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#### **Graphical Abstract**

Syntheses, spectroscopy, electrochemistry, EPR, PXRD-structure and DFT/TD-DFT of *bis*[2-oxo-1-naphthaldehydato-ĸO,O']copper(II)

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# Syntheses, spectroscopy, electrochemistry, EPR, PXRD-structure and DFT/TD-DFT of *bis*[2-oxo-1-naphthaldehydato-κO,O']copper(II)

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#### Abstract

Reaction of N-2-(R-pyridyl)-2-hydroxy-1-naphthaldimine {R = H (HL1), 4-CH<sub>3</sub> (HL2) and 6-CH<sub>3</sub> (HL3)} with copper(II) nitrate provides the new complex of bis[2-oxo-1naphthaldehydato-KO,O']copper(II) (1) via in-situ hydrolysis of the Schiff base back to 2hydroxy-1-naphthaldehyde (HL'). Elemental analyses reveal that there are no nitrogen atoms in the complex. X-ray diffraction (PXRD) data indicate that the complex is monoclinic with space group  $P2_1/a$  and Z = 2 and that the ligand acts as bidentate through O^O-chelate system forming a bis-complex with O<sub>2</sub>O<sub>2</sub>-coordination sphere around the copper(II) ion. Electrochemical results showed two quasi-reversible one electron charge transfer processes attributed to  $[Cu(L')_2]^2/[Cu(L')_2]^-$  and  $[Cu(L')_2]^-/[Cu(L')_2]$  (L' = deprotonated aldehyde) couples in acetonitrile. The magnetic data confirmed the paramagnetic property of the complex with one unpaired electron in the metallic centre. The results suggest that the complex assumes a geometry between tetrahedral and square-planar supported by DFT calculations. Thermal analysis shows an irreversible phase transformation from solid to isotropic liquid phase. EPR spectrum in chloroform exhibits an isotropic pattern with four lines due to nuclear hyperfine splitting from the copper(II) ion with spin 3/2. The structural analyses, electrochemical and paramagnetic properties of these complexes explore greater interests for their use in the supramolecular chemistry.

*Keywords:* Copper(II)-2-oxo-1-naphthaldehydate; PXRD structure; *In-situ* hydrolysis of Schiff base; Electrochemistry; EPR and DSC analyses

#### 1. Introduction

Synthesis of the Schiff base from aldehyde and amine is a reversible process, and hydrolysis shifts the equilibrium to the reverse direction to yield the aldehyde [1,2]. The *in-situ* hydrolysis of

Schiff base during complexation and/or slow crystallization process, due to presence of a small amounts of water, has been reported in details [1-3,4,5]. However, the metal ion-induced hydrolytic cleavage of the imine-bond in Schiff base reproduces the aldehyde, which in turn leads to the formation of the metal(II)-aldehydate complexes [2,5]. We have recently reported a case of *in-situ* hydrolysis of the R-pyridyl Schiff base, N-2-(R-pyridyl)salicylaldimine during complexation with the copper(II)-nitrate, which provides the *bis*[salicylaldehydato- $\kappa$ O,O']copper(II) [6]. Similar reaction with the chiral Schiff base (*R*)-N-(*p*-BrC<sub>6</sub>H<sub>4</sub>)ethyl-salicylaldimine in presence of 2,2'-bipyridine (bipy) provides the dinuclear ( $\mu$ -salicylaldehydato)(bipy)(nitrato)-copper(II) [6].

