



Azo-based iminopyridine ligands: synthesis, optical properties, theoretical calculations and complexation studies



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ABSTRACT

We describe herein the full characterization of azobenzene based iminopyridine ligands (**L1**–**L4**) synthesized by a condensation reaction between *N,N*-Dimethyl-4,4'-azodianiline or 4-(4-nitrophenylazo)aniline and 2-pyridinecarboxaldehyde or 2,6-pyridinedicarboxaldehyde. The UV–visible absorption bands of these ligands were fully assigned using DFT and TD-DFT computations. The complexation of ligand **L1** and ligand **L2** with AgNO₃ afforded two neutral silver metal complexes formulated as [Ag**L1**NO₃] and [Ag**L2**NO₃], respectively. The crystal structure analysis of the two complexes indicate the presence of a Y-shaped tricoordinated silver (I) ion for [Ag**L1**NO₃] and a tetracoordinated silver(I) ion displaying rather rare and distorted square planar geometry for [Ag**L2**NO₃]. In solid state, for both complexes, a 3D supramolecular architecture is generated via hydrogen bonds of type C–H⋯O and C–H⋯π. The UV–visible spectrophotometric titration studies of ligands **L1**–**L4**, by increasing amount of AgNO₃ or of ZnCl₂ indicates the possibility of forming transition metal complexes with these ligands.

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1. Introduction

Azobenzene^{1,2} and its numerous derivatives are widely commercially available, currently used as dyes and represent 60–70% of the world production of 'absorbing molecules'.³ They are known to possess unique photochromic properties with stable *cis* and *trans* geometries related by two efficient and reversible photoisomerization processes. This *trans*-to-*cis* photoisomerization occurs usually by UV light irradiation of the π – π^* absorption band while the reverse *cis*-to-*trans* isomerization takes place by blue light irradiation resulting in the n – π^* absorption band.^{4,5} Such remarkable property is the basis of many applications in, for example, nonlinear optics,⁶ optical storage media,⁷ chemosensors,⁸ optical switches^{9,10} as well as trigger for protein folding.¹¹ One of the ongoing challenges lies in the preparation of multifunctional molecular materials that are based on combinations of two molecular units bearing two different physical properties. This recent activity is due to the potential of these materials to exhibit coexistence and synergy between two different physical properties or to provide new advanced

molecular functions. On this ground, many efforts have been devoted to the association of a coordinating or binding unit to an azobenzene photofunctional unit to produce azo-conjugated transition metal complexes. For example, metal complexes of dithiolates,¹² catecholates,¹³ bipyridines,⁹ terpyridines,^{14,15} salens,^{16–18} diamines¹⁹ and, more recently, iminopyridine-based ligands have been reported.^{20,21} Such pyridine based Schiff bases ligands with chelating abilities are well known to form stable complexes with a large variety of transition metals. They have therefore found wide use, for example, in metallo-organic self-assembling media generating different topologies like discrete metallo-supramolecular helicates,^{22–24} cages²⁵ and capsules.²⁶ In addition, they have been utilized with a variety of transition metals as catalysts for ethylene polymerization²⁷ or oxidation of secondary alcohols.²⁸

Recently we have reported the preparation of an electroactive bisiminopyridine ligand²⁹ and demonstrated the positive effect of the metal complexation with zinc(II) ion on the nonlinear optical properties of this ligand.³⁰ Moreover we have shown a dramatic enhancement of the nonlinear optical absorption of an azo-based iminopyridine ligand upon complexation with ZnCl₂.²⁰ As a continuation of our work, we report herein the synthesis and full characterization of a series of iminopyridine-appended azobenzene

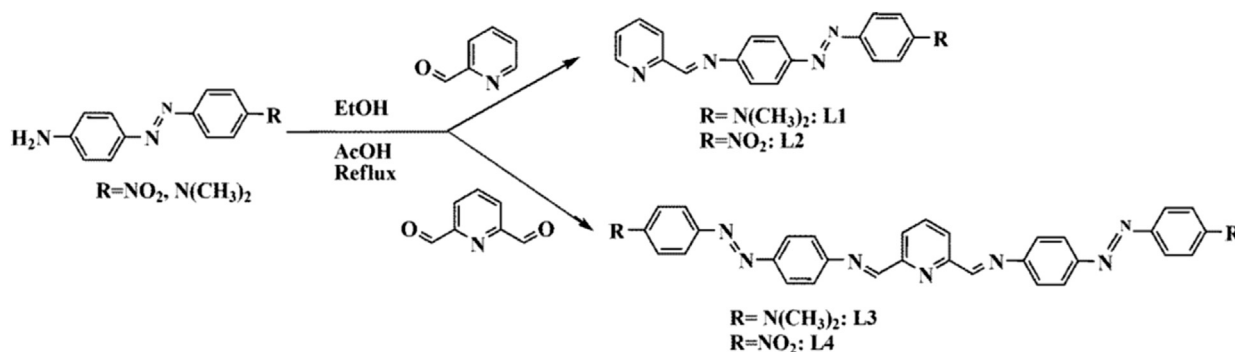
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ligands, complexation studies as well as the preparation of two new silver(I) metal complexes.

