films [1–4]. For example, metal porphyrin and phthalocyanine molecules were employed to obtain optical and electronic devices [1]. Also the Langmuir–Blodgett films have been prepared using Schiff base complexes derived from *N*,*N*′-ethylene-bis(salicylaldimine) [2–4], but in these cases the films present low stability.

In addition, salicylaldimine complexes of copper, nickel, iron and palladium show metallomesogen properties [5,6] useful in electronic devices and liquid crystals. Schiff base

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ligands, in thermotropic liquid crystals, are generally made by condensing the appropriate 4-substituted ether or 2,4-hydroxybenzaldehyde with 4-substituted anilines or primary amines. The related bis(*N*-R-2-hydroxy-1-naphthaldiminato)-copper(II) complexes, R = *n*-octyl, *n*-dodecyl, are described including synthesis, conventional characterization, cyclic voltammetry in nitrogen and carbon dioxide media, a magnetic study and theoretical calculations (DFT). The X-ray crystal structure has been determined for the *n*-octyl derivative.

2. Experimental

2.1. Synthesis of copper complexes

Bis(*N*-alkyl-2-hydroxy-1-naphthaldiminato)-copper(II) complexes were prepared by the reaction of bis(1-formyl-2-naphthalato)-copper(II), and the monoamines: *n*-octylamine, or *n*-dodecylamine, following the reported procedures [7–9]. Suitable crystals for X-ray studies have been obtained for bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II).

2.2. Instruments

The FT-IR spectra were obtained with a Bruker IFS 66V spectrophotometer using KBr pellets in the 4000–400 cm^{-1} range. The UV–Vis spectra were recorded using a Variant Cary 1E Spectrophotometer in the 900–190 nm region, and a Carl Zeiss Model DMR-22 Instrument between 2000 and 350 nm. Zero-field cooled magnetic susceptibility was measured in the temperature range 10–300 K for the 2 compounds. Measurements were performed at 1 KOe, using a Quantum Design Squid susceptometer-magnetometer She 906. The susceptibility data were corrected by the diamagnetic contributions using the Pascal constants [10]. Cyclic voltammetry was measured using a Pine bipotentiostate model AFCB-1. A two compartment-three electrode locally built cell was used, using a Glassy Carbon as the working electrode and a platinum wire as the auxiliary electrode. All potentials were measured versus a Ag/AgCl/KCl(1 M) reference electrode. Measurements were performed in *N*,*N*′-dimethylformamide (Merck p.a.), and $(C_2H_5)_4NClO_4$ was used as the supporting electrolyte.

2.3. X-ray structure determination of bis(N-n-octyl-2-hydroxy-1-naphthaldiminato)-copper(II)

Initial crystal data were collected with a Syntex $P2_1$ diffractometer, however, the level of resolution was low ($R_f = 0.062$) due to the small crystal thickness and the final data were collected on a Bruker SMART diffractometer having a CCD detector. Data were reduced and corrected by absorption, Lorentz and polarization effects with the package of programs furnished by Bruker. The structure was solved with the heavy atom method (Patterson and Fourier maps) and refined with CAOS [11]. H atoms were riding on attached C atoms at 0.96 Å and hydrogen B_{iso} fixed. Table 1 contains additional crystal data.

Table 1
Crystal data and refinement details of bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II)

Elemental formula	$C_{38}H_{48}N_2O_2Cu$
M_f	628.36
a (Å)	42.273(25)
b (Å)	42.273(25)
c (Å)	5.164(3)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	7992
Z	9
Crystal system, space group	rhombohedral (hexagonal setting), R-9 (#148)
Radiation, λ (Å)	Mo Kα, 0.71069
Temperature (K)	298
Crystal growth method	evaporation
Crystal size, color	0.30 × 0.10 × 0.10 mm, brown
D_c (g cm^{-3})	1.175
$F(000)$	3015
μ (Mo Kα)	0.674 cm^{-1}
Absorption (ψ-scan), T_{min}–T_{max}	0.97–1.00
Data collection apparatus, method	Bruker SMART CCDC area detector, phi omega scans
X-ray source	fine focus sealed X-ray tube
Monochromator	graphite
$H_{min,max}/K_{min,max}/L_{min,max}$	0,54/−46,0/−6,6
θ_{min}–θ_{max}	1.53–28.30
Total number of reflections	4025
Reflections with [$F_o > 6\sigma(F_o)$]	2020
R (R_w)	0.052 (0.069)
Decay correction	none
Number of parameters refined	196
Highest/lowest difference Fourier peak	0.231/−0.329