The (R-pyridyl)-Schiff base mainly reacts with the transition metal(II) ions to give mononuclear  $[M(L)_2]$  or polynuclear  $[(ML)_n]^{n+}$  {M = Cu/Ni/Zn(II), L = deprotonated Schiff base} complexes. The structural analyses, electrochemical and magnetic properties of these complexes have been attracted the interests for the use in the supramolecular chemistry area [7,8,9]. In this connection, we have reported the syntheses, characterizations and molecular structures of copper/zinc(II)-complexes with the N-2-(R-pyridyl)-salicylaldimine or N-2-(R-pyridyl)-2hydroxy-1-naphthaldimine [10,11,12]. Molecular structure demonstrates that the two molecules of N^O-chelates form a N<sub>2</sub>O<sub>2</sub>-coordination sphere around the zinc atom with pseudo-tetrahedral geometry in *bis*[N-2-(pyridyl)salicylaldiminato- $\kappa^2$ N^O]zinc(II) [10a]. This compound explores spontaneous resolution to a racemic conglomerate with two opposite chiral space groups,  $P4_{1}2_{1}2_{1}$ (P-helix) and  $P4_{3}2_{1}2$  (M-helix) via supramolecular weak C-H···O bonding between the neighbouring molecules. However, an additional weak coordination between the one or two pyridyl-nitrogen atoms and the metal atom results in variable coordination number of 4+1 (R = 4-CH<sub>3</sub>) or 4+2 (R = 6-CH<sub>3</sub>) in *bis*[N-2-(R-pyridyl)salicylaldiminato- $\kappa^2$ N^O]zinc(II) [10b]. The difference in coordination mode is based on the position of the methyl group on the pyridyl ring leading to the supramolecular weak C-H··· $\pi$  and  $\pi$ ··· $\pi$  interactions in 4-CH<sub>3</sub> substituted or C-H···O and  $\pi$ ··· $\pi$  interactions in 6-CH<sub>3</sub> substituted compound. An inversion-symmetric complex pair with opposite  $\Lambda$ - and  $\Delta$ -configurations at-metal centre is reported in *bis*[N-2-(R-pyridyl)-2oxo-1-naphthaldiminato- $\kappa^2$ N,O]zinc(II) [11]. Packing analysis reveals one of the Zn-N^O-chelate ring forms a reciprocal and strong supramolecular  $\pi - \pi$  interaction with the pyridyl ring of an adjacent molecule. While the analogues bis[N-2-(R-pyridyl)-2-oxo-1-naphthaldiminato- $\kappa^2 N^O$  [copper(II) show a roughly square-planar geometry around the metal atom with weak  $\pi \cdots \pi$ interactions between the two parallel naphthyl- or pyridyl-moieties [12a].

The present paper, in continuation, reports the results of synthesis and characterizations of bis[2-oxo-1-naphthaldehydato- $\kappa$ O,O']copper(II) (1) from reaction between N-2-(R-pyridyl)-2-hydroxy-1-naphthaldimine and copper(II) nitrate via *in-situ* hydrolysis of the Schiff base (Scheme 1). Powder X-ray diffraction (PXRD) was employed to determine the molecular structure of the compound. Further, the optimized structure and excited state properties were studied by DFT/TD-DFT and compared with the experimental results.



Scheme 1. Synthetic route to the formation of bis[2-oxo-1-naphthaldehydato- $\kappa$ O,O']copper(II) (1)

#### 2. Experimental

#### 2.1. Materials and methods

Electronic spectra of the compound were obtained with Shimadzu UV 1800 spectrophotometer in chloroform, dichloromethane and acetonitrile at 25 °C. FT-IR spectra were recorded on a Nicolet iS10 (Thermo Scientific) spectrometer as KBr disc at ambient temperature. Differential scanning calorimeter (DSC) analyses were performed on a Shimadzu DSC-60 at the range of 30–290 °C (i.e., up to decomposition temperature) with a rate of 10 K min<sup>-1</sup> under a nitrogen flow. Elemental analyses were performed on a VarioEL from Elementar Analysensystem. An Epsilon<sup>TM</sup> Instruments (BASi) electrochemical analyzer was used for cyclic voltammetry experiments in acetonitrile containing tetra-N-butyl-ammonium-hexaflorophosphate (TBAP) as supporting electrolyte. The three-electrode measurement was carried out at 25 °C with a platinum disc working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference

electrode. The solution containing the copper(II)-complex and TBAP was deoxygenated with nitrogen gas for 10 minutes prior to use. The X-band EPR spectra were recorded on a ECS-EMX (Bruker) spectrometer in chloroform at 22 °C using diphenylpicrylhydrazine (DPPH) as the reference compound. <sup>1</sup>H NMR spectra were recorded on a Bruker AC 400 spectrometer, operating at 400 MHz (<sup>1</sup>H) in CDCl<sub>3</sub> and dmso-d<sub>6</sub>/CDCl<sub>3</sub> (*ca.* 1 % dmso-d<sub>6</sub>, v/v) at 20 °C, respectively. For magnetic measurements, a sealed coaxial insert containing 1% TMS in acetone-d<sub>6</sub> was used as an external standard and instrument lock. Magnetic susceptibility ( $\chi$ /[M]) and moment ( $\mu_{expt}$ /[ $\mu$ B]) of **1** (9.8x10<sup>-4</sup> mol dm<sup>-3</sup>) were measured based on the Evans method [13] in dichloromethane at 25 °C, containing cyclohexane (0.5% v/v) as an internal reference. Syntheses of the Schiff bases N-2-(R-pyridyl)-2-hydroxy-1-naphthaldimine {R = H (HL1), 4/6-CH<sub>3</sub> (HL2/HL3)} were reported in our previous communications [12a].