2. Results and discussion

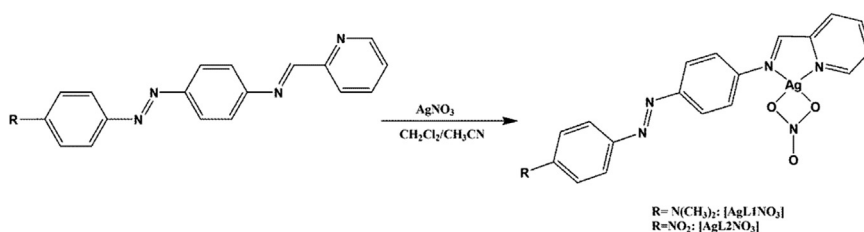
2.1. Synthesis

Ligands **L1–L4** were prepared by a condensation reaction between *N,N*-Dimethyl-4,4'-azodianiline or 4-(4-nitrophenylazo)aniline with 2-formylpyridine or 2,6-pyridinedicarboxaldehyde in ethanol and a catalytic amount of acetic acid in 63%–80% yield (Scheme 1).



Scheme 1. Synthetic scheme of ligands **L1–L4**.

In a recent work published by us, the complexation of ligand **L1** with zinc chloride (ZnCl_2) afforded a mononuclear complex $[\text{ZnL1Cl}_2]$ showing a stronger nonlinear absorption than its ligand.²⁰ Here, the reaction between ligand **L1** or **L2** and the silver nitrate in a 1:1 ratio lead to the formation of monomeric complexes described here by the formula, $[\text{AgL1NO}_3]$ or $[\text{AgL2NO}_3]$ (Scheme 2). Note that the complexation of ligand **L2** with zinc chloride (ZnCl_2) afforded the corresponding zinc (II) complex as evidenced by mass spectrometry analysis. These results indicate a negligible effect of the electron-withdrawing effect of the nitro groups regarding the complexation ability of ligand **L2**.



Scheme 2. Synthetic scheme of complex $[\text{AgL1NO}_3]$ and $[\text{AgL2NO}_3]$.

2.2. Crystal structure description

Suitable X-ray crystals were obtained for the two complexes $[\text{AgL1NO}_3]$ and $[\text{AgL2NO}_3]$ enabling us to determine their crystal structure (Fig. 1). Selected parameters of the X-ray diffraction data collection and refinement are gathered in Table 1.

Within the crystal structure of $[\text{AgL1NO}_3]$ ligand **L1** chelates $\text{Ag}(\text{O}1)$ through its two nitrogen atoms from the iminopyridine fragment and together with a third oxygen atom provided by the

nitrate anion, define a distorted Y-shaped coordination geometry around $\text{Ag}(\text{I})$ metal ion. In $[\text{AgL2NO}_3]$ the silver(I) ion is tetra-coordinated displaying rather rare and distorted square planar geometry, being chelated by both ligand **L2** and a nitrate ion. It is obvious that the cause of the distortion of the geometry around the silver(I) ion, in both complexes, is due to the chelating coordination mode of ligand **L1** in complex $[\text{AgL1NO}_3]$, and **L2** and nitrate ion in complex $[\text{AgL2NO}_3]$, where the small bite angle determines angle values (see Table 2) significantly inferior to the corresponding values in a trigonal and, respectively square planar stereochemistry. Furthermore, in the description of the environment of the silver (I) in $[\text{AgL1NO}_3]$, the weak $\text{Ag}\cdots\text{O}$ and $\text{Ag}\cdots\text{N}$ interactions ($\text{AgO}1\cdots\text{O}1$

2.8447 (25) Å and $\text{AgO}1\cdots\text{N}4$ 2.6970 (28) Å) between the metal center and one oxygen atom from the nitrate ion and, respectively one nitrogen atom from the azo fragment of ligand **L1** from a vicinal molecule, were not taken into consideration.

Analyzing the crystal packing of complex $[\text{AgL1NO}_3]$ a 3D supramolecular network constructed by intermolecular $\