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# Zinc and copper complexes of stilbene iminopyridine ligands with η2-Olefin binding mode

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## ABSTRACT

Two stilbene based iminopyridine ligands (**L1-L2**) synthesized by a condensation reaction between N,N-Dimethyl-4,4′-azodianiline and 2-pyridinecarboxaldehyde or 2,6-pyridinedicarboxaldehyde, with 73% and 65% yield, are described. The two ligands have been characterized by elemental analysis and spectroscopic techniques. The complexation of ligand **L1** with ZnCl$_2$ afforded neutral tetrahedral zinc(II) metal complex **C1** formulated as **[ZnL1Cl$_2$]** with a 2D supramolecular architecture reinforced by $\pi\cdots\pi$ stacking and hydrogen bonding in the solid state. Interestingly in the case of copper(I) complex **C2**, ligand **L1** acts as a ditopic ligand since it coordinates one Cu(I) with an iminopyridyl fragment and a second metal center with an $\eta^2$-olefin binding mode giving rise to a 1D-polymeric structure. The coordination sphere is completed with an acetonitrile solvent molecule leading to a distorted tetrahedral geometry around copper cation and the resulting coordination polymer can be formulated as **{[Cu(L1)$_2$CH$_3$CN] BF$_4$}**. In addition complexation of **L2** with zinc chloride afforded complex **C3** formulated as **[ZnL2Cl$_2$]**. DFT and TDDFT computations permitted to investigate the frontier MOs of all species and to assign their UV–visible absorption bands.

## 1. Introduction

Photochromic compounds are defined as being chemical species that undergo a reversible chemical transformation between two forms having different absorption spectra by light irradiation [1]. Different types of transformations such as *cis*–*trans* isomerization, ionization, pericyclic ring-opening and ring-closing reactions, as well as intramolecular group transfer reactions, are known [2]. Such chemical changes have been the basis of a variety of applications ranging from consumer and cosmetic products, photochromic inks, ophthalmic and sunglass lenses, optical filters, optoelectronic devices and optical memories [3]. Thus, azobenzene and stilbene derivatives have been reported to possess unique photochromic properties with stable *cis* and *trans* geometries related with two efficient and reversible photoisomerization processes on their –N=N– and –C=C– double bonds, respectively [4]. Moreover, this above mentioned reversible isomerization is the basis for many functional materials with applications in nonlinear optics [5], optical storage media [6], chemosensors [7] and optical switches [8]. In contrast, combining photochromic units with a coordinating or a binding unit is a very successful strategy for the design of photochromic transition metal complexes [9]. On this ground, pyridine containing Schiff bases, such as 2-iminopyridyls and 2,6-bisiminopyridyls form stable complexes with various transition metals. They have been used, for instance, in metallo-organic self-assembling media to produce discrete metallo-supramolecular helicates [10], cages [11] and capsules [12] and have also been utilized with a variety of transition metals in catalysis [13]. In addition, d$^{10}$ metal complexes of Schiff base ligands have been successfully used in co-sensitized solar cells [14]. In addition, d$^{10}$ copper(I) cation is known to interact with ethylene in biological systems [15] and this has inspired a great deal of work to prepare and isolate stable copper(1) olefin complexes. This has been achieved using neutral N-donor heterocyclic compounds, including bis(pyrazolyl)methanes [16], dipyridylamine [17]

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phenanthroline [18] and bipyridines [16–19].

Recently, we described the synthesis of a tetrathiafulvalene based iminopyridine ligand and demonstrated the increase in its nonlinear optical response upon metal complexation with zinc(II) ion [20]. Moreover, we have shown a dramatic increase in the nonlinear optical absorption of an azo-based iminopyridine ligand upon complexation with $ZnCl_2$ [21]. As a continuation of our work, we are reporting herein the synthesis and full characterization of two iminopyridine-appended stilbene ligands **L1**, which has been reported in the literature during the ongoing of the present work [22], and **L2** as well as the preparation of two new zinc(II) and copper(I) metal complexes with ligand **L1** and a zinc(II) complex of ligand **L2**. Interestingly, coordination of copper(I) with ligand **L1** gives rise to a stable copper(I)-olefin coordination polymer where **L1** is acting as a ditopic ligand coordinating with both the iminopyridyl and olefin fragments. DFT computations were carried out in order to investigate the electronic structure and properties of the species under consideration. The nonlinear optical properties of these compounds which will be compared with the corresponding azo-based materials are currently under investigations and will be published in due time.