# 2.2. Synthesis of bis[2-oxo-1-naphthaldehydato-кO,O']copper(II) (1)

Two equivalents of N-2-(pyridyl)-2-hydroxy-1-naphthaldimine (HL1) (249 mg, 1.00 mmol) dissolved in 10 mL of methanol (yellow color solution), and stirred this solution for 30 min. at room temperature. Dissolved Cu(NO<sub>3</sub>)<sub>2</sub>'4H<sub>2</sub>O (130 mg, 0.50 mmol) into 10 mL of warm methanol, and poured this solution into the ligand solution, color changed to green immediately. The mixture was then stirred for 6-7 hours at room temperature, and finally color changed to light greenish brown. Reduced the volume of the solvent to *ca*. 50% in *vacuo* and left standing this concentrated solution for crystallization *via* slow evaporation of solvent at room temperature. Greenish brown microcrystals were precipitated out within 4-5 days, filtered off and washed three times with methanol (2 ml in each). Dried the microcrystals in air for 3-4 days and obtained the *bis*[2-oxo-1-naphthaldehydato- $\kappa$ O,O']copper(II) (1). The same procedure was followed to synthesise the complexes using the ligands, N-2-(4/6-CH<sub>3</sub>-pyridyl)-2-hydroxy-1-naphthaldimine (HL2/HL3), respectively. In all cases, we obtained only the identical greenish brown microcrystals as of 1, evidenced from elemental data and other analytical methods (discussed below). However, several attempts were made to grow X-ray quality single crystals for 1, but none were succeeded.

#### 2.2.1. Compound 1 synthesized from HL1 (Batch 1)

Yield: 170 mg (82 %). – IR (KBr, cm<sup>-1</sup>): 3065, 2905w (H–C), 1621, 1603, 1584vs, (C=O), and 1540s (C=C). –  $C_{22}H_{14}O_4Cu \cdot 0.5H_2O$  (414.89): calcd. C, 63.69; H, 3.64 found C 63.05, H 3.49.

2.2.2. Compound 1 synthesized from HL2 (Batch 2)

Yield: 155 mg (75%). – IR (KBr, cm<sup>-1</sup>): 3062, 2902w (H–C), 1620, 1603, 1584vs (C=O), and 1540s (C=C). –  $C_{22}H_{14}O_4Cu$  (405.89): calcd. C, 65.10; H 3.48 found C 64.40, H 3.47.

2.2.3. Compound 1 synthesized from HL3 (Batch 3)

Yield: 160 mg (72 %). – IR (KBr, cm<sup>-1</sup>): 3065, 2902w (H–C), 1620, 1603, 1584vs (C=O), and 1540s (C=C). –  $C_{22}H_{14}O_4Cu$  (405.89): calcd. C, 65.10; H, 3.48 found C 64.85, H 3.34.

#### 2.3. Hydrolysis of the Schiff base

To check *in-situ* hydrolysis of the Schiff base, <sup>1</sup>H NMR spectra were taken within *ca*. 5 min of HL2 dissolution in CDCl<sub>3</sub> and in dmso-d<sub>6</sub>/CDCl<sub>3</sub> (*ca*. 1%, v/v), respectively. Spectra were further taken within 3 h of dissolution in dmso-d<sub>6</sub>/CDCl<sub>3</sub> (*ca*. 1%, v/v) to follow the progress of hydrolysis with time.

#### 2.3.1. HL2 in CDCl<sub>3</sub> (only Schiff base)

<sup>1</sup>H NMR (400 MHz, within 5 min):  $\delta = 2.42$  (s, 3H, CH<sub>3</sub>) 6.92 (d,  $J_{\text{HH}} = 9.6$  Hz, 1H,  $H_{3'}$ ), 7.00 (s, 1H,  $H_3$ ), 7.01 (d,  $J_{\text{HH}} = 4.8$  Hz, 1H,  $H_5$ ), 7.13 (2dd,  $J_{\text{HH}} = 7.6$ , 8.0 Hz,  $J_{\text{HH}} = 0.8$ , 0.8 Hz, 1H,  $H_{7'}$ ), 7.51 (2dd,  $J_{\text{HH}} = 7.2$ , 8.4 Hz,  $J_{\text{HH}} = 1.6$ , 1.2 Hz, 1H,  $H_{8'}$ ), 7.62 (d,  $J_{\text{HH}} = 7.6$  Hz, 1H,  $H_{9'}$ ), 7.75 (d,  $J_{\text{HH}} = 9.6$  Hz, 1H,  $H_{6'}$ ), 8.15 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H,  $H_{4'}$ ), 8.35 (d,  $J_{\text{HH}} = 5.6$  Hz, 1H,  $H_6$ ), 9.94 (d,  $J_{\text{HH}} = 8.0$  Hz, 1H, CHN), and 15.39 (d,  $J_{\text{HH}} = 6.4$ , 1H, OH) (see Scheme 1 for atoms numbering).