2.4. Computational details

Spin density and electrostatic potential for bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II) were calculated in gas phase with a single point calculation at a density functional theory (DFT) level using the B3LYP exchange-correlation functional and a LACVP** basis set (TITAN Package) [12]. LACVP** uses an effective core potential (LACVP) for the copper atom and a 6-31G basis set for the remaining atoms (C, N, O, H), The two stars (**) indicate the inclusion of (d,p) polarization functions with the aim of minimizing the electronic repulsion. Atomic coordinates for the single point calculation were obtained from the X-ray structure. A restricted open shell calculation was performed due to the doublet multiplicity of the complex.

3. Results and discussion

3.1. FT-IR and UV–Vis spectra

FT-IR and UV–Vis spectra for the 2 complexes are summarized:

3.1.1. Bis(N-n-octyl-2-hydroxy-1-naphthaldiminato)-copper(II)

FT-IR (KBr, cm^{-1}): 2920–2853 (ν_{C-H}), 1617 ($\nu_{C=N}$), 420 (ν_{Cu-N}), 270 (ν_{Cu-O}); UV–Vis (*N*-*N*′-dimethylformamide, λ_{max}, nm ($\varepsilon = M^{-1}\,cm^{-1}$)): 630(100); UV–Vis (Nujol, λ_{max}, nm): 630.

3.1.2. Bis(N-n-dodecyl-2-hydroxy-1-naphthaldiminato)-copper(II)

FT-IR (KBr, cm^{-1}): 2920–2850 (ν_{C-H}), 1619 ($\nu_{C=N}$), 418 (ν_{Cu-N}), 273 (ν_{Cu-O}); UV–Vis (*N*,*N*′-dimethylformamide, λ_{max}, nm ($\varepsilon = M^{-1}\,cm^{-1}$)): 640(90); UV–Vis (Nujol, λ_{max}, nm): 645.

The FT-IR spectra show several vibration modes of which the most typical correspond to ν_{C-H}, $\nu_{C=N}$, ν_{Cu-N}, and ν_{Cu-O}. The $\nu_{C=N}$ stretching is shifted 10–15 cm^{-1} to lower energies upon coordination of the Schiff base to the metal, in agreement with the coordination of the nitrogen atom to the metal. The UV–Vis in the solid state and in *N*,*N*′-dimethylformamide solutions showed only one broad band at 630–645 nm corresponding to the d–d transition region [13,14]. Therefore, these copper(II) complexes have the ligands in an essentially square-planar stereochemistry.

3.2. Cyclic voltammetry

Fig. 1 shows the cyclic voltammogram for bis(*N*-*n*-dodecyl-1-hydroxy-2-naphthaldiminato)-copper(II) in N_2 and CO_2 atmospheres. The voltammogram recorded in N_2 has one cathodic peak at −0.90 V associated to an anodic peak located at −0.80 V versus Ag/AgCl (3 M KCl), which corresponds to a Cu(II)/Cu(I) *quasi*-reversible process [15]. An additional, irreversible, cathodic peak was observed at −1.75 V associated with a ligand reduction process [16].

Drastic changes are observed when N_2 is replaced by CO_2 as can be seen in Fig. 1: the cathodic current peak at −1.30 V increases, the anodic peak at −0.80 disappears and the process becomes totally irreversible.

The CO_2 is reduced at −1.30 V, and −1.40 V versus Ag/AgCl using bis(*N*-*n*-octyl-1-hydroxy-2-naphthaldiminato)-copper(II) and bis(*N*-*n*-dodecyl-1-hydroxy-2-naphthaldiminato)-copper(II), respectively. We have also found that CO_2 reduction is not a selective process as a competition with hydrogen evolution has been observed [17].

