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# Synthesis, spectroscopy, electrochemistry, and molecular structure of *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide

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# Synthesis, spectroscopy, electrochemistry, and molecular structure of *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide

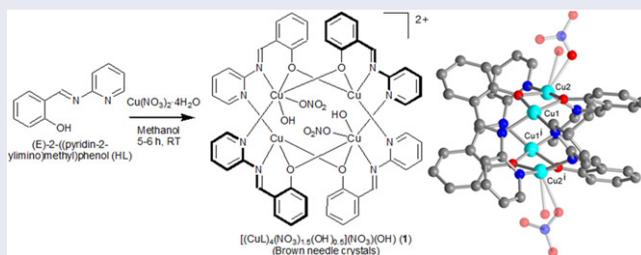
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## ABSTRACT

Reaction between (E)-2-((pyridin-2-ylimino)methyl)phenol (HL) and copper(II) nitrate provides *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide, [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>](NO<sub>3</sub>)(OH) (1). ESI-mass spectra show the ion peaks for the dinuclear species at *m/z* 565 for [(CuL)<sub>2</sub>(HCO<sub>2</sub>)<sup>+</sup> and 521 for [(CuL)<sub>2</sub>+H]<sup>+</sup> and the mononuclear species at *m/z* 260 for [(CuL)]<sup>+</sup>. Vibrational spectra show very strong bands at 1604/1546 cm<sup>-1</sup> for ν(C=N/C=C) and at 1384, 1351 cm<sup>-1</sup> for ν(NO<sub>3</sub><sup>-</sup>). Cyclic voltammograms demonstrate an irreversible redox processes for the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples in acetonitrile. X-ray molecular structure determination explores the formation of a cationic tetranuclear copper(II)-complex, in which a deprotonated ligand molecule chelates to one copper ion with the phenolate-O and imino-N atoms. In addition, a phenolate-O atom bridges between two neighboring copper ions and a pyridine-N atom coordinates to a third copper ion, so that each ligand bridges among three copper ions in a κ<sup>2</sup>N,O:κO:κN' coordination sphere. Thus, the four copper ions and four chelating-bridging ligands assemble primarily into a cationic [(CuL)<sub>4</sub>]<sup>4+</sup> complex. The two copper ions are further coordinated by either a nitrate anion (75% occupancy) or a hydroxide anion (25% occupancy) and form the core of a tetranuclear [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>]<sup>2+</sup> cation.

## GRAPHICAL ABSTRACT



## ARTICLE HISTORY

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## KEYWORDS

(E)-2-((Pyridin-2-ylimino)methyl)phenol; tetranuclear [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>]<sup>2+</sup> cation; spectroscopy; electrochemistry; X-ray structure

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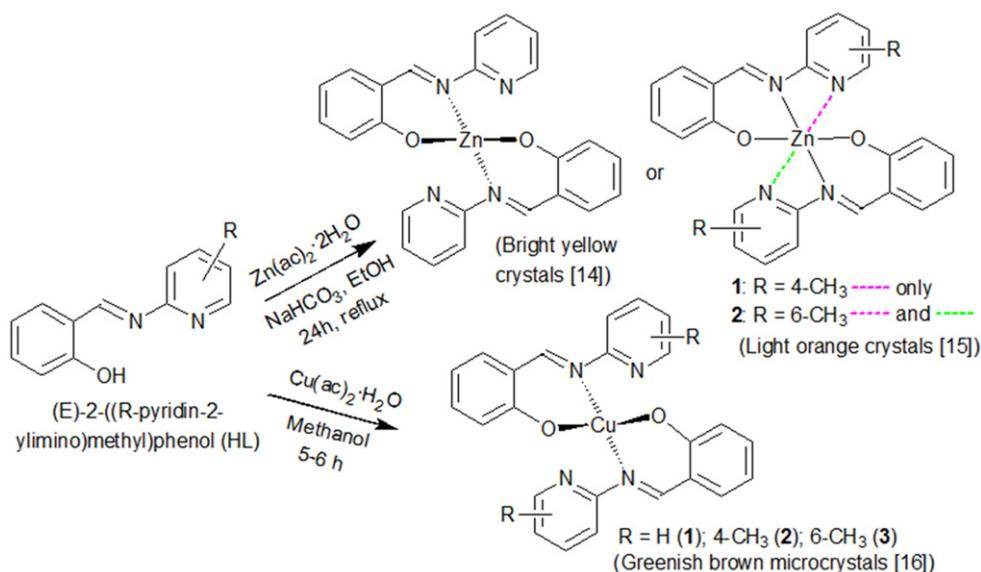
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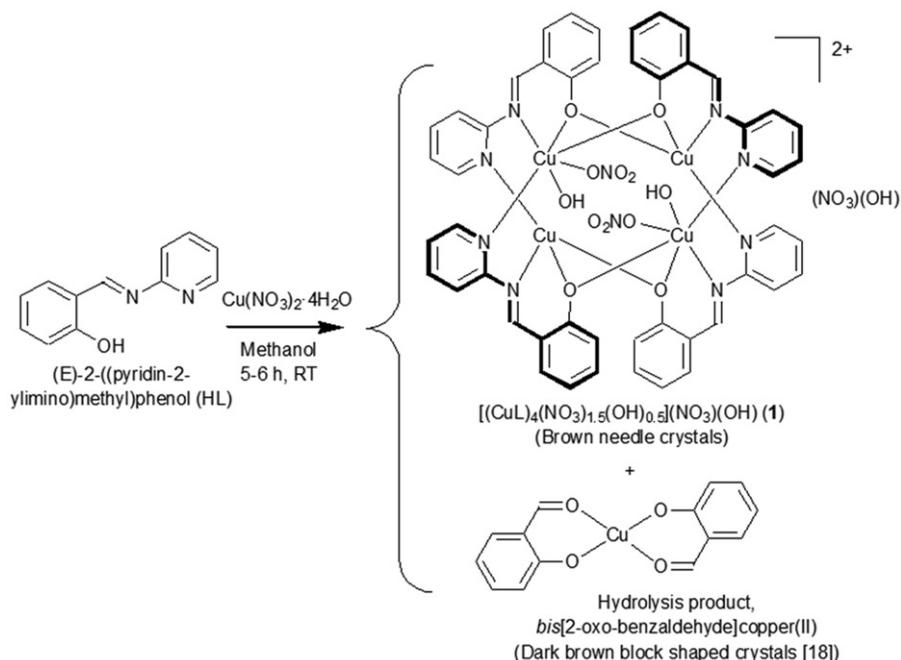
## 1. Introduction