#### 2.3.2. HL2 in dmso-d<sub>6</sub>/CDCl<sub>3</sub> (ca. 1%, v/v) (mixture products from hydrolysis of Schiff base)

<sup>1</sup>H NMR (400 MHz, within 5 min):  $\delta = 2.26$  (s, 3H, *CH*<sub>3</sub>), 9.79 (s, 1H, *CH*N), 14.23 (br, 1H, OH) for HL2; 2.16 (s, 3H, *CH*<sub>3</sub>), 2.40 (br, 2H, NH<sub>2</sub>) for 2-amino-(4-CH<sub>3</sub>)pyridine, and 10.65 (s, 1H, *CHO*), 12.87 (br, 1H, OH) for 2-hydroxy-1-naphthaldehyde (arometic protons are not listed).

<sup>1</sup>H NMR (400 MHz, within 3 h):  $\delta = 2.24$  (s, 3H, *CH*<sub>3</sub>), 9.75 (d,  $J_{\text{HH}} = 7.6$  Hz, 1H, *CH*N) for HL2; 2.18 (s, 3H, *CH*<sub>3</sub>), 2.41 (br, 2H, *NH*<sub>2</sub>) for 2-amino-(4-CH<sub>3</sub>)pyridine, and 10.67 (s, 1H, *CH*O), 12.92 (br, 1H, *OH*) for 2-hydroxy-1-naphthaldehyde (arometic protons are not listed).

#### 2.4. Powder X-ray diffraction (PXRD)

PXRD data for compounds **1** and 2-hydroxy-1-naphthaldehyde were collected on GNR Expolrer Powder X-ray Diffractometer operating in the Bragg-Brentano geometry with CuKα

radiation ( $\lambda = 1.5406$  Å). The experiment was carried out at 40 kV and 30 mA using standard Aluminum sample holder. Data were collected at 25 °C with 20 step size 0.02° and integration time 3.0 s over an angular range of  $5-50^{\circ}$  (2 $\theta$ ). Partial recollection of data was taken to confirm sample integrity, which showed no significant evidence of sample degradation upon exposure to the X-ray beam. Structure was solved using the direct space approach and refined by the Rietveld method implemented in the program EXPO 2014 [14]. The background of PXRD patterns was modeled by a shifted Chebyshev function and indexed using the N-TREOR09 code [15] for the most intense 18 peaks yielding monoclinic unit cell. Considering the unit cell volume and density, the number of formula units in the unit cell were found Z = 2. Using the FINDSPACE module, the most probable space groups based on the highest frequency of occurrences in CSD (version 5.35, 2014 release) and the FoM-values are  $P2_1/a$ ,  $P2_1/n$ ,  $P2_1/c$ , P2/a and  $P2_1$ . The space group  $P2_1$  is for chiral symmetry and P2/a is very rare in CSD (0.65%). Thus, the probable space groups are considered to  $P2_1/a$ ,  $P2_1/n$  and  $P2_1/c$ , which show same frequency of occurrences in CSD (ca. 34.57%), but the highest MoF-value is for  $P2_1/a$ . All these three space groups are tested for structure determinations, respectively. The structure solution was carried out by global optimization of structural models using simulated annealing technique. Finally, the structure with lowest cost function was submitted for Rietveld refinement [16,17,18], where only planar restraints were applied to the naphthyl ring [17,19]. The summary of crystal data and structure refinement parameters are listed in Table 1.

Compound	$C_{22}H_{14}CuO_4$
Formula weight	405.02
Temperature (K)	298
Crystal system	monoclinic
Wavelength (Å)	1.54056
Space group	$P2_1/a$ (14)
a (Å)	25.9929
b (Å)	5.4563
c (Å)	5.7279
α (°)	90
β (°)	95.297
γ (°)	90
Volume (Å <sup>3</sup> )	808.89
Ζ	2
Density (calculated) g cm <sup>-3</sup>	1.535

**Table 1.** Crystal data and structure refinement parameters for compound 1.

2θ interval (°)	4.994-50.004
Step size $(2\theta)^{o}$	0.02
Counting time (sec)	3
No. of Counts	4502
No. of Reflections	135
No. of background points	21
R <sub>p</sub>	4.967
$R_{\rm wp}/R_{\rm exp}$	6.283/6.616
$\chi^2$	0.902
Goodness-of-fit	0.950

#### 2.5. Computational method

Computational procedure on compound **1** was performed with the Gaussian 09 software package [20]. For computation, the initial geometry of the compound was generated from the PXRD structure. DFT optimization was done using the functional B3LYP and the basis sets 6-31G(d) and SDD, respectively [6,12,21]. To rationalize the experimental electronic spectrum, excited state properties by TD-DFT were employed using different functionals B3LYP, cam-B3LYP and M06 and the basis sets TZVP and SDD on the optimized structure, respectively. PCM (Polarization Continuum Model) was incorporated using chloroform as solvent and 72 excitation states were considered for computation (Table S2). The computed spectra thus obtained were compared with the experimental spectrum, and the maximum fit was found with M06/TZVP//B3LYP/6-31G(d) calculations (MOs) calculations were performed at the same level of theory.