## 2. Experimental

### 2.1. *General remarks*

Commercially available reagents and all solvents for synthesis were of analytical grade and were used without further purification. Reactions were carried out under nitrogen. Nuclear magnetic resonance spectra were recorded on a Bruker 300 MHz spectrometer. The following abbreviations are used to represent the multiplicity of the signals: s (singlet), d (doublet), the spin-spin coupling constants (J) were measured. Infrared spectra were recorded on a Bruker vertex 70 spectrometer; the measurements were recorded in 400–4000 $cm^{-1}$ range. Elemental analyses (C, H and N) were performed on a Thermo-Scientific Flash 2000 Organic. Mass spectrometry measurements were carried out on a Bruker Biflex-III TM which uses 1,8,9-trihydroxyanthracene as a matrix. UV–Visible absorption spectra were recorded at room temperature in quartz cuvettes using a Perkin Elmer spectrophotometer.

### 2.2. *Crystallography*

Experimental X-ray diffraction data on single crystals were collected at room temperature using a Bruker Nonius Kappa CCD diffractometer operating with Mo-K$\alpha$ ($\lambda = 0.71073$ Å) for complexes **C1** and **C2**. For complex **C3** data were collected at 150 K on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector and mirror monochromated micro-focus Cu-K$\alpha$ radiation ($\lambda = 1.54184$ Å). All the structures were solved by direct methods, expanded and refined on $F^2$ by full matrix least-square techniques using SHELX97 programs. All non-H atoms were refined anisotropically and the H atoms were included in the calculation without refinement. Multi-scan empirical absorption was corrected using the SADABS program (Bruker AXS area detector scaling and absorption correction,v2008/1) for complexes **C1** and **C2** and using the CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.37.35 g, 2014) for complex **C3**. Details of the single crystal X-ray experiments and crystal data are summarized in Table 1.

### 2.3. *Synthesis of compounds* ***L1*****,** ***C1*****,** ***C2*****,** ***L2*** *and* ***C3***

#### 2.3.1. *Synthesis of N, N-dimethyl-4-((E)-(pyridin-2-ylmethylene) amino)styryl) aniline (**L1**)*

This ligand **L1** has been prepared with a slight modification from the procedure described earlier [22].

A solution of (E)-4-(4-aminostyryl)-N,N-dimethylaniline (0.200 g, 0.61 mmol) and 2-formylpyridine (0.065 g, 0.61 mmol) in ethanol (20 mL) and a few drops of acetic acid were heated under reflux overnight. After cooling to room temperature, the precipitate formed was filtered off and washed with ethanol. The desired product **L1** was obtained as an orange powder with 73% yield (0.147 g, 0.449 mmol). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$/ppm: 8.72 (d, 1H, $J = 4.20$ Hz, H1), 8.66 (s, 1H, H6), 8.22 (d, 1H, $J = 7.92$ Hz, H4), 7.85 (m, 1H, H2), 7.53 (d, 2H, $J = 8.40$ Hz, H9 and H11), 7.43 (d, 2H, $J = 8.80$ Hz, H16 and H20), 7.35 (m, 1H, H3), 7.31 (d, 2H, $J = 8.50$ Hz, H8 and H12), 7.08 (d, 1H, $J = 16.30$ Hz, H13 or H14), 6.93 (d, 1H, $J = 16.30$ Hz, H14 or H13), 6.85 (d, 2H, $J = 8.80$ Hz, H17 and H19), 2.99 (s, 6H, H21 and H22). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$/ppm: 159.46 (C6), 154.80 (C18), 150.21(C5), 149.74 (C1), 149.14 (C7), 137.23 (C3), 136.67 (C10), 128.99 (C13 or C14), 127.65 (C9 and C11), 126.85 (C16 and C20), 125.73 (C2), 125.01 (C15), 123.69 (C13 or C14), 121.88 (C8 and C12), 121.74 (4), 115.31 (C17 or C19), 112.47 (C17 or C19), 40.48 (C21 and C22). Anal. Calc. for $C_{22}H_{21}N_3$: C, 80.70%; H, 6.46%; N, 12.83%. Found: C, 80.72%; H, 6.21%; N, 12.56%. Selected IR bands ($cm^{-1}$): $\nu = 1603$, 1519, 1348, 1076, 828. MALDI-TOF MS calcd: $m/z = 327.17$ Da. Found: $m/z = 327.4$. HR-MS (M): for $C_{22}H_{21}N_3$: 327.1735. Found 327.1730 ($M^+$).