The complexes of transition metal(II) ions with R-pyridyl Schiff base ligands, (E)-2-((R-pyridin-2-ylimino)methyl)phenol (HL, R=H or CH<sub>3</sub>), are of continued interest due to their easy synthesis, spectroscopy, electrochemistry, catalytic and thermal behaviors, paramagnetism, molecular structures, and supramolecular chemistry [1–3]. In the *bis*-ligated form with four coordinated mononuclear [Cu(L)<sub>2</sub>] {L<sup>−</sup> = (E)-2-((R-pyridin-2-ylimino)methyl)phenolate}, the ligands are bound to the metal ion *via* phenolic-O and imine-N atoms in a square-planar geometry [1a, 1b]. The pyridyl-N atoms are not involved in the metal coordination sphere, but rather enter into intramolecular hydrogen bonding with the imine-H atom [1a]. The  $\pi$ - $\pi$  stacking between the phenolate aryl rings and the pyridyl rings orients the molecules into 1-D supramolecular strands.

We have recently focused on the syntheses of transition metal(II) complexes with *chiral*-N<sup>∧</sup>O chelating Schiff base ligands such as [M(R/S-N<sup>∧</sup>O)<sub>2</sub>] (M = Cu/Ni/Zn) [4–8] and mixed ligated [Rh( $\eta^4$ -cod)(chiral-N<sup>∧</sup>O)] [9–13]. Molecular structure determination demonstrates a six-membered *bis* N<sup>∧</sup>O-chelation to the metal(II) ion in distorted tetrahedral/square-planar geometry. We reported zinc(II) complexes with (E)-2-((R-pyridin-2-ylimino)methyl)phenol, showing variable coordination number of the metal(II) ion from four (R = H) to 4 + 1 (R = 4-methyl) or 4 + 2 (R = 6-methyl), +1 and +2 being weaker extended coordinations from the pyridyl-N atom to the metal(II) ion [14, 15] (Scheme 1). X-ray analyses demonstrate an N<sub>2</sub>O<sub>2</sub>-chromophore from two deprotonated N<sup>∧</sup>O-chelates around the metal(II) ion to form the four-coordinate pseudo-tetrahedral *bis*[(E)-2-((pyridin-2-ylimino)methyl)phenolato]zinc(II) [14]. One or two additional weak Zn-N(R-pyridyl) contacts were revealed to provide coordination number five (R = 4-methyl) or six (R = 6-methyl) in



**Scheme 1.** Synthetic route to the formation of *bis*[(E)-2-((R-pyridin-2-ylimino)methyl)phenolato]-zinc/copper(II) complexes.



**Scheme 2.** Synthetic route to the formation of the *tetrakis*[(*E*)-2-((pyridin-2-ylimino)methyl)phenolato](hydroxido)<sub>0.5</sub>(nitrato)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide,  $[(\text{CuL})_4(\text{NO}_3)_{1.5}(\text{OH})_{0.5}](\text{NO}_3)(\text{OH})$  (**1**).