#### 3. Results and discussion

Reaction of pyridyl Schiff bases N-2-(R-pyridyl)-2-hydroxy-1-naphthaldimine {HL: R = H (HL1) or 4/6-CH<sub>3</sub> (HL2/HL3)} with copper(II) nitrate provides the *bis*[2-oxo-1-naphthaldehydato- $\kappa$ O,O']copper(II), [Cu(L')<sub>2</sub>] (1) (L' = 2-oxo-1-naphthaldehydato) (Scheme 1). The *in-situ* hydrolysis of the Schiff bases reproduces the aldehyde, 2-hydroxy-1-naphthaldehyde (HL') due to presence of a small amount of water in the system. This aldehyde in turn coordinates to the copper(II) ion as 2-oxo-1-naphthaldehydate (L') to produce the compound 1. Elemental data show no nitrogen atoms in 1 (synthesized from three batches of reactions using three ligands) and reproduce well to the calculated values, respectively (see

experimental section). Vibrational spectra show very strong bands/shoulders at 1610/1596 and 1527 cm<sup>-1</sup>, attributed to  $\nu$ (C=O) and  $\nu$ (C=C), respectively.

#### 3.1. Hydrolysis of the Schiff base

To check *in-situ* hydrolysis of the Schiff base, we run <sup>1</sup>H NMR spectra of N-2-(4-CH<sub>3</sub>-pyridyl)-2-hydroxy-1-naphthaldimine (HL2) in CDCl<sub>3</sub> and dmso-d<sub>6</sub>/CDCl<sub>3</sub> (*ca.* 1 % dmso-d<sub>6</sub>, v/v), respectively (Fig. 1 and Table 2). The spectrum in CDCl<sub>3</sub> corresponds well to the peaks associated to the HL2 [12a]. However, the spectra in dmso-d<sub>6</sub>/CDCl<sub>3</sub> show several peaks resulting from mixture products of HL2, 2-hydroxy-1-naphthaldehyde (HL') and 2-amino-(4-CH<sub>3</sub>)pyridine, respectively (Fig. 1 and Table 2). The O–H (phenolic) peak in HL2 is found at  $\delta$  15.39 ppm in CDCl<sub>3</sub>, which is disappeared in dmso-d<sub>6</sub>/CDCl<sub>3</sub> within 3 h of dissolution, while the O–H (aldehyde) peak is appeared at  $\delta$  12.92 ppm in HL'. Spectra taken within *ca.* 5 min and 3 h of HL2 dissolution in dmso-d<sub>6</sub>/CDCl<sub>3</sub> show that the ratios of CH<sub>3</sub>-peaks integration values in HL2 to 2-amino-(4-CH<sub>3</sub>)pyridine are *ca.* 5:1 (5 min) or *ca.* 2:1 (3 h). The same ratios of CHN/CHO-peaks integration values are found in HL2 to HL'. The results strongly suggest *in-situ* hydrolysis of the Schiff base (HL2) back to the aldehyde (HL') and 2-amino-(4-CH<sub>3</sub>)pyridine in reaction mixture (Scheme 1), due to presence of a small amount of water in dmso-d<sub>6</sub> (see H<sub>2</sub>O peak in Fig. 1).





**Fig. 1.** <sup>1</sup>H NMR (400 MHz) spectra of HL2 in CDCl<sub>3</sub> (top) and in dmso-d<sub>6</sub>/CDCl<sub>3</sub> (*ca.* 1 % dmso-d<sub>6</sub>, v/v) within *ca.* 5 min (middle) and 3 h (bottom) dissolution (formation of hydrolyzed mixture products) at 20  $^{\circ}$ C.

# Table 2.

<sup>1</sup>H NMR (400 MHz) spectral data for HL2 in CDCl<sub>3</sub> and dmso-d<sub>6</sub>/CDCl<sub>3</sub> (*ca.* 1 %, v/v), respectively at 20  $^{\circ}$ C.<sup>#</sup>

Entity (solvent)	Time	$CH_3 (CH_3)^a$	$(NH_2)^a$	CHN (CHO) <sup>b</sup>	OH (OH) <sup>b</sup>
HL2 (CDCl <sub>3</sub> )	within 5	2.42s	-	9.94 (d, $J_{\rm HH}$ = 8.0	15.39 (d,
	min			Hz)	$J_{\rm HH}=6.4)$
Mixture products of	within 5	2.26s (2.16s)	2.40br	9.79s (10.65s)	14.23br
hydrolysis in solution: HL2, 2-hydroxy-1-	min	(Ratio ca. 5:1		(Ratio 5:1)	(12.87br)
naphthaldehyde, 2-amino-(4-	within 3 h	2.24s (2.18s)	2.41br	9.75 (d, $J_{\rm HH}$ = 7.6	Not seen
CH <sub>3</sub> )pyridine (dmso-		(Ratio ca. 2:1)		Hz) (10.67s)	(12.92br)
d <sub>6</sub> /CDCl <sub>3</sub> )				(Ratio <i>ca</i> .2:1	