It is the first time that a CO_2 reduction process is observed using an acyclic complex as electrocatalyst in this region of the potentials [18,19]. In a previous work, Fujiwara et al. studied the CO_2 reduction using simple acyclic copper complexes obtained from copper carbonate, 2,2-bipyridyl and phosphines [18]. These complexes exhibited a significant electrocatalytic activity for CO_2 reduction around −1.98 V versus Ag/AgCl, affording HCOOH, $(COOH)_2$ and CO as the main reduction products.

It has been indicated that catalytic CO_2 reduction activity is given when the second electron does not lead to complex decomposition and the ligand structure affects such stability [9a,15,18b].

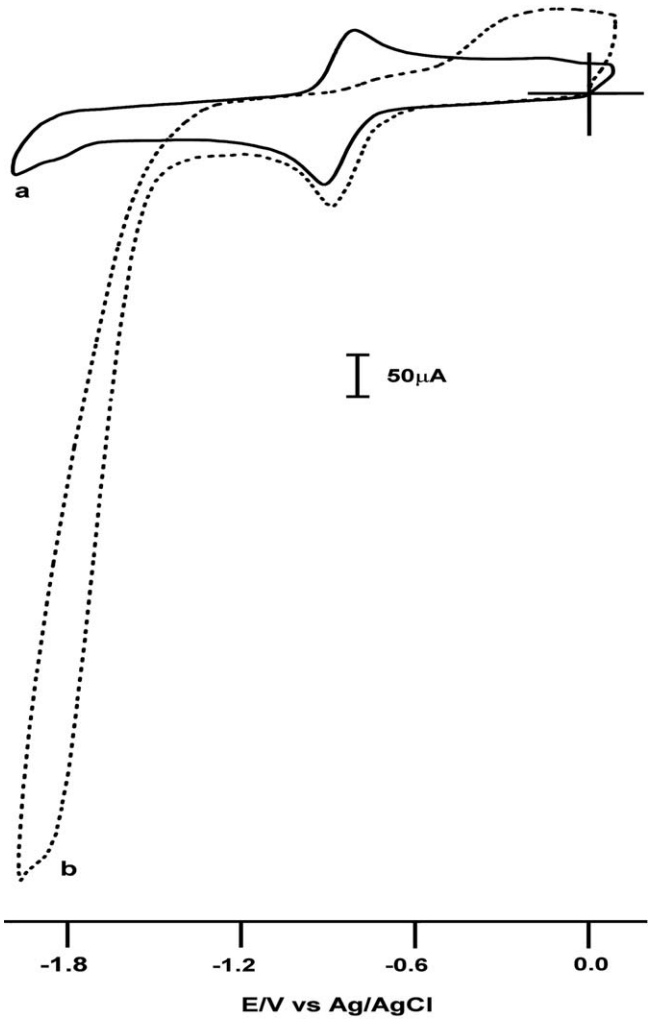

Fig. 1. Cyclic voltammetry of bis(*N*-*n*-dodecyl-2-hydroxy-1-naphthaldiminato)-copper(II): (a) in N_2; (b) in CO_2.

Further studies are in progress for preparative scale electrolysis at −1.40 V versus Ag/AgCl, to characterize the CO_2 reduction products using bis(*N*-*n*-octyl-1-hydroxy-2-naphthaldiminato-)copper(II) and bis(*N*-*n*-dodecyl-1-hydroxy-2-naphthaldiminato)-copper(II) as electrocatalysts.

3.3. X-ray structure of bis(N-n-octyl-1-hydroxy-2-naphthaldiminato)-copper(II)

Fig. 2 depicts the molecular structure, Fig. 3 illustrates a stacking arrangement and Table 2 shows relevant bond distances and angles. The Cu atom is located at the center of symmetry so that the asymmetric unit is half the molecule. The Cu coordination sphere is made up of two naphthaldiminato ligands that chelate the metal through their O and N atoms, so that each pair of oxygen and nitrogen atoms is *trans* displayed and the inversion center at Cu makes its coordination sphere exactly planar 4-coordinate.