#### 2.3.2. *Zinc(II) complex [ZnL1Cl$_2$] (**C1**)*

In a test tube, a solution of ligand **L1** (0.020 g, 0.06 mmol) in $CH_2Cl_2$ (5 mL) was mixed with a solution of $ZnCl_2$ (0.008 g, 0.06 mmol) in $CH_3CN$ (5 mL) and ultrasonicated for 2 min. On top of the resulting solution, a layer of diethyl ether was added, which led to the formation of single crystals of complex **C1** after two days. Yield: 81% (0.023 g, 0.049 mmol). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$/ppm: 8.86 (d, 1H, $J = 4.4$ Hz, H1), 8.76 (s, 1H, H6), 8.17 (m, 1H, H2), 7.92 (d, 1H, $J = 7.60$ Hz, H4), 7.75 (d, 2H, $J = 8.5$ Hz, H9 and H11), 7.75 (m, 1H, H3), 7.56 (d, 2H, $J = 8.4$ Hz, H8 and H12), 7.44 (d, 2H, $J = 8.7$ Hz, H16 and H20), 7.13 (d, 1H, $J = 16.4$ Hz, H13 or H14), 6.90 (d, 1H, $J = 16.0$ Hz, H14 or H13) 6.72 (d, 2H, $J = 8.8$ Hz, H17 and H19), 3.01 (s, 6H, H21 and H22)· $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$/ppm: 159.46 (C6), 154.76 (C18), 150.19 (C5), 149.74 (C1), 149.11 (C7), 137.23 (C3), 136.70 (C10), 128.98 (C13 or C14), 127.66 (C9 or C11), 127.19 (C9 and C11), 126.85 (C16 and C20), 125.70 (C2), 125.39 (C15), 125.04, 124.63, 123.66, 121.90, 121.75, 115.32, 112.46, 40.49. Anal. Calc. for $C_{22}H_{21}N_3ZnCl_2$: C, 56.98%; H, 4.36%; N, 7.21%. Found: C, 56.61%; H, 4.31%; N, 6.95%. Selected IR bands ($cm^{-1}$): $\nu = 1591$, 1520, 1363, 1098, 827. MALDI-TOF MS calcd: $m/z = 425.59$ Da. Found: $m/z = 426.0$ HR-MS (M): for $C_{22}H_{21}N_3ZnCl$: 426.0715. Found 426.0722 ($[ZnL1Cl]^+$).

#### 2.3.3. *Copper (I) complex* **{[Cu(L1)$_2$CH$_3$CN]BF$_4$}** *(**C2**)*

In a test tube, a solution of ligand **L1** (0.020 g, 0.06 mmol) in $CH_2Cl_2$ (5 mL) was mixed with a solution of $Cu(CH_3CN)_4BF_4$ (0.0094 g, 0.03 mmol) in $CH_3CN$ (5 mL) and sonicated for 2 min. On top of the resulting solution, a layer of diethyl ether was added which led to the formation of single crystals of complex **{[Cu(L1)$_2$CH$_3$CN]BF$_4$} C2** after one week. Yield: 57% (0.013 g, 0.017 mmol). Anal. Calc. for $C_{46}H_{45}N_7CuBF_4$: C, 65.29%; H, 5.36%; N, 11.56%. Found: C, 64.97%; H, 4.92%; N, 11.13%. Selected IR bands ($cm^{-1}$): $\nu = 1593$, 1597, 1473, 1440, 1050, 848. MALDI-TOF MS calcd: $m/z = 717.28$ Da. Found: $m/z = 717.5$ HR-MS (M): for $C_{44}H_{42}N_6Cu$: 717.2767. Found: 717.2763 ($[Cu(L1)_2]+$).

#### 2.3.4. *Synthesis of 4,4′-((1E,1′E)-(((1E,1′E)-(pyridine-2,6-diylbis(methanylylidene)) bis(azanylylidene))bis(4,1-phenylene)) bis(ethene-2,1-diyl))bis(N,N-dimethylaniline) (**L2**)*

The synthesis of ligand **L2** was similar to that of ligand **L1**. Thus, 4-(4-aminostyryl)-N,N-dimethyaniline (0.200 g, 0.61 mmol) was