<sup>#</sup> Aromatic protons are not listed; Values in parentheses are for <sup>a</sup> 2-amino-(4-CH<sub>3</sub>)pyridine and <sup>b</sup> 2-hydroxy-1-naphthaldehyde.

# 3.2. Electronic spectra and excited state properties

Electronic spectrum of **1** in chloroform (Fig. 2) features very strong bands/shoulders below 300 nm due to intra-ligand  $n \rightarrow \pi^*/\pi \rightarrow \pi^*$  (L-L) transitions. A moderate broad band at 300-450

nm is attributed to ligand-to-metal (L-M) charge transfer transitions. Further, a weak broad band at visible region (450-800 nm) is assigned for superposition of several metal-centered dd electrons transitions (Fig. 2, inset) [6,11,12,21]. Computed electronic spectrum by DFT/TD-DFT (Fig. 2) shows similar patterns of several bands/shoulders at varying position to the experimental spectrum. It has been reported that a simplified and straightforward assignments on computed spectrum are complicated for the open-shell copper(II)-complex (due to spin contamination) and the existences of a large number of transitions at a single excitation state (Table S2) [6,12,21,22]. Thus, a combined band composed of d-d and L-M transitions is found at *ca*. 639 nm ( $\lambda_{max}$ ) with the highest MOs contributions. This band is attributed to HOMO–12 to LUMO transitions, which is close to the experimental band at *ca*. 625 nm (Fig. 2, inset and Table 3). However, a few selected and simplified assignments, based on orbital and population analyses, relevant to the experimental data are listed in Table 3. The HOMO–12 and LUMO for  $\beta$ -spin consideration are presented in Fig. 3.



Fig. 2. Experimental  $(1.16 \times 10^{-4} \text{ mol dm}^{-3})$  and computed electronic spectra for 1 in chloroform at 25 °C (computed at M06/TZVP//B3LYP/6-31G(d)).

#### Table 3.

Excited state properties for compound 1, computed with M06/TZVP//B3LYP/6-31G(d) for  $\beta$ -spin consideration in chloroform.

$\lambda/nm^{a}$	Oscillator	MOs contributions (%) $^{D}$	Assignments <sup>c</sup>
	strength (f)		
639 (625)	0.0023	H-12→L (92), H-9→L (19)	d-d, L-M
469 (385, 415sh)	0.1228	H-4→L (41), H→L (85)	d-d, L-M
348 (337)	0.5825	H-16→L (24), H-4→L (82)	L-M
271 (270sh)	0.1455	H-11→L (65), H→L+3 (33)	d-d, L-M, L-L
252 (260sh)	0.1868	H-2→L+3 (21), H→L+5 (22)	d-d, L-M, L-L
236 (245sh)	0.5960	H-6→L+2 (18), H-5→L+1 (43)	L-M, L-L

<sup>a</sup> Values in parentheses are from experimental spectrum; <sup>b</sup> H = HOMO and L = LUMO; <sup>c</sup> d-d = metal-centred, L-M = ligand-to-metal and L-L = ligand-ligand transitions bands.



Fig. 3. The HOMO–12 and LUMO for compound 1 for  $\beta$ -spin consideration, computed with M06/TZVP//B3LYP/6-31G(d) in chloroform.

#### 3.3. PXRD and optimized structure

Powder X-ray diffraction (PXRD) patterns (Fig. 4) confirm the crystalline nature of the compound **1** and the 2-hydroxy-1-naphthaldehyde (HL'). Comparison studies of PXRD patterns show several identical peaks at slightly shifting positions, and few new peaks in **1** (e.g.,  $2\theta = 6.79$ , 21.25, 27.48 and 29.65), merely indicate a different structure for the product [17,18,23,24]. The crystal structure has been solved using the direct space approach and Rietveld refinement method integrated in the program EXPO 2014 [14,17,18,19]. The Rietveld refinement plots exhibit good agreement between the experimental and calculated PXRD profiles (Fig. 5) [17,18]. The compound crystallizes in a monoclinic system with a = 25.9929 Å, b = 5.4563 Å, c = 5.7279 Å,  $\beta = 95.30^{\circ}$ , space group  $P2_1/a$  and Z = 2. The molecular structure (Fig. 6) explores that two O^O-chelate ligands form a non-planar O<sub>2</sub>O<sub>2</sub>-coordination sphere around the copper atom. Moreover, as Z = 2, the Cu centre must be on a symmetry element (i.e., possesses an inversion centre and asymmetric unit must be half of the molecule) and therefore only two Cu–O distances are independent. Indeed, in Tab. 4, the Cu–O distances are equally pairwise. The observed bond lengths and angles are comparable to those reported from X-ray single crystal structure for the related *bis*[salicy]aldehydato-

 $\kappa$ O,O']copper(II) [6]. DFT optimized structure, calculated with b3lyp/6-31g(d) [6,12,21], is identical to PXRD structure of the compound (Fig. 6, Table 4). However, little differences between these two structures, specially in the largest angles values by *ca*. 7°, could be because of PXRD results refer to the molecule in the solid state, while DFT implies isolated molecule in gaseous phase.

For quantitative analysis of coordination geometry, along with the optimized structure, we measured the degree of distortion from tetrahedral to square-planar based on the dihedral angle ( $\theta'^{\circ}$ ) and its normalized function  $\tau_{\text{tet-sq}}$  ( $\theta'90^{\circ}$ ) [21,25,26]. The values of  $\theta$  are 0° (or  $\tau_{\text{tet-sq}} = \text{zero}$ ) for square-planar and 90° (or  $\tau_{\text{tet-sq}} = 1.0$ ) for tetrahedral geometry (not considering the inherent distortion induced by the chelate ring formation). In compound **1**, these values are 39.06° ( $\theta$ ) and 0.43 ( $\tau_{\text{tet-sq}}$ ), close to the optimized structure (i.e., 37.44° and 0.42). Based on these results, we conclude the geometry of the compound to more or less in-between tetrahedral and square-planar around the copper atom.



Fig. 4. PXRD patterns for the aldehyde (HL') and compound (1).



Fig. 5. PXRD patterns for compound 1: experimental, calculated, difference and background after final Rietveld refinement.



**Fig. 6**. PXRD (top) and DFT optimized (botom) structures, calculated at B3LYP/6-31G(d), for compound **1**.

**Table 4**. Selected bond lengths (Å) and angles (°) in compound **1**.

PXRD structure	DFT structure	X-ray crystal
		structure <sup>#</sup>

Cu1-O1/Cu1-O2	1.8525/1.8526	1.8760	1.8891
Cu1-O3/Cu1-O4	1.9405/1.9429	1.9081	1.9423
C3-O1/C14-O2	1.2876/1.2890	1.2882	1.3042
C2-O3/C13-O4	1.2648/1.2638	1.2643	1.2462
01-Cu-O3	92.87	93.15	93.40
O2-Cu-O4	92.82	93.15	93.40
01-Cu-O2	161.56	154.19	180.00
O3-Cu-O4	144.93	151.92	180.00
04-Cu-O1	92.68	93.06	86.60
O3-Cu-O2	92.70	93.06	86.60

<sup>#</sup>For *bis*[salicylaldehydato-κO,O']copper(II) [6].

#### 3.4. Thermal stability

Transition metal(II)-O,O/N,O-chelate complexes exhibited thermally induced phase transformation from solid (low temperature) to isotropic liquid phase (high temperature, well studied by Differential Scanning Calorimeter (DSC) [12,21,25-26]. DSC analyses curves show identical thermal behavior for **1**, synthesized from three batches of reactions (Fig. 7). The compound shows thermal stability up to *ca*. 255 °C and a subsequent phase change with both exo- and endo-thermic heat of transformation at *ca*. 274 °C [12]. While, the cooling curve shows no peaks on the reverse direction, suggesting an irreversible phase transformation.



Fig. 7. DSC curves for compound 1 (heating: solid line, cooling: dashed line).

#### 3.5. Cyclic voltammograms (CV)

CV for 1 were recorded at -1.00 to 0.60 V (vs. Ag/AgCl) with varying scans rates in acetonitrile at 25 °C, respectively (Figs. 8, S1 and Table S1). The cathodic wave shows a strong broad reductive peak (Ic) at ca. - 0.70 V (Ec), corresponds to two electrons charge transfer processes for  $[Cu(L')_2]/[Cu(L')_2]^-$  and  $[Cu(L')_2]^{-/[Cu(L')_2]^{2-}}$  (L' = 2-oxo-1naphthaldehydate) couples (one electron in each). The potential difference between these two peaks is very narrow, results in overlapping to provide a strong broad peak. On the other hand, the anodic wave shows two separate oxidative peaks (Ia2 and Ia1) at ca. - 0.20 (Ea2) and 0.40 V (Ea1) for  $[Cu(L')_2]^2/[Cu(L')_2]^-$  and  $[Cu(L')_2]^-/[Cu(L')_2]$  couples, respectively. Analyses of voltammograms demonstrate that the cathodic peak current (Ic) or anodic to cathodic peak current ratio (Ia1/Ic) increases with faster scans rates, while Ia2/Ic ratio decreases (Figs. 9A-C, S2 and Table S1). The peaks potential difference  $\Delta Ea1$  (Ec - Ea1) or  $\Delta Ea2$  (Ec - Ea2) is independent of faster scans rates (Fig. 9D and Table S1). Thus, CV results best describe two quasi-reversible one electron charge transfer processes for  $Cu^{2+}/Cu^{+}$  and  $Cu^{+}/Cu^{0}$  couples. respectively, as reported for the related copper(II)-compounds [6,11,12,21]. Further, the linear relationships between peak current and square root of scans rate ( $v^{1/2}$ ) (Figs. 9A-C) demonstrate a diffusion-controlled electrochemical process in acetonitrile.



**Fig. 8.** Cyclic voltammograms for compound **1** (synthesized from HL1; 0.5 mmol dm<sup>-3</sup>) with varying scan rates ( $\nu/Vs^{-1}$ ); TBAP (0.1 mol dm<sup>-3</sup>) in acetonitrile at 25 °C.



**Fig. 9.** Plots of *Ic vs.*  $v^{1/2}$  (A), *Ia*1/*Ic* or *Ia*2/*Ic vs.*  $v^{1/2}$  (B or C) and  $\Delta E1$  (or  $\Delta E2$ ) *vs.*  $v^{1/2}$  (D) for compound **1** (synthesized from HL1) in acetonitrile at 25 °C.

#### 3.6. EPR spectra and paramagnetism

X-band EPR spectrum for **1** (Fig. 10) displays an isotropic pattern resulting from tumbling motion of the molecules in chloroform solution as expected for the copper(II)-complexes with distorted tetrahedral to square-planar geometry [12b,27,28]. Spectrum with four lines represents a nuclear hyperfine splitting from the copper(II) ion with spin 3/2 [12b,27,28a]. The relatively low  $g_{iso}$  value (2.13 < 2.30) indicates considerable covalent character in the metal–ligand bonds [12b,27,28b]. The hyperfine coupling splitting value of *ca*. 7.6 mT (*A*) indicates an electron interacting with only one copper nucleus [12b,27]. The copper(II)-complex with one unpaired electron is essentially paramagnetic in tetrahedral or square-planar geometry. The observed magnetic moment value 1.35  $\mu$ B ( $\mu_{expt.}$ ) in dichloromethane at 25 °C, calculated with the Evans' method [12,13,29], indicates the paramagnetic nature of the copper(II)-complex [12,27,30].



Fig. 10. EPR spectrum for compound 1 (from HL1) in chloroform at 22 °C.

#### 4. Conclusions

The *bis*[2-oxo-1-naphthaldehydato- $\kappa$ O,O']copper(II) (1) is isolated via *in-situ* hydrolysis of N-2-(R-pyridyl)-2-hydroxy-1-naphthaldimine back to the 2-hydroxy-1-naphthaldehyde. Powder X-ray diffraction (PXRD) structure explored the formation of a O<sub>2</sub>O<sub>2</sub>-chromophore around the copper atom in-between tetrahedral and square-planar geometry as supported by the DFT optimized structure. The excited state properties by DFT/TDDFT are comparable to the electronic spectrum in chloroform. CV studies in acetonitrile demonstrate two quasi-reversible one electron charge transfer processes for  $[Cu(L')_2]^2$ -/ $[Cu(L')_2]^-$  and  $[Cu(L')_2]^-/[Cu(L')_2]$  (L' = 2-oxo-1-naphthaldehydato) couples, respectively. DSC analysis reveals an irreversible phase transformation from solid to an isotropic liquid-phase. The EPR spectrum in chloroform shows the *g*<sub>iso</sub> value of 2.13, characteristic of tetrahedral and square planar copper(II)-complexes. The magnetic moment value ( $\mu_{expt.} = 1.35 \ \mu B$ ) in dichloromethane indicates paramagnetic nature of the copper(II)-complex with one unpaired electron.

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# <u>Highlights</u>

- > PXRD structure of *bis*[2-oxo-1-naphthaldehydato-κO,O']copper(II).
- > *In-situ* hydrolysis of the Schiff base back to aldehyde.
- EPR spectrum showing isotropic pattern with four lines from nuclear hyperfine splitting of copper(II) with spin 3/2.
- Two quasi-reversible one electron charge transfer processes for [Cu(L')<sub>2</sub>]/[Cu(L')<sub>2</sub>]<sup>-</sup> and [Cu(L')<sub>2</sub>]<sup>-</sup>/[Cu(L')<sub>2</sub>]<sup>2-</sup> couples.