A study by our group on the molecular structure of bis(3,5-dibromo-*N*-*p*-tolylsalicylaldiminato)-copper(II) [20]

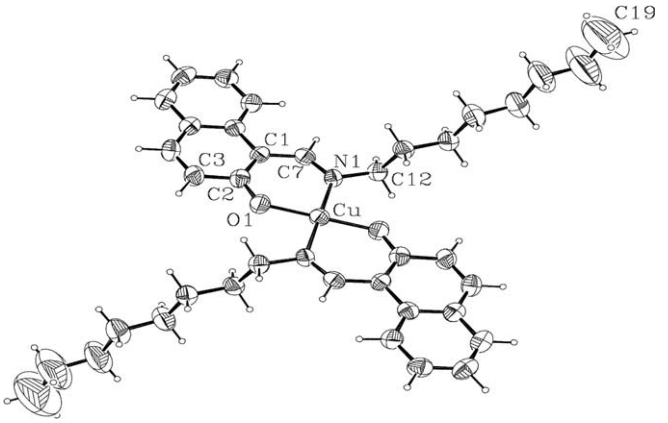

Fig. 2. Ortep molecular structure of bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II).

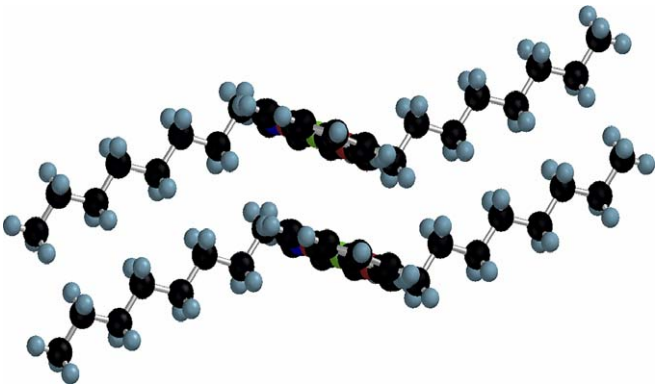

Fig. 3. Stacking arrangement for two molecules of bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II).

Table 2
Selected bond distances and bond angles of bis(*N*-*n*-octyl-1-hydroxy-2-naphthaldiminato)-copper(II)

Bond distances (Å)		Bond angles (°)	
Cu–O	1.887(4)	N–Cu–O	90.80(2)
Cu–O′	1.887(4)	N–Cu–O′	89.2(2)
Cu–N	1.995(4)	N′–Cu–O	89.2(2)
Cu–N′	1.995(4)	N′–Cu–O′	90.8(2)
O–C(2)	1.300(7)	N–Cu–N′	180
N–C(7)	1.295(8)	O–Cu–O′	180
N–C(12)	1.483(7)	C(2)–O–Cu	131.3(3)
		C(12)–N–Cu	120.7(4)
		C(7)–N–Cu	124.2(3)
		C(7)–N–C(12)	115.1(4)

also shows only two ligands coordinated to Cu in a similar way, but its coordination sphere is distorted tetrahedral. Both species have equal Cu–O and Cu–N bonds but their bite angles O–Cu–N differ (93.8° and 93.1° in bis(3,5-dibromo-*N*-*p*-tolylsalicylaldiminato)-copper(II), and 90.8(2)° in the title compound). It was shown that the tetrahedral distortion in bis(3,5-dibromo-*N*-*p*-tolylsalicylaldiminato)-copper(II) is related to steric hindrance between the *N*-*p*-tolyl group of one salicylaldiminato ligand and one Br atom from the other salicylaldiminato [20]. In the title compound, such hindrance is not present and both ligands prefer the more stable planar coordination sphere. Bis(5-bromo-*N*-*m*-tolylsalicylaldiminato)-copper(II) [20] also shows no planar distortion in the CuO_2N_2 moiety as the title compound but has additional interactions to the metal (Jahn-Teller effect) stemming from 2 Br atoms, so establishing an octahedral species. However, these additional bonds do not make the "CuO_2N_2" bond distances and angles different than in the title compound.

Packing of the title compound shows graphite-like interactions. For instance, the separation between O and its equivalent O($-x$, $-y$, $-z-1$) is 3.416(4) Å; N is almost equidistant to the related Ph ring C1′–C6′ (N–C5′ 3.497(7) Å, N–C6′ 3.494(7) Å, N–C1′ 3.690(7) Å, N–C2′ 3.879(7) Å, N–C3′ 3.884(7) Å and N–C4′ 3.691(7) Å). Analysis of other naphthaldiminato Cu compounds shows that stacking is feasible. A series of planar guest molecules in co-crystallized material also fit stacking. Thus, the slightly stepped complex bis(1-methyliminomethyl-2-naphthalato)-copper(II) bis(tetrachlorobenzoquinone) stabilizes a π–π intercalation between the Cu complex and tetrachlorobenzoquinone. The same architecture is shown in the other 2 crystals having 1,3,5-trinitrobenzene and 7,7,8,8-tetracyanoquinodimethane instead of tetrachlorobenzoquinone [21a]. These two complexes are more stepped than the former and the separation between planar groups is shorter than 3.4 Å.

An interesting case is bis(*N*-*iso*-propyl-2-oxy-1-naphthylidene-aminato)-copper(II), a complex containing isopropyl as N-substituent [21b]. If co-crystallized with 7,7,8,8-tetracyanoquinodimethane there is π–π intercalation, similarly to the previous case, but the pure complex shows the Cu atom tetrahedrally distorted, which indicates that adding planar entities induces stacking. Generally, small N-substituents induce stacking of planar guests with the aromatic area of the complex (the naphthyl moiety), while crowded N-substituents tend to avoid that. However, π–π interaction can even exist in crowded non-planar systems as in bis(*N*-(*p*-dimethylaminophenyl)-2-oxy-1-naphthaldiminato)-copper(II) [22] that shows a dinuclear arrangement where one dimethylaminophenyl moiety stacks the 2-oxy-1-naphthaldiminato part of a second Cu moiety with separations N–C of 3.77 Å and C–C of 3.43 Å.

Five-coordination on Cu makes other units closer in bis(μ_2-*N*-methyl-2-hydroxy-1-naphthaldiminato)-bis(*N*-methyl-2-hydroxy-1-naphthaldiminato-copper(II)) [23], which is a dinuclear species having additional Cu–O bonds (2.60 Å) and C–C π–π interactions of about 3.4 Å. The arrangement is slightly stepped and there is no π–π stacking between dinuclear units, which suggests that crystal packing does not help for stacked structures.

As mentioned above, a co-crystallized molecule can induce a supramolecular structure inducing complex coplanarity and π–π stacking. Additional aromatic groups in the ligand can also induce π–π stacking because of their intrinsic planarity.

Our complex possesses a very long non-aromatic N-substituent and we then explore related Cu complexes to see if a supramolecular architecture depends on the chain length. There are four salicylaldiminato structures having long chains solved with diffraction methods. The C_8-length complex (*N*-octylsalicylideneaminato-*N*,*O*)-copper(II) [24] is slightly stepped and shows no stacking; the C_{10}-length complex (*N*-*n*-decyl-*o*-hydroxyacetophenoniminato)-copper(II) [25] and the C_8-length complex bis(*o*-hydroxyacetophenone-(*N*-octyl)iminato)-copper(II) [26] are markedly stepped and have no stacking; the C_6-length complex bis(*N*-*n*-hexyl-2-oxy-4-(1-naphthoyloxy)benzaldiminato)-copper(II) [27] is planar and has no stacking. Therefore, a long chain does not induce π–π interaction in salen Cu compounds. Some help in promoting stacking comes if extra aromatic groups are added, as in the C_6-length complex bis(*N*-*n*-hexyl-2-oxy-4-(1-naphthoyloxy)benzaldiminato)-copper(II) [28] which has a co-crystallized 1,3,5-trinitrobenzene planar molecule that intercalates with separations of about 3.5 Å.

Analysis of shorter *N*-alkyl chains shows that for a *N*-methyl group, there are 3 crystal forms in bis(*N*-methylsalicylaldiminato)-copper(II). In the 1st, there is important π–π interaction including a Cu–Cu short distance of 3.33 Å [29]; in the 2nd crystalline form, there is similar stacking and shorter Cu–Cu separation (3.29 Å) [29] and the 3rd crystal shows no stacking [30]. For a *N*-ethyl chain, the complex bis(*N*-ethylsalicylaldiminato)-copper(II) shows π–π stacking with C–C separations of about 3.48 Å [31]; a similar arrangement is found in its *n*-propyl derivative [32].

Secondary N-alkyl chains tend to disrupt the π–π stacking because the Cu coordination spheres are pushed away. So it appears that the title compound is unique in inducing stacking as long chains do not do that in related complexes. However, thus far studied Cu complexes of long *N*-alkyl chains are salen derivatives, which possess less aromaticity than the title compound. Therefore, the additional aromatic nucleus may be responsible for the observed π–π stacking. The whole matter can then be rationalized as follows: if there is enough aromaticity in the system, provided by co-crystallized planar solvents or increased nuclearity in the ligand (meanwhile helped by short *N*-alkyl substituents), there will be more probability of π–π interaction. A demonstration of this is seen when comparing the structures of bis(*N*-diphenylmethylsalicylideneaminato)-copper(II) and bis(*N*-diphenylmethyl-1,2-naphthaldiminato)-copper(II) [33]. The N-substituent is $-CHPH_2$ in both ligands, a group that does not induce stacking because of its hindrance effect as seen in the former complex (containing a salicyl ligand). However, for the latter complex (containing a naphthyl ligand e.g. having an additional aromatic nucleus) a slight stacking with C–C distances between 3.6 and 4.0 Å is induced.

In the title compound the *n*-octyl chains show marked disorder, mainly in the terminal C atoms as seen by anisotropic displacement parameters in the Ortep picture (see Fig. 2). Although this feature is commonly observed when some room is available in the crystal [34], which is not necessarily implied, for instance, it is not present in the crystal structure of the related Cu(II) species bis(5-hexadecyloxytropolonato)-copper(II) [34].

Correlation between mesogen properties and alkyl chain length has been recently described for 5-alkoxytropolonate copper(II) compounds, as the alkoxy length C_8 derivative, bis(5-octyloxytropolonato)-copper(II), is not mesogen [36] but those longer than C_8 are [35]. In the title compound, the chain protrudes almost perpendicular to the coordination plane with the corresponding torsion angle of 92.2°, quite different than 15.5° in bis(5-octyloxytropolonato)-copper(II) [36] but closer to 55.2° in the mesogen species bis(5-hexadecyloxytropolonato)-copper(II) [35]. Further comparison between layers shows O–O, Cu–Cu and Cu–O separations of 3.41 Å, 5.16 Å and 3.95 Å, respectively, in the title compound, 3.50 Å, 6.41 Å and 4.03 Å in bis(5-octyloxytropolonato)-copper(II), 3.76 Å, 4.16 Å and 3.31 Å in bis(5-hexadecyloxytropolonato)-copper(II). Therefore, the title compound shows structural features closer to the active mesogen [35], even though its chain length compares well with the inactive reported species [36]. A short Cu···O interaction is considered to be needed in the tropolonate series to generate a mesophase. In the title compound, the Cu···O separation (3.95 Å) although shorter than in the inactive mesogen (4.03 Å) [36] does not seem strong enough to induce a mesophase.

3.4. Magnetic studies and theoretical calculations

Fig. 4 shows effective moment between 10 K and 300 K for bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)copper(II), and bis(*N*-*n*-dodecyl-2-hydroxy-1-naphthaldiminato)copper-(II), in the solid state. Magnetic susceptibilities results do not show evident intermolecular magnetic interactions in the range of studied temperatures, as may be suggested by the crystal packing. The small variations observed in the calculated magnetic moments cannot be attributed to any intermolecular exchange phenomenon.

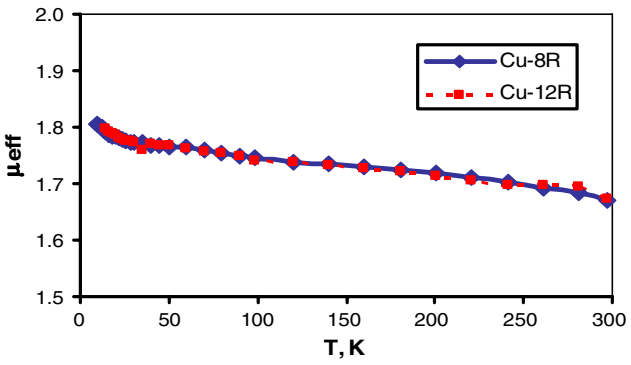

Fig. 4. Magnetic moments (Bohr magnetrons) of bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II) [Cu-8R] and bis(*N*-*n*-dodecyl-2-hydroxy-1-naphthaldiminato)-copper(II) [Cu-12R] between 10 and 300 K.

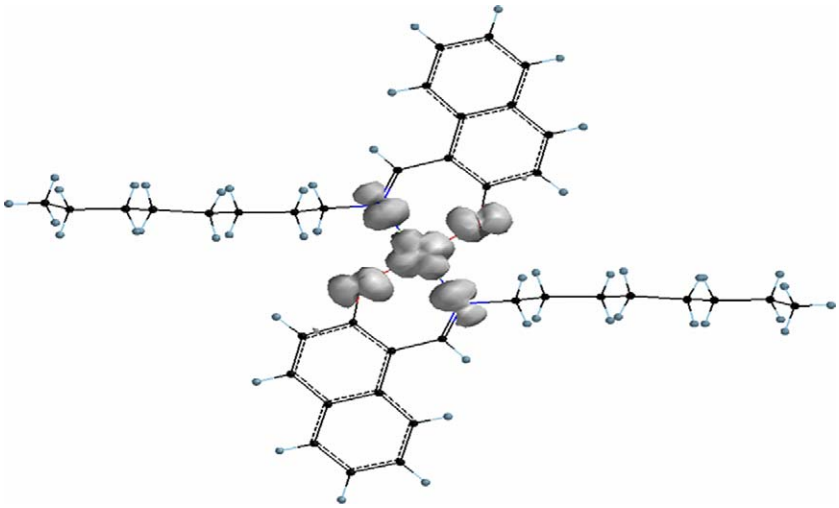

Fig. 5. B3LYP/LACVP** surface of spin density for bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II).

Besides, spin density and electrostatic potential surface were obtained at B3LYP/LACVP** level of theory for bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II) using the atomic coordinates provided by the X-ray structure determination (Section 3.1). Fig. 5 depicts the calculated spin density showing the unpaired electron localized on the CuO_2N_2moiety. The presence of spin density on the first coordination sphere of the copper atom (N_2O_2) is due to a delocalization process.

Fig. 6 shows the electrostatic potential, in which the red zone represents the richest electron density region and the blue zone represents the poorest one. The red zone corresponds to the 2 *trans* displayed oxygen atoms of the CuO_2N_2 moiety, in agreement with the anionic nature of the phenoxo groups. In conclusion, the surfaces of spin density and electrostatic potential suggest that if any interaction exists between two packed molecules, this would occur through the planar CuN_2O_2 centers (see Fig. 3). Further, the results of spin density surface show good agreement with the paramagnetic nature of the studied complexes.

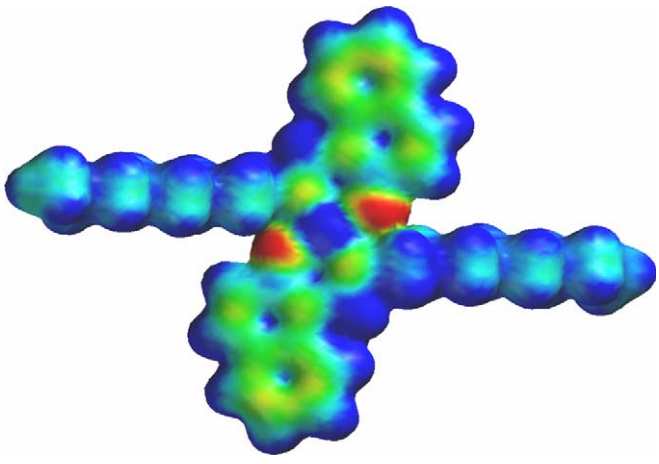

Fig. 6. B3LYP/LACVP** surface of electrostatic potential mapped into the electron density isosurface of 0.002 electrons/au^3 for bis(*N*-*n*-octyl-2-hydroxy-1-naphthaldiminato)-copper(II). Red color represents rich electron regions, blue color represents poor electron regions and green color shows intermediate regions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Acknowledgements

Financial support from: CONICYT, FONDECYT Líneas Complementarias, Project No. 8010006 is acknowledged. E.S and D.V-Y. thank FONDAP, Project No. 11980002, ECOS/CONICYT. A.R.-E. thanks CONICYT and DIGEGRA for a doctorate fellowship.

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