*bis*[(*E*)-2-((*R*-pyridin-2-ylimino)methyl)phenolato]zinc(II) [15]. The former four-coordinated compound shows spontaneous resolution to a racemic conglomerate – from achiral  $\text{N}^{\wedge}\text{O}$  chelate to chiral enantiomeric right-handed (*P*-helix) and left-handed (*M*-helix) helical chain due to weak  $\text{C-H}\cdots\text{O}$  hydrogen bonding interactions [14]. On the other hand, the latter two compounds demonstrate supramolecular packing organized by  $\text{C-H}\cdots\pi$  and  $\pi\cdots\pi$  interactions in 4-methyl substituted and  $\text{C-H}\cdots\text{O}$  and  $\pi\cdots\pi$  interactions in 6-methyl substituted compound [15].

Reaction of *R*-pyridyl Schiff base ligands, (*E*)-2-((*R*-pyridin-2-ylimino)methyl)-phenol/-naphthol (HL) with copper(II) acetate provides the typical four-coordinate mononuclear *bis*[(*E*)-2-((*R*-pyridin-2-ylimino)methyl)-phenolato/-naphtholato]copper(II) [1a, 1b, 16, 17] (Scheme 1). The use of copper(II) nitrate instead affords a mixture of products of the mononuclear *bis*[2-oxo-benzaldehyde]copper(II) *via* hydrolysis of the Schiff base ligands [18] and the present tetranuclear cationic *tetrakis*[(*E*)-2-((pyridin-2-ylimino)methyl)phenolato](hydroxido)<sub>0.5</sub>(nitrato)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide,  $[(\text{CuL})_4(\text{NO}_3)_{1.5}(\text{OH})_{0.5}](\text{NO}_3)(\text{OH})$  (**1**) (Scheme 2). Indeed, there have been considerable interests on syntheses, characterization, and physicochemical properties of multinuclear copper(II)-Schiff base complexes [19, 20]. In this connection, a few multinuclear copper(II)-pyridyl Schiff base complexes along with their molecular structures have been reported [21, 22]. Reactions of (*E*)-2-((pyridin-2-ylimino)methyl)-phenol with the copper(II) nitrate or perchlorate provide the tetranuclear cationic  $\{[\text{Cu}(\text{H}_2\text{O})(\text{L})]_4\}(\text{NO}_3)_4$  or  $(\text{ClO}_4)_4$  [21]. This article outlines the results of syntheses, spectroscopy, electrochemistry, and X-ray molecular structure of tetranuclear cationic complex **1**.

## 2. Experimental

### 2.1. Materials and methods

Copper(II) nitrate, salicylaldehyde, and R-pyridyl amine were used as received from Merck. HPLC grade acetonitrile from Fisher Scientific and tetrabutylammonium hexafluorophosphate (TBAP) from Sigma-Aldrich were used as received. Commercial grade methanol was refluxed over CaO for several days. FT-IR spectra were recorded on a Nicolet iS10 (Thermo Scientific) spectrometer as KBr discs at ambient temperature. UV-Vis spectra were obtained with a Shimadzu UV 1800 spectrophotometer in acetonitrile at 25 °C. An Epsilon<sup>TM</sup> Instruments (BASi) electrochemical analyzer was used for cyclic voltammogram experiments in acetonitrile containing 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. It has been reported in our previous communication [16] that the electrolyte (TBAP) solution shows two oxidation peaks at ca. 0.70, 0.90 V and the Schiff base shows one oxidation peak at ca. 1.20 V. To avoid overlapping with these peaks, we limited the CV range at -0.80 to 0.50 V. The solution containing the copper(II)-complex and TBAP was deoxygenated for 10 min with nitrogen gas prior to use. The working electrode was cleaned with the supplied solution and dried prior to use between the scans. Reproducibility of CV was checked at a scan rate of 0.10 V/s. The ESI-mass (positive mode) spectrum was taken on a Shimadzu LCMS-2020. Isotopic distributions patterns for the <sup>63/65</sup>Cu containing ions are clearly visible in the mass spectrum. Synthesis of the R-pyridyl Schiff base ligand, (E)-2-((R-pyridin-2-ylimino)methyl)phenol, was reported in our previous communication [15].

### 2.2. Syntheses of the complex

Two equivalents of (E)-2-((pyridin-2-ylimino)methyl)phenol (HL) (400 mg, 2.00 mmol) were dissolved in 10 mL methanol and added into 10 mL of a hot methanol solution of Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (200 mg, 1.0 mmol). The solution was stirred for 5–6 h at room temperature. The color changed from light green to greenish brown. The volume of the solvent was reduced to 50% in vacuo and this solution was left standing for crystallization by slow evaporation of the solvent at room temperature. Dark brown, block-shaped crystals of bis[2-oxo-benzaldehyde]copper(II) [17] formed after 4–5 days and the crystals were filtered off. The light brown filtrate was left standing for further crystallization via slow evaporation of solvent at room temperature. After 5–6 days, light brown needle crystals of tetrakis{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide (1), suitable for X-ray measurement, were obtained. The crystals were washed with methanol two times (2 mL each) and dried in air for 2–3 days.

*Tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide, [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>](NO<sub>3</sub>)(OH) (1). Yield: 142 mg (46%). IR data (KBr, cm<sup>-1</sup>): 3055, 3023, 2917w (C-H), 1604vs (C=N), 1546s (C=C) and 1384, 1351vs (NO<sub>3</sub><sup>-</sup>). MS (ESI<sup>+</sup>): *m/z* = 565 [(CuL)<sub>2</sub>(HCO<sub>2</sub>)<sup>+</sup>], 521 [(CuL)<sub>2</sub>+H]<sup>+</sup>, 458 [Cu(L)<sub>2</sub>+H]<sup>+</sup>, 354 [(CuL)(C<sub>6</sub>H<sub>5</sub>O)+H]<sup>+</sup>, 260 [(CuL)]<sup>+</sup> and 200 [HL + H]<sup>+</sup>.

### 2.3. X-ray crystallography

A single crystal of **1** was carefully selected under a polarizing microscope. *Data collection*: Bruker APEX-II CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 K; multilayer mirror monochromator,  $\omega$ -scans. Data collection and cell refinement with APEX [23], data reduction with SAINT (Bruker) [24]. *Structure analysis and refinement*: The structure was solved by direct method (SHELXS-97) [25], refinement was done by full-matrix least squares on  $F^2$  using the SHELXL-97 program suite [25] empirical (multiscan) absorption correction with SADABS (Bruker) [26]. All nonhydrogen positions were refined with anisotropic temperature factors. The hydrogen atoms for aromatic CH, aliphatic CH<sub>2</sub> were positioned geometrically and refined using corresponding riding models: C–H = 0.95  $\text{\AA}$  with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  for aromatic CH (AFIX 43).

The cationic tetranuclear Cu(II)-ligand(-1) complex could be unequivocally refined. The four Cu<sup>2+</sup> ions together with the four uninegative ligands give a 4+ charge for the complex cation. This requires four negative anionic charges. The asymmetric unit consists of two Cu<sup>2+</sup> ions and two ligands. Two symmetry independent possible NO<sub>3</sub><sup>−</sup> anions were initially found but refined to less than full occupancy for each nitrate anion. The NO<sub>3</sub><sup>−</sup> anion with N6, O7, O8, and O9 was situated near a glide plane and a twofold rotation axis. The symmetry operations then gave a symmetry-related NO<sub>3</sub><sup>−</sup> anion at an O...O' distance of 1.41  $\text{\AA}$ . Consequently, this NO<sub>3</sub><sup>−</sup> anion refined to about 50% occupation (except for O7) when the occupation factors of its atoms were refined. The occupation factor of O7 refined to full occupation.

The other nitrate anion with N5, O3, O4, and O5 was refined to *ca.* 0.75 occupancy. The NO<sub>3</sub><sup>−</sup> anion is also coordinated to Cu2 with Cu2...O3 = 2.318  $\text{\AA}$ . Simultaneously, an oxygen atom (O10) was refined near N5 at Cu2...O10 = 2.252  $\text{\AA}$  with its occupation factor refining to *ca.* 0.25. Together, the two found partially occupied nitrate anions account for a charge of −1.25 out of −2 which is needed for electroneutrality of the asymmetric unit. No further nitrate ions could be localized within the residual electron density.

To account for the missing −0.75 charge, 50% of O7 is taken as the oxygen atom of a hydroxide ion, OH<sup>−</sup>, when the NO<sub>3</sub><sup>−</sup> anion assumes the position on the "other side" of the symmetry element. This adds a −0.5 charge. Similarly, the oxygen atom O10 is assigned to a coordinated hydroxide ion. Atom O10 with its occupation factor of 0.25 adds the remaining −0.25 charge.

In addition, an oxygen atom with 12.5% occupation was refined in a hydrogen-bonded distance (O...O = 2.84  $\text{\AA}$ ) to O7 and near the half-occupied NO<sub>3</sub><sup>−</sup> anion. Thus, the axial ligand of square-pyramidal Cu2 is either a nitrate ion (75%) or a hydroxide ligand (25%). The formula of the asymmetric unit is then [(Cu<sub>2</sub>L<sub>2</sub>)(NO<sub>3</sub>)<sub>0.75</sub>(OH)<sub>0.25</sub>](NO<sub>3</sub>)<sub>0.5</sub>(OH)<sub>0.5</sub>(H<sub>2</sub>O)<sub>0.125</sub>(solvent)<sub>x</sub>. The doubled molecular formula is [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>](NO<sub>3</sub>)(OH)(H<sub>2</sub>O)<sub>0.25</sub>(solvent)<sub>x</sub>. The residual electron density was severely disordered and, thus, was treated (removed) by the SQUEZZE routine with PLATON. Repeated efforts to obtain a better quality data set were not successful, probably due to solvent loss and possibly some variation in the nitrate and hydroxide anions ratio in the crystal. Details of X-ray structure determinations and refinements are provided in Table 1. Graphics were drawn with

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

Empirical formula	$(C_{48}H_{36}Cu_4N_8O_4) \cdot 2(NO_3)_{0.50} \cdot 2(NO_3)_{0.75} \cdot 2(O_{0.50}) \cdot 2(O_{0.25}) \cdot 2(O_{0.125})$
<i>M</i> / g mol <sup>-1</sup>	1226.03
Crystal size / mm <sup>3</sup>	0.07 × 0.03 × 0.03
Color/Shape	Brown/Needle
Temperature /K	150
$\theta$ range /°	$\theta = 2.5\text{--}24.4$
<i>h</i> ; <i>k</i> ; <i>l</i> range	-16, 15; -19, 28; $\pm 18$
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> / Å	13.9592(8)
<i>b</i> / Å	24.7378(10)
<i>c</i> / Å	16.1352(8)
<i>V</i> / Å <sup>3</sup>	5571.8(5)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> / g cm <sup>-3</sup>	1.462
$\mu$ (Mo K $\alpha$ ) / mm <sup>-1</sup>	1.57
<i>F</i> (000)	2478
Max. / min. transmission	0.745 / 0.699
Reflections collected	23626
Independent reflect. ( <i>R</i> <sub>int</sub> )	4646 (0.141)
Data / restraints / parameters	4646 / 0 / 369
Max. / min. $\Delta\rho$ / e.Å <sup>-3</sup> <sup>a</sup>	0.66 / -0.89
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.061/ 0.151
Goodness-of-fit on <i>F</i> <sup>2c</sup>	1.10

<sup>a</sup>Largest difference peak and hole.

<sup>b</sup> $R_1 = [\sum(|F_0| - |F_c|) / \sum |F_0|]$ ;  $wR_2 = [\sum[w(F_0^2 - F_c^2)^2] / \sum (F_0^2)]^{1/2}$ .

<sup>c</sup>Goodness-of-fit =  $[\sum(w(F_0^2 - F_c^2)^2) / (n-p)]^{1/2}$ .

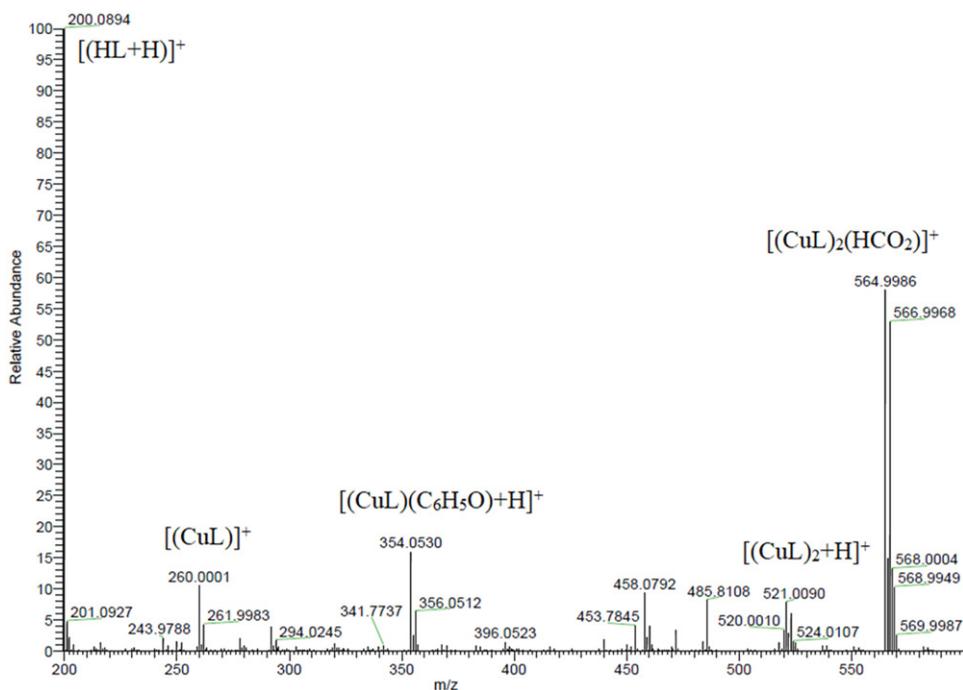
DIAMOND (Version 3.2) [27]. Computations on the supramolecular interactions were carried out with PLATON for Windows [28].

### 3. Results and discussion

The (E)-2-((pyridin-2-ylimino)methyl)phenol (HL) coordinates to the copper(II) nitrate to give the tetranuclear cationic *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato} (hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide, [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>](NO<sub>3</sub>) (OH) (1) (Scheme 2). The vibrational spectrum (supporting information Figure S1) shows two very strong bands at 1604 and 1546 cm<sup>-1</sup>, attributed to the  $\nu C=N$  and  $\nu C=C$ , respectively [4–11]. The counter nitrate anions show two very strong bands at 1384 and 1351 cm<sup>-1</sup> for  $\nu(NO_3^-)$ . The spectrum further shows weak bands/shoulders at the range of 3055–2917 cm<sup>-1</sup> for  $\nu C-H$ .

#### 3.1. Mass spectra

ESI-mass spectrum (Figure 1) shows the ion peaks for the dinuclear species at *m/z* 565 for [(CuL)<sub>2</sub>(HCO<sub>2</sub>)]<sup>+</sup> and 521 for [(CuL)<sub>2</sub>+H]<sup>+</sup>, and the mononuclear species at *m/z* 354 for [(CuL)(C<sub>6</sub>H<sub>5</sub>O)+H]<sup>+</sup> and 260 for [(CuL)]<sup>+</sup>. The spectrum further shows the ion peak for the protonated Schiff base ligand at *m/z* 200 for [HL + H]<sup>+</sup>.



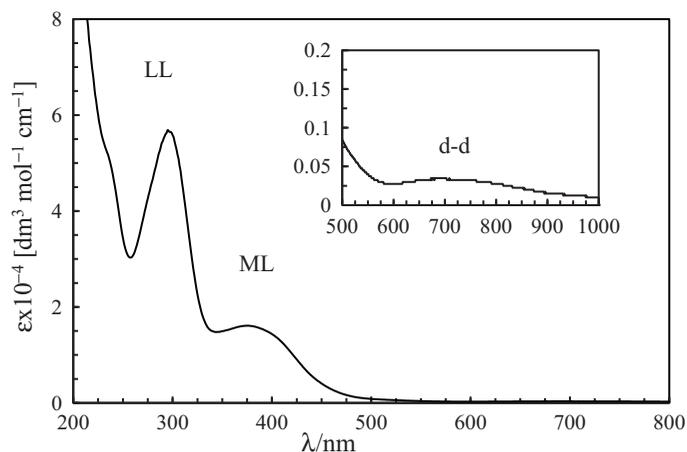
**Figure 1.** ESI-mass spectrum for *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrato)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide (**1**).

### 3.2. Electronic spectra

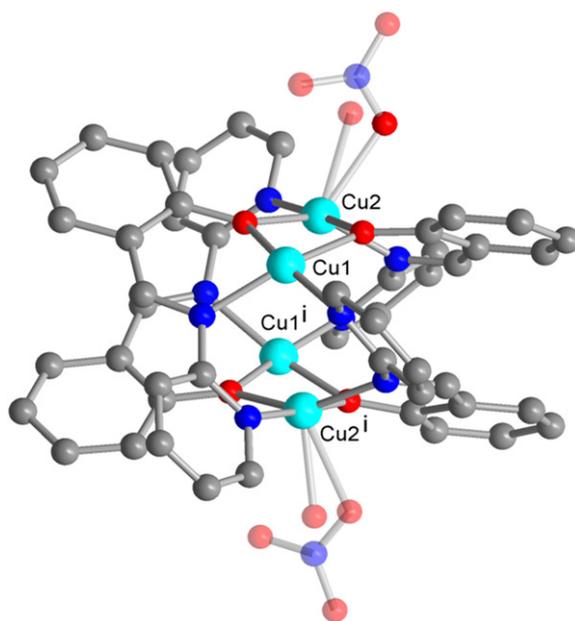
The electronic spectrum of **1** in acetonitrile (Figure 2) shows very strong bands/shoulders below 330 nm with absorption maxima at 295 nm ( $\lambda_{\text{max}}$ ) due to ligand-centered  $n \rightarrow \pi^*/\pi \rightarrow \pi^*$  (LL) transitions. A moderate broad band at 330–550 nm ( $\lambda_{\text{max}} = 376$  nm) is assigned to the metal-ligand (ML) charge transfer transitions. The spectrum further features a very weak broad band in the visible region at 550–1000 nm ( $\lambda_{\text{max}} = 675$  nm) due to the superposition of several metal-centered d-d (MM) transitions (Figure 2, inset) [5, 8b, 16–18].

### 3.3. Structural analysis

X-ray molecular structure determination demonstrates the formation of tetranuclear cationic *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrato)<sub>1.5</sub>-tetra copper(II) nitrate hydroxide, [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>](NO<sub>3</sub>)(OH) (**1**) (Figure 3). The selected bond lengths (Å) and angles (°) are listed in Table 2 and are comparable to the reported values in the literature [21]. The deprotonated ligand (E)-2-((pyridin-2-ylimino)methyl)phenolate (L<sup>-</sup>) does not only chelate to one copper ion with the phenolate-O and imino-N atoms, but also bridges between two neighboring copper ions with the phenolate-O atom. Further, the pyridine-N atom coordinates to a third copper ion, so that each ligand molecule bridges among three copper ions in a  $\kappa^2\text{N,O}:\kappa\text{O}:\kappa\text{N}'$  coordination sphere. Hence, the four copper ions and four chelating-bridging ligands



**Figure 2.** Electronic spectrum of **1** ( $3.2 \text{ mmol dm}^{-3}$ ) in acetonitrile at  $25^\circ\text{C}$ .

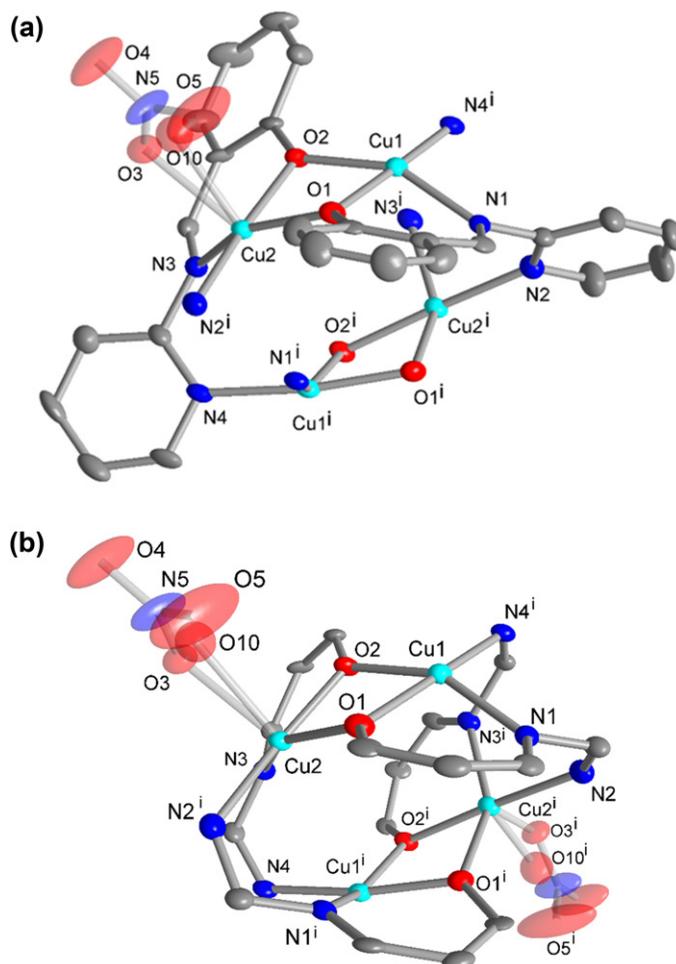


**Figure 3.** X-ray molecular structure for tetranuclear *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide (**1**). The coordinated nitrate anion (75% occupancy) or hydroxide ligand (O10, 25% occupancy) to Cu2 is shown transparent. Symmetry transformation  $i = -x + 1, y, -z + 1/2$ . Hydrogen atoms are not shown for clarity. Selected bond lengths and angles are reported in Table 2.

assemble into a cationic  $[(\text{CuL})_4]^{4+}$  complex. An extended asymmetric unit showing the two unique Cu ions and ligands with their respective full first coordination sphere is shown in Figure 4a. Cu2 is also coordinated by either a nitrate anion (75% occupancy) or a hydroxide ligand (O10, 25% occupancy), which are shown as transparent in Figure 4a. The core of the tetranuclear  $[(\text{CuL})_4(\text{NO}_3)_{1.5}(\text{OH})_{0.5}]^{2+}$  cation thus formed, showing only the coordinating and bridging part of the ligands and the anions, is shown in Figure 4b.

**Table 2.** Selected bond lengths (Å) and angles (°) in 1.

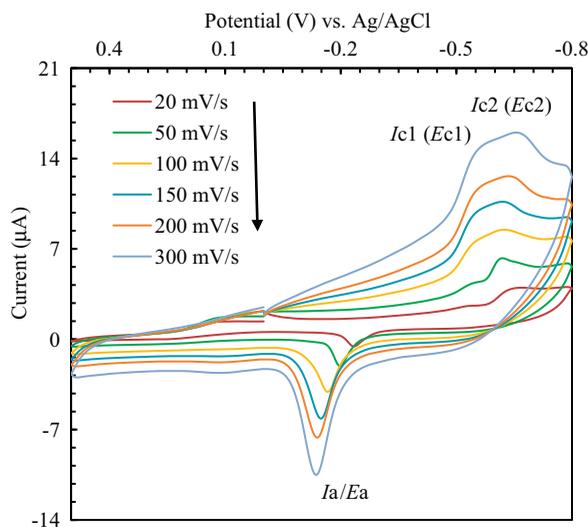
Cu1—O1	1.957(4)	Cu2—N3	1.993(5)
Cu1—O2	1.980(4)	Cu2—N2 <sup>i</sup>	2.008(5)
Cu1—N1	1.989(4)	Cu2—O10	2.25(3)
Cu1—N4 <sup>i</sup>	2.035(5)	Cu2—O3	2.317(6)
Cu2—O2	1.953(4)	N2—Cu2 <sup>i</sup>	2.008(5)
Cu2—O1	1.965(4)	N4—Cu1 <sup>i</sup>	2.035(5)
O1—Cu1—O2	74.90(15)	N3—Cu2—N2 <sup>i</sup>	94.77(19)
O1—Cu1—N1	89.05(17)	O2—Cu2—O10	86.0(7)
O2—Cu1—N1	152.77(17)	O1—Cu2—O10	100.3(8)
O1—Cu1—N4 <sup>i</sup>	171.06(17)	N3—Cu2—O10	107.3(8)
O2—Cu1—N4 <sup>i</sup>	97.60(17)	N2 <sup>i</sup> —Cu2—O10	95.8(7)
N1—Cu1—N4 <sup>i</sup>	95.96(18)	O2—Cu2—O3	89.25(19)
O2—Cu2—O1	75.30(15)	O1—Cu2—O3	122.1(2)
O2—Cu2—N3	89.80(17)	N3—Cu2—O3	85.5(2)
O1—Cu2—N3	147.62(17)	N2 <sup>i</sup> —Cu2—O3	94.5(2)
O2—Cu2—N2 <sup>i</sup>	174.32(18)	Cu1—O1—Cu2	102.58(17)
O1—Cu2—N2 <sup>i</sup>	99.06(18)	Cu2—O2—Cu1	102.18(16)

Symmetry code: (i)  $-x + 1, y, -z + 1/2$ .**Figure 4.** (a) An extended asymmetric unit showing the two unique Cu ions and ligands with their respective full first coordination sphere (50% thermal ellipsoids). Hydrogen atoms are not shown for clarity. (b) Core of the tetranuclear [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>]<sup>2+</sup> cation showing only the coordinating and bridging part of the ligands and the anions (50% thermal ellipsoids). Hydrogen atoms are not shown for clarity.

The packing diagram for the compound is presented in supporting information Figure S2. Only part of the nitrate counteranions and solvent molecules (water) could be located in the voids. The major part of the electron density of 478 electrons/cell in the total potential solvent area volume of 1106 Å<sup>3</sup> (or 19.9% of the unit cell volume of 5571.8 Å<sup>3</sup>) was treated/removed by the SQUEEZE option in PLATON.

### 3.4. Electrochemistry

Cyclic voltammograms of **1** were recorded in acetonitrile at 25 °C over the range of –0.80 to 0.50 V versus Ag/AgCl using variable scans rates, respectively (Figure 5). The reductive wave shows two broad cathodic peaks (*I*<sub>c1</sub> and *I*<sub>c2</sub>) centered at ca. –0.54 V (*E*<sub>c1</sub>) and –0.63 V (*E*<sub>c2</sub>), which become less distinct at higher scan rates. These, most likely, result from one-electron charge transfer processes for the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples, respectively [4, 5, 16, 17, 29, 30]. All four Cu(II) or Cu(I) ions in the cluster are in different chemical environments and are not reduced at exactly the same potential values, but at very close values (overlapped), resulting in a broad peak centering at ca. –0.54 V or –0.63 V. During the anodic wave, it is most likely that there is oxidation of electrodeposited Cu(0), depending on the ligands and solvent which would give either Cu(I) or Cu(II) and provide an anodic peak at ca. –0.23 V (*E*<sub>a</sub>). Thus, the results indicate an irreversible redox process in acetonitrile. Analyses of voltammograms at different scans rates demonstrate that both the reduction and oxidation peaks become intense with shifting to lower and higher potentials, respectively, with faster scans rates (Figure 5 and supporting information Table S1). The results are in accord with related copper(II)-N,O chelate Schiff base complexes [4, 5, 16, 17, 29, 30].



**Figure 5.** Cyclic voltammograms for **1** (ca. 0.5 mmol dm<sup>-3</sup>) at varying scan rates (v/mVs<sup>-1</sup>); TBAP (0.1 mol dm<sup>-3</sup>) in acetonitrile at 25 °C.

## 4. Conclusions

Reaction between (E)-2-((pyridin-2-ylimino)methyl)phenol and copper(II) nitrate provides the tetranuclear *tetrakis*{(E)-2-((pyridin-2-ylimino)methyl)phenolato}(hydroxido)<sub>0.5</sub>(nitrate)<sub>1.5</sub>-tetracopper(II) nitrate hydroxide, [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>](NO<sub>3</sub>)(OH) (1). X-ray molecular structure determination explores the geometry of the complex in which the deprotonated ligand molecule does not only chelate to one copper ion with the phenolate-O and imino-N atoms, but also bridges between two neighboring copper ions with the phenolate-O atom. In addition, the pyridine-N atom coordinates to a third copper ion in such a way that each ligand molecule bridges among three copper ions in a κ<sup>2</sup>N,O:κO:κN' coordination sphere. Hence, four copper ions and four chelating-bridging ligands assemble to form a tetranuclear cationic [(CuL)<sub>4</sub>]<sup>4+</sup>. The two copper ions are further coordinated by either a nitrate or a hydroxide to form the tetranuclear [(CuL)<sub>4</sub>(NO<sub>3</sub>)<sub>1.5</sub>(OH)<sub>0.5</sub>]<sup>2+</sup> cation. CV analysis reveals an irreversible redox process for the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples in acetonitrile.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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