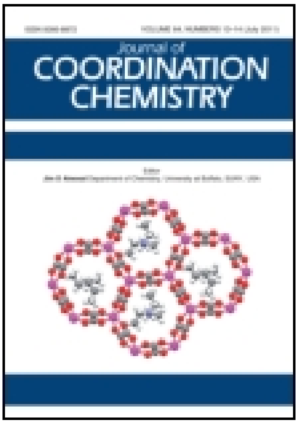

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Structure, electronic, and CV properties of hydroxy-naphthaldehyde Schiff-base copper(II) complexes derived from alkyl amines: X-ray structure of bis(n-i-propyl-3-hydroxy-2-naphthaldiminato)copper(II)

Manuel Villagrán [a], Francesco Caruso [b], Miriam Rossi [c], José Zagal [a] & Juan Costamagna [a]

[a] Faculty of Chemistry and Biology, Universidad de Santiago, Santiago-33, Chile

[b] Istituto de Chimica Biomolecolare, Consiglio Nazionale delle Ricerche, Università di Roma “La Sapienza”, Vecchio Istituto Chimico, Ple. Aldo Moro 5, 00185, Rome, Italy

[c] Department of Chemistry, Vassar College, Poughkeepsie, NY 12604-0484, USA

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Structure, electronic, and CV properties of hydroxy-naphthaldehyde Schiff-base copper(II) complexes derived from alkyl amines: X-ray structure of bis(n-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II)

MANUEL VILLAGRÁN†, FRANCESCO CARUSO‡, MIRIAM ROSSI§,
JOSÉ ZAGAL† and JUAN COSTAMAGNA*†

†Faculty of Chemistry and Biology, Universidad de Santiago, Santiago-33, Chile
‡Istituto de Chimica Biomolecolare, Consiglio Nazionale delle Ricerche, Università di Roma "La Sapienza", Vecchio Istituto Chimico, Ple. Aldo Moro 5, 00185, Rome, Italy
§Department of Chemistry, Vassar College, Poughkeepsie, NY 12604-0484, USA

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Copper(II) complexes with Schiff bases derived from linear and branched amines with 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde were synthesized and characterized by IR and electronic spectroscopies, magnetic susceptibilities, electrochemistry, cyclic voltammetry (CV), X-ray diffraction, and theoretical calculations. Electronic spectra are a function of the R group on the imine nitrogen of the ligand that determines steric effects. Complexes obtained from 3-hydroxy-2-naphthaldehyde ligand are more distorted from planarity in dimethylformamide solutions than those of 2-hydroxy-1-naphthaldehyde for the same R group. As a result, the former are easier to reduce to the related copper(I) complexes than those of 2-hydroxy-1-naphthaldiminate. The structure of bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) was determined by single-crystal X-ray diffraction. Its molecular structure can be described as distorted flat tetrahedral influenced by important packing effects and is flatter than that calculated with density functional theory methods. Additional related flat tetrahedral complexes were studied by theoretical calculations and it has been found that electronic effects also play a significant role.

Keywords: Naphthaldiminato; Cyclic voltammetry; Substituent effects

1. Introduction

The synthesis and characterization of copper(II) complexes with Schiff bases remains of interest. They are important as model complexes for metalloenzymes, copper proteins, and compounds having antibacterial, antifungal, and antitumor properties [1–7].

Another important characteristic of these complexes is related to the versatility and changes observed in electronic, structural, and electrochemical properties upon subtle modifications of the ligands. The Cu(II)/Cu(I) redox process can be modulated by

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*Corresponding author. Email: juan.costamagna@usach.cl

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changing some substituents on the ligands. These properties mimic biological systems [8] and the changes are related to steric as well as electronic properties. In general, some effects observed in solid phases are not present in solution [9–12].

Cu(II) complexes with Schiff bases derived from 2-hydroxy-1-naphthaldehyde, 3-hydroxy-2-naphthaldehyde, and salicylaldehyde (named here 2,1-Napht, 3,2-Napht and Sal, respectively) have been widely reported in the literature [13, 14]. Substituent effects on structural, electronic, and redox properties have been described for bis(N-alkyl-2-hydroxy-1-naphthaldiminato)copper(II) in earlier work [9]. Non-equivalence between solid and solution state structures, as determined by electronic spectra and X-ray diffraction, were explained by density functional theory (DFT) data.

Syntheses, electronic, electrochemical, X-ray, and DFT results for several (N-alkyl-3-hydroxy-2-naphthaldiminate)copper(II) are described here and compared to similar complexes derived from (N-alkyl-2-hydroxy-1-naphthaldiminate)copper(II) (scheme 1) and (N-alkyl-salicylaldiminato)copper(II) complexes. The differences are outlined in terms of steric and electronic effects.

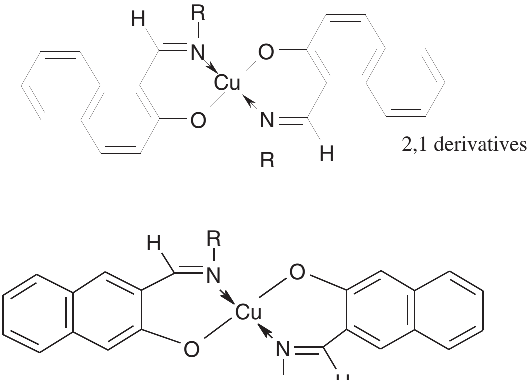
2. Experimental

2.1. *Materials*

Copper(II) acetate monohydrate, methylamine, ethylamine, isopropylamine, tert-butylamine, ethanol, *N*,*N*′-dimethylformamide (DMF), 2-hydroxy-1-naphthaldehyde, and tetraethylammonium perchlorate (TEAP) were purchased from Aldrich Chemical Co. Inc. 3-Hydroxy-2-naphthaldehyde was prepared as described previously [15].

2.2. *Measurements and methods*

2.2.1. Melting points. Melting points were determined on a Thomas Hoover 6427-F10 Melting point apparatus.



Scheme 1. Complexes derived from (*n*-alkyl-2-hydroxy-1-naphthaldiminate) copper(II) and (*n*-alkyl-3-hydroxy-2-naphthaldiminate)copper(II).

2.2.2. Magnetic susceptibility. Solid phase magnetic susceptibilities were determined in a Cahn Ventron microbalance using the Faraday method. Magnetic susceptibilities in solution were determined by the Evans method [16].

2.2.3. Spectroscopy. UV-Vis spectra were recorded on a Karl Zeiss DMR-22 spectrometer using 1 cm quartz cell in DMF for solutions, and nujol mulls on Whatman paper No. 52 for solids. IR range was 4000–400 cm^{-1}.

2.2.4. Electrochemistry. Cyclic voltammetry (CV) measurements were performed on a potentiostat/galvanostat PAR-173, Universal Programmer PAR-175, and a digital Coulometer PAR-179 from Princeton Applied Research. An H cell was used with three electrodes, glassy carbon, platinum wire, and saturated calomel electrode, as working, auxiliary, and reference electrodes, respectively. The solvent and supporting electrolyte were DMF and TEAP, respectively. All measurements were carried out under nitrogen at 25°C. Rotating disc electrode (RDE) measurements were made in an H-type cell using a glassy carbon of area 2.85 cm^2 inserted on a Pine Analytical rotator, model PIR with rotation rates of 900, 1600, 2500, and 3600 rpm. Controlled potential electrolysis measurements were carried out on a PAR 179 coulometer coupled to PAR 173 potentiostat using platinum gauze as working electrode.

2.3. *Synthesis of copper(II) complexes*

Bis(2-hydroxy-1-naphthaldehydate)copper(II) and bis(3-hydroxy-2-naphthaldehydate) copper(II) complexes (scheme 1) were prepared as described [17].

bis(o-hydroxy-naphthaldehyde)copper(II) + $2H_2NR$ (R = Met, Et, *i*-Pr, *t*-Bu) → Cu-complex (shown in scheme 1) + 2 H_2O.

In a 100 mL two-necked flask, equipped with a condenser, magnetic stirring, bis(o-hydroxy-naphthaldehyde)copper(II) and the respective amine, H_2NR (R = methyl, ethyl, *i*-Pr, *t*-Bu) were refluxed in ethanol for 8 h and cooled to room temperature. Solid was collected by filtration, washed with ethanol, and dried in an oven for 6 h following reported procedures [18–21]. Recrystallization from chloroform gave *ca* 80% yield in all cases.

2.3.1. Bis(N-methyl-2-hydroxy-1-naphthaldiminato)copper(II) (1). $C_{24}H_{20}N_2O_2Cu$ (MW = 431.974), m.p. = 233°C. $\mu_{eff}(s) = 1.72$ BM, $\mu_{eff}(sol) = 1.87$ BM. Analysis, (calculated, %), found: C, (65.03), 65.70; H, (4.50), 4.60; N, (6.50), 6.40; Cu, (14.70), 14.70.

2.3.2. Bis(N-methyl-3-hydroxy-2-naphthaldiminate)copper(II) (1′). $C_{24}H_{20}N_2O_2Cu$ (MW = 431.974), m.p. = 214°C, $\mu_{eff}(s) = 1.78$ BM, $\mu_{eff}(sol) = 1.91$ BM. Analysis, (calculated, %), found: C, (65.03), 66.00; H, (4.50), 5.00; N, (6.50), 7.40; Cu, (14.70), 14.60.

2.3.3. Bis(N-ethyl-2-hydroxy-1-naphthaldiminato)copper(II) (2). $C_{26}H_{24}N_2O_2Cu$ (MW = 460.028), m.p. = 220°C, $\mu_{eff}(s) = 1.78$ BM, $\mu_{eff}(sol) = 1.97$ BM. Analysis, (calculated, %), found: C, (67.80), 67.40; H, (5.25), 5.00; N, (6.00), 5.70; Cu, (13.80), 13.60.

2.3.4. Bis(N-ethyl-3-hydroxy-2-naphthaldiminato)copper(II) (2′).

$C_{26}H_{24}N_2O_2Cu$ (MW = 460.028), m.p. = 222°C. μ_{eff}(s) = 1.82 BM, μ_{eff}(sol) = 1.90 BM. Analysis, (calculated, %), found: C, (67.80), 67.70; H, (5.25), 6.00; N, (6.00), 6.00; Cu, (13.80), 13.70.

2.3.5. Bis(N-*i*-propyl-2-hydroxy-1-naphthaldiminato)copper(II) (3).

$C_{28}H_{28}N_2O_2Cu$ (MW = 488.082), m.p. = 197°C, μ_{eff}(s) = 1.81 BM, μ_{eff}(sol) = 1.98 BM. Analysis, (calculated, %), found: C, (69.47), 68.60; H, (5.73), 5.80; N, (5.73), 5.70; Cu, (13.10), 13.20.

2.3.6. Bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) (3′).

$C_{28}H_{28}N_2O_2Cu$ (MW = 488.082), m.p. = 190°C, μ_{eff}(s) = 1.74 BM, μ_{eff}(sol) = 1.85 BM. Analysis, (calculated, %), found: C, (69.47), 68.60; H, (5.73), 5.80; N, (5.73), 5.80; Cu, (13.10), 13.00.

2.3.7. Bis(N-*t*-butyl-2-hydroxy-1-naphthaldiminato)copper(II) (4).

$C_{30}H_{32}N_2O_2Cu$ (MW = 516.136), m.p. = 202°C, μ_{eff}(s) = 1.73 BM, μ_{eff} (sol) = 1.81 BM. Analysis, (calculated, %), found: C, (69.81), 69.90; H, (6.25), 6.00; N, (5.43), 6.00; Cu, (12.30), 12.40.

2.3.8. Bis(N-*t*-butyl-3-hydroxy-2-naphthaldiminato)copper(II) (4′).

$C_{30}H_{32}N_2O_2Cu$ (MW = 516.136), m.p. = 210°C, μ_{eff}(s) = 1.98 BM, μ_{eff}(sol) = 1.85 BM. Analysis, (calculated, %), found: C, (69.81), 69.70; H, (6.25), 6.15; N, (5.43), 5.90; Cu, (12.30), 12.40.

2.4. *X-ray diffraction*

Suitable crystals for X-ray diffraction of bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) (**3′**) were obtained from a toluene solution on standing at room temperature about a week. Diffraction data were collected at 125 K using a Bruker SMART APEX II CCD X-ray diffractometer. Structure resolution and refinement were performed using SHELXTL [22]; details are included in table 1. Hydrogen atoms not found in Fourier maps were included from models and constrained as riding on their bound atoms. This crystal structure has been deposited as CCDC 826 763.

2.5. *Theoretical study*

Calculations were done using software from Accelrys [23]. DFT code DMol3 was applied to calculate geometries, energies, and frequencies, see below, implemented in Materials Studio 5.5 (PC platform) [24]. We employed double numerical polarized basis

Table 1. Crystal data and refinement details of bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) (**3′**).

Empirical formula	$C_{28}H_{28}CuN_2O_2$
Formula weight	488.06
Temperature (K)	125(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Crystal color	Brown
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	19.3813(16)
b	6.7559(6)
c	18.7371(15)
β	106.241(1)
Volume (Å^3), Z	2355.5(3), 4
Calculated density (Mg m^{-3})	1.376
Absorption coefficient (mm^{-1})	0.955
Crystal size (mm^3)	$0.29 \times 0.26 \times 0.10$
θ range for data collection (°)	1.46, 29.13
Limiting indices	$-26 \leq h \leq 26$; $-9 \leq k \leq 9$; $-25 \leq l \leq 25$
Data collected	33,583
Independent reflection	6341
Max. and min. transmission	0.77 and 0.91
Refinement method	F^2
Refined data/parameters	4723/410
Goodness-of-fit on F^2	1.031
Final R, wR $[I > 2\sigma(I)]$	0.0446, 0.1000

set that includes all occupied atomic orbitals plus a second set of valence atomic orbitals plus polarized d-valence orbitals [25], and correlation generalized gradient approximation was applied in the manner suggested by Perdew–Burke–Ernzerhof [26]; the recent inclusion of a dispersion term that deals with O–H interactions was also applied. Spin unrestricted approach was exploited with all electrons being considered explicitly. The real space cutoff of 5 Å was imposed for numerical integration of the Hamiltonian matrix elements. The self-consistent-field convergence criterion was set to the root-mean square change in the electronic density to be less than 10^{-6} e Å^{-3}. The convergence criteria applied during geometry optimizations were 2.72 10^{-4} eV for energy and 0.054 eV Å^{-1} for force.

3. Results and discussion

3.1. *Synthesis and chemical characterization*

Elemental analyses are in good agreement with a 2 : 1 ligand to metal ratio. The magnetic moments for the complexes in solid phase as well as in solution at room temperature are in the 1.72–1.98 BM range. These values indicate the presence of monomeric species in the solid and in solution, and are consistent with square planar or pseudo-tetrahedral mononuclear copper(II) complexes with $S = ½$ spin states [27, 28].

3.2. *Solid electronic spectra*

Copper(II) complexes generally present bands in the visible region assigned to d–d transitions. The number and positions depends on the nature of the alkyl group linked to the imine nitrogen of the Schiff-base ligand. In the complexes derived from 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde the bulky, *i*-Pr and *t*-Bu groups induce distortion of the planar symmetry and electronic spectra show a continuous shift of the d–d band to lower energy with increasing R bulkiness. The *i*-propyl-2-hydroxy-1-naphthaldehyde derivative presents two d–d bands at 12,500–14,900 cm^{-1} whereas the *i*-propyl-3-hydroxy-2-naphthaldehyde complex shows a broad signal. The 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde derivatives, with the *t*-Bu group, show two d–d bands at 10,200–14,600 cm^{-1} and 13,300–16,600 cm^{-1}, respectively (table 2). X-ray results (*vide infra*) suggest that the broad signal of *i*-propyl-3-hydroxy-2-naphthaldehyde (14,800 cm^{-1}) may be an overlap of two bands.

In the ultraviolet region both series of complexes present similar number and positions of bands that depend on intraligand π–π* transitions (see tables 2 and 3) [9].

Table 2. Electronic spectra for Schiff-base complexes derived from o-hydroxy-naphthaldehyde in solid phase (values in cm^{-1}).

Compound	d–d	π–π*	π–π*	π–π*
1	14,800	25,900–26,600	31,800	32,800
1′	15,700	23,300	31,700	32,300
2	15,300	23,500–25,100	31,300	32,500
2′	15,200	22,200	32,300	36,400
3	12,500–14,900	25,900	31,800	32,800
3′	14,800 (*)	22,200	31,500	32,800
4	10,200–14,600	26,000	31,800	32,300
4′	13,300–16,600	22,200	31,700	32,500

(**1′**), (**2′**), (**3′**), and (**4′**) are the corresponding bis(N-R-3-hydroxy-2-naphthaldiminato)copper(II) complexes. (**1**) bis(N-methyl-2-hydroxy-1-naphthaldiminato)copper(II); (**2**) bis(N-ethyl-2-hydroxy-1-naphthaldiminato)copper(II); (**3**) bis(N-*i*-propyl-2-hydroxy-1-naphthaldiminato)copper(II); (**4**) bis(N-*t*-butyl-2-hydroxy-1-naphthaldiminato)copper(II).
(*)Wide band.

Table 3. Electronic spectra for Schiff-base complexes derived from o-hydroxy-naphthaldehyde in DMF (values in cm^{-1}, ε = molar coefficient LM^{-1}cm^{-1}).

Compound	d–d(ε)	π–π*(ε)	π–π*(ε)	π–π*(ε)
1	16,500(140)	25,600(4700)–26,600(5100)	32,100(9100)	32,800(9400)
1′	16,600(200)	23,000(8000)	32,800(10,000)	36,400(15,200)
2	16,600(90)	25,600(4300)–26,600(4600)	32,500(9500)	32,800(9700)
2′	16,600(150)	25,400(7400)–27,000(8100)	32,300(15,000)	
3	15,300(190) (*)	25,100(4400)–26,300(4200)	31,800(9100)	32,800(9200)
3′	14,300(180)–17,800(500)	23,400(7000)	31,200(10,000)	32,600(12,300)
4	13,900(250)–21,700(1400)	25,500(4900)–26,300(4012)	31,800(9300)	32,800(9500)
4′	12,500(190)–16,949(850)	22,200(9700)	31,200(15,200)	32,500(20,000)

Compound names defined in table 2.
(*)Wide band.

3.3. *Electronic spectra in solution*

Electronic spectra in DMF and in solid state are similar but the complexes derived from 3-hydroxy-2-naphthaldehyde show d–d bands at lower energy. For the *i*-Pr substituent d–d bands are at 14,300–17,800 cm^{-1}. For *t*-Bu, the electronic spectrum of the 3-hydroxy-2-naphthaldehyde complex shows two d–d bands located at 12,500–16,949 cm^{-1}, while for the 2-hydroxy-1-naphthaldehyde the values are 13,900–21,700 cm^{-1} (table 2). So, the complexes derived from 3-hydroxy-2-naphthaldehyde are more distorted from planarity than the series derived from 2-hydroxy-1-naphthaldehyde in DMF solution.

Differences in the solid can be explained in terms of the role played by crystal packing forces in the latter, which are stabilized by intermolecular contacts and/or electronic π–π stacking interactions among naphthalene ring of the ligands. In solution, this effect has no influence on the structures of the complexes studied, as recently discussed [9].

3.4. *Electrochemical results*

Electrochemical study of the copper(II) complexes derived from 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde was carried out following the experimental conditions reported previously [9]. All compounds studied show that the system deviates strongly from reversibility at high scan rates, i.e. over 0.500 $V\,s^{-1}$. Taking into account the Nicholson–Shain criteria, this behavior is consistent with a quasi-reversible electrochemical process [29]. Controlled potential electrolysis reveals that a single electron is involved in this reduction step, and therefore the electrochemical reduction response in these complexes is consistent with a one electron, diffusion-controlled, quasi-reversible Cu(II)/Cu(I) couple. Table 4 shows the potentials and electrode kinetic parameters associated with the electron transfer process studied, such as the Tafel slope (b), approximately 120 $mV\,dec^{-1}$, obtained from RDE experiments, electronic coefficient transfer (α), between 0.45 and 0.59, and the heterogeneous rate constant (k_s) ranging from 2.3 to $5.5 \times 10^{-3}\,cm\,s^{-1}$. The heterogeneous rate constant (k_s) values are within the extreme case of reversible ($k_s > 2 \times 10^{-2}\,cm\,s^{-1}$) and

Table 4. Electrochemical parameters for Cu(II)/Cu(I) couple in bis(N-R-2-hydroxy-1-naphthaldiminate) copper(II) and bis(N-R-3-hydroxy-2-naphthaldiminate)copper(II) complexes.

Compound[a]	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)[b]	b ($mV\,dec^{-1}$)[c]	A[d]	10^3 ks $cm\,s^{-1}$[e]
1	−0.95	−0.87	−0.91	120	0.49	5.1
1′	−0.81	−0.88	−0.85	140	0.45	4.5
2	− 0.95	−0.87	−0.91	120	0.49	5.1
2′	−0.76	−0.86	−0.83	112	0.53	2.3
3	−0.78	−0.70	−0.74	120	0.49	5.5
3′	−0.63	−0.72	−0.69	110	0.54	3.2
4	−0.73	−0.65	−0.69	100	0.59	5.5
4′	−0.55	−0.64	−0.61	130	0.45	3.5

Compound names defined in table 2.
[a] 1 $mmol\,L^{-1}$ in DMF; 0.1 $mol\,L^{-1}$ TEAP.
[b] $E_{1/2}$ values calculated as $\frac{1}{2}(E_{pc} + E_{pa})$.
[c] Tafel slope obtained from RDE experiments.
[d] α, electronic coefficient transfer.
[e] Heterogeneous rate constant from CV experiment described in ref [14].

irreversible ($k_s < 3 \times 10^{-5}\,\mathrm{cm\,s^{-1}}$) electrode kinetics [30]. These results show that the Cu(II)/Cu(I) couple is a reduction process that has a moderately fast electron transfer, not complicated by side chemical or electrochemical reactions, and hence the determining step of the rate is the electron transfer process. Therefore, the Cu(II)/Cu(I) couple in the complexes derived from 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde is a quasi-reversible process in electrochemical terms without significant stereochemical reorganization under the conditions used in this study. The k_s values are in the range reported for Cu(2,2-dithiodianiline)Cl, $6.87 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$, and for copper(II) Schiff-base complexes derived from salicylaldehyde and aniline halogen substituted, Cu(5-BrSal-2-Cl-aniline), $4.91 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$ [31, 32].

3.5. *Correlations between electronic spectra and half-wave potentials ($E_{1/2}$)*

As shown in table 3, electronic spectra of the complexes derived from 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde, in DMF solution, are a function of the ligand R steric effects at the imine nitrogen. With non-bulky R groups (methyl, ethyl) only one d–d band typical for square planar Cu(II) complexes is seen. For bulky R (*i*-Pr, *t*-Bu) the electronic spectra show two d–d bands (or a broad one) at low energy corresponding to planar-distorted or pseudo-tetrahedral symmetry [9]. In this work, complexes derived from 3-hydroxy-2-naphthaldehyde show the d–d band at lower energy. Therefore, compared to the 2-hydroxy-1-naphthaldehyde for the same R group, these compounds are more distorted from planarity in DMF solutions (table 3).

Table 4 shows that the $E_{1/2}$ for Cu(II)/Cu(I) couple for the complexes derived from 3-hydroxy-2-naphthaldehyde are systematically shifted to anodic regions for all R substituents with the differences ranging from 50 to 80 mV. These figures suggest that these copper(II) complexes are easier to reduce to copper(I) than the 2-hydroxy-1-naphthaldiminato derivatives. The tendency to planarity in copper complexes stabilizes Cu(II) as previously observed [31].

3.6. *X-ray crystallography*

Figure 1 depicts the molecular structure of bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) (**3′**), which can be described as distorted flat tetrahedral due to steric hindrance between *i*-Pr and the opposite oxygen. The UV-Vis spectrum is consistent with this flat tetrahedral arrangement. The coordination sphere is less distorted than in bis(N-*t*-butyl-salicylaldiminate)copper(II) [33] as seen from the dihedral angles between the planes, including Cu–N1–O2 and Cu–N2–O2 (Dih) of 51.4° and 61.6°, respectively, as expected for the larger *t*-Bu group. Comparison with bis(N-*t*-butyl-2-hydroxy-1-naphthaldiminato)copper(II) (**4**) shows, in contrast, a smaller dihedral angle, 45.4°. This inconsistency can be explained through marked packing effects that these types of complexes show, as noted previously [9]. We explore the CSD database to see if the differences in related flat tetrahedral complexes, containing acyclic secondary N-alkyl substituents, are also due to electronic effects (table 5).

Statistically speaking, table 5 suggests 3,2-Napht-Cu(II) complexes preference for wider Dih angles than 2,1-Napht-Cu(II) complexes. When comparing 2,1-Napht complexes with Sal related species there is no trend. In the title compound the torsion angle H12–C12–N1–C11, figure 1, and its equivalent H62–C62–N2–C61 are −15.9° and

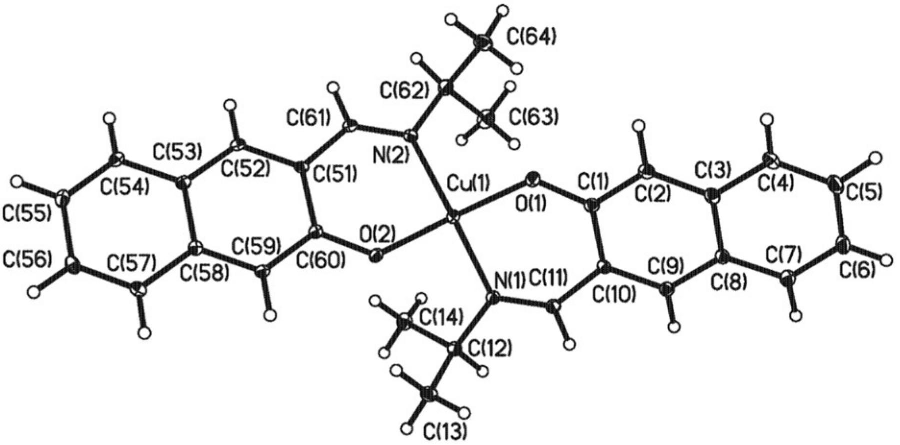


Figure 1. X-ray structure of bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) (**3′**).

Table 5. Selected X-ray structural parameters of CuL_2, L = N-R-hydroxy-naphthaldiminato and N-R-salicylaldiminato for secondary acyclic C R groups.

R	Ligand[a]	Dih[b]	OCuO[c]	NCuN[d]	Refcode,[e] Reference
i-Pr	3,2-Napht	51.5	141.38(7)	144.20(8)	This work
i-Pr	2,1-Napht	38.6	151.6	153.6	IPRNCU, [34]
i-Pr	Sal	58.9	137.2	137.9	ISALCU01, [35]
i-Bu	3,2-Napht	44.6	145.2	150.5	LEHCEH, LEJVAY, [13d]
i-Bu[f]	2,1-Napht	39.6 34.8	149.7 155.5	154.4 154.5	LEHCAD, LEJTUQ, [13d]
i-Bu	Sal	42.4	147.3	151.8	LEHBUW, [13d]
3-*i*-Pentyl	3,2-Napht	50.0	143.4	144.5	MUGVAL, [12a]
3-*i*-Pentyl[f]	2,1-Napht	25.7 34.0	159.5 155.0	164.1 156.2	MUGTUD, [12a]
3-*i*-Pentyl	Sal	27.5	159.4	160.8	MUGTOX, [13d]
$PhCHCH_3$	3,2-Napht	49.3	145.6	143.2	ODEMAM, TIDZEM, [36]
$PhCHCH_3$	2,1-Napht	28.4	158.9	160.5	ODELUF [36], QAMFEQ [37]
$PhCHCH_3$	Sal	39.8	151.8	151.3	DPESCU11 [37], QAMGAN [38]

[a] Ligands: 3,2-Napht = 3-hydroxy-2-naphthaldiminato, 2,1-Napht = 2-hydroxy-1-naphthaldiminato, Sal = salicylaldiminato.
[b] Dih, dihedral angle between the planes N1–Cu–O1 and N2–Cu–O2 (labels consistent with figure 1) in the flat tetrahedral configuration.
[c] OCuO = bond angle O1–Cu–O2.
[d] NCuN = bond angle N1–Cu–N2.
[e] Refcode is the ID name reported in the CSD database.
[f] Two molecules in the asymmetric unit.

−16.4°, respectively, consistent with a statistical analysis on Cu(II) complexes of 3,2-Napht, 2,1-Napht, and Sal containing secondary acyclic C on N, as most values fall in the range −30° to 30°, or its equivalent 150° to 180°, and −150° to −180°, i.e., the unique H(*i*-Pr) tends to be coplanar with its attached aromatic ring.

Table 6 summarizes structural details for N ligands with increasingly bulky R groups, primary (ethyl), secondary (*i*-Pr) and tertiary (*t*-Bu), in 3,2-Napht, 2,1-Napht, and Sal derivatives. It also includes DFT calculations performed for bis(N-ethyl-3-hydroxy-2-naphthaldiminato)copper(II) (**2′**), bis(N-ethyl-2-hydroxy-1-naphthaldiminato) copper(II) (**2**), and bis(N-ethyl-salicylaldiminato)copper(II). These geometry

Table 6. Structural details for increasing bulkiness of R groups on N ligand, ethyl, *i*-Pr, and *t*-Bu in the three ligands, 3,2-Napht, 2,1-Napht, and Sal.

Refcode/Ligand	R	Dih	OCuO	NCuN	Cu–O[a]	Cu–N[b]
DFT (this work)	Et	0	180	180	1.948	2.044
3,2-Napht					1.948	2.044
KUPBIH [9]	Et	1.7	178.9(1)	178.6(1)	1.893(2)	1.989(2)
2,1-Napht					1.899(2)	1.993(2)
DFT (this work)	Et	0	180	180	1.953	2.018
2,1-Napht						
CUESAL02 [38]	Et[a]	9.3	171.0	177.1	1.888	2.000
SAL					1.888	2.006
DFT (this work)	Et	0	180	180	1.952	2.036
SAL						
X-ray (this work)	*i*-Pr	51.5	141.38(7)	144.20(8)	1.873(1)	2.005(2)
3,2-Napht					1.886(1)	2.007(2)
DFT (this work)	*i*-Pr	58.7	137.0	139.3	1.948	2.038
3,2-Napht					1.951	2.043
IPRNCU [34]	*i*-Pr	38.3	151.6	153.6	1.8918(6)	1.9696(4)
2,1-Napht					1.8936(5)	1.9651(6)
IPONTC[c] [34]	*i*-Pr	0	180	180	1.8937(5)	1.9967(3)
2,1-Napht					1.8937(5)	1.9967(3)
DFT (this work)	*i*-Pr	53.2	139.0	146.0	1.963	2.007
2,1-Napht					1.963	2.007
ISALCU01 [35]	*i*-Pr[a]	59.7	137.2	137.9	1.8710(3)	1.973(1)
SAL					1.8843(4)	1.9824(4)
DFT (this work)	*t*-Bu	62.1	131.1	140.4	1.959	2.036
3,2-Napht					1.959	2.036
KUPBON [9]	*t*-Bu	45.4	143.3(1)	152.6(1)	1.906(2)	1.967(3)
2,1-Napht					1.909(2)	1.966(3)
DFT (this work)[d]	*t*-Bu	54.7	134.4	149.6	1.988	1.999
2,1-Napht					1.984	1.999
TNBSCU [33]	*t*-Bu[a]	61.6	131.1	139.7	1.889(3)	1.963(4)
SAL					1.888(4)	1.970(3)

Unless marked in the first column each line refers to X-ray structure determination.

[a] Cu–O are Cu–O1 and Cu–O2 bond distances, as shown in figure 1.

[b] Cu–N are Cu–N1 and Cu–N2 bond distances.

[c] There is an intercalated flat solvent in the crystal.

[d] Mistyped value in [9].

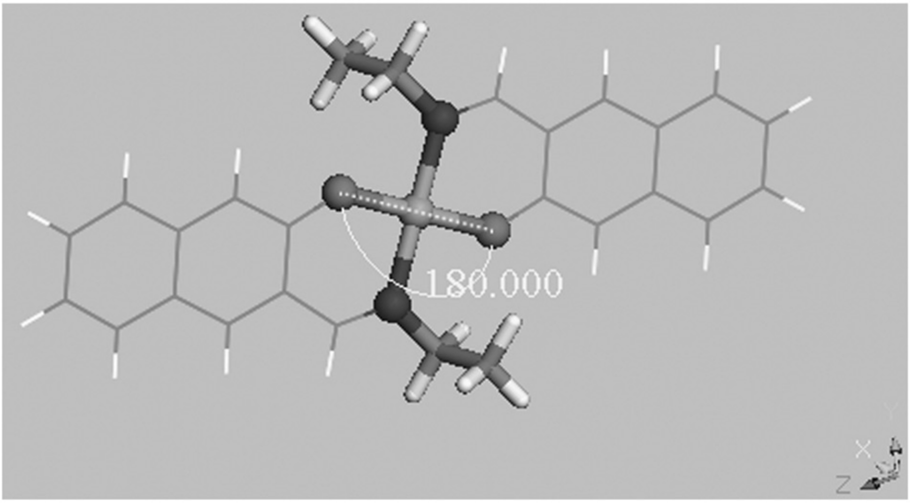


Figure 2. C_i planar geometry optimized DFT structure of bis(N-ethyl-3-hydroxy-2-naphthaldiminato) copper(II) (**2′**).

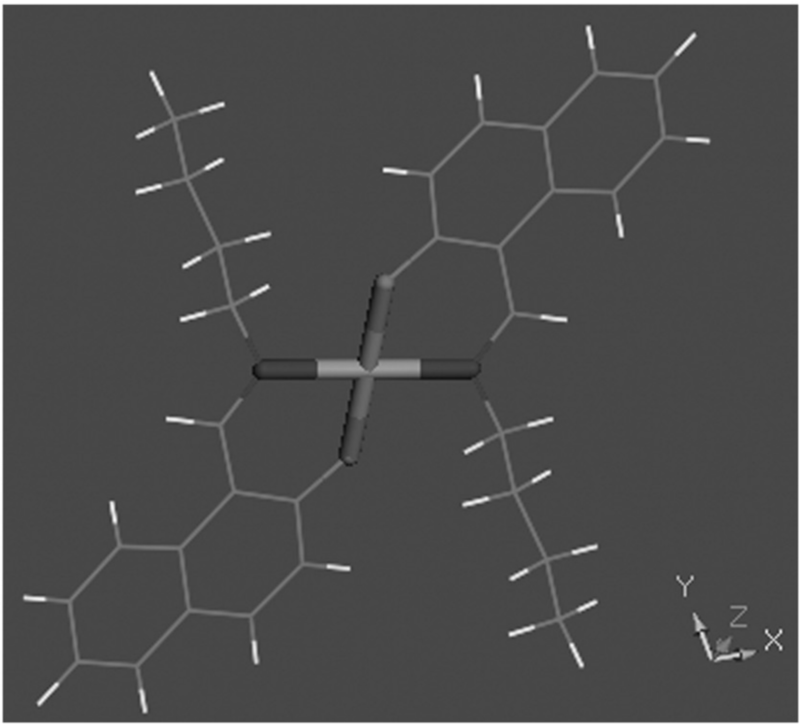


Figure 3. Bis(N-*n*-butyl-2-hydroxy-1-naphthaldiminato)copper(II) optimized DFT structure.

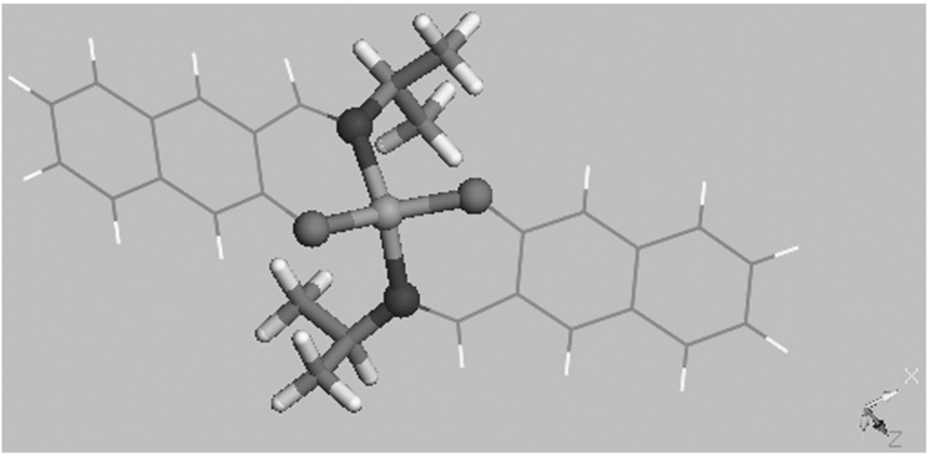


Figure 4. Bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) (**3′**) optimized DFT structure.

optimizations converged to minimum planar C_i arrangements, one, bis(N-ethyl-3-hydroxy-2-naphthaldiminato)copper(II) (**2′**), is depicted in figure 2. The minimum geometry of bis(N-ethyl-2-hydroxy-1-naphthaldiminato)copper(II) (**2**) is in contrast with the corresponding structure calculated earlier [9], whose equivalent C_i planar configuration had one negative frequency, characteristic of a transition state. The

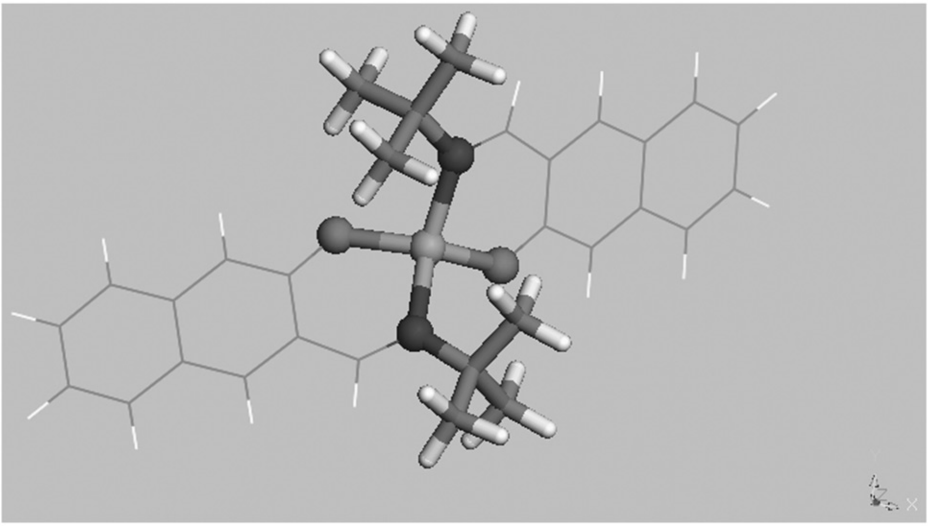


Figure 5. DFT molecular structure of bis(N-*t*-butyl-3-hydroxy-2-naphthaldiminato)copper(II) (**4′**).

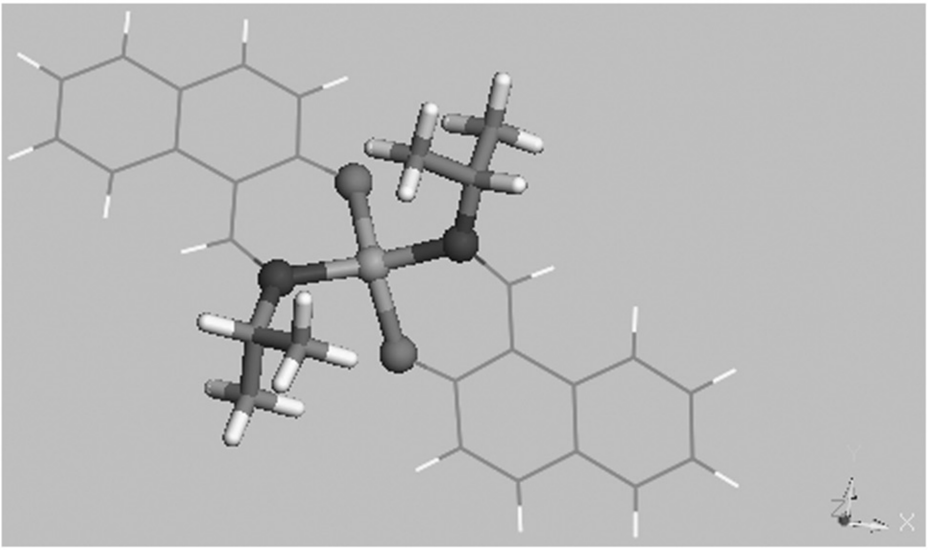


Figure 6. DFT optimized molecular structure of bis(N-*i*-propyl-2-hydroxy-1-naphthaldiminato) copper(II) (**3**).

introduction of an improved algorithm, see section 2.5, in the program DMol3 may be responsible for this more accurate calculation. The DFT C_i planar arrangement of these ethyl complexes is consistent with other N-alkyl (primary) substituents in the literature obtained using diffraction methods [11e, 39–41]. There are two exceptions, however, bis(N-ethyl-2-hydroxy-1-naphthaldiminato)copper(II) (**2**), Dih = 1.7° and bis(N-ethylsalicylaldiminato)copper(II) (Dih = 9.3°). Our DFT calculation for bis(N-*n*-butyl-3-

hydroxy-2-naphthaldiminato)copper(II), having the longer than ethyl primary N-alkyl substituent *n*-Bu, confirmed the C_i planar configuration as a minimum (figure 3). In table 6, DFT calculations for complexes having the bulkier *i*-Pr and *t*-Bu groups show more distorted flat tetrahedral arrangements than seen in the crystals, which can be explained in terms of packing pressure. DFT minimum structures for bis(N-*i*-propyl-3-hydroxy-2-naphthaldiminato)copper(II) (**3′**) and bis(N-*t*-butyl-3-hydroxy-2-naphthaldiminato)copper(II) (**4′**) are depicted in figures 4 and 5, respectively.

Crystals of the latter complex, obtained from toluene solutions, are extremely sensitive to X-rays, preventing a solid state structural determination. Finally, the flat tetrahedral DFT calculated structure of bis(N-*i*-propyl-2-hydroxy-1-naphthaldiminato) copper(II) (**3**) is depicted in figure 6.

4. Conclusion

Comparison between X-ray and DFT methods for the title compound shows that distortion in the solid state is enhanced by packing forces. DFT calculations show that primary alkyl groups on N stabilize C_i structures, which can be distorted in the solid due to packing. However, interpretations of distortions in certain solvents cannot be explained using packing arguments. To obtain valid conclusions regarding the relationship between molecular structure and redox potential it is necessary to obtain solution configurations using UV-Vis spectra and DFT calculations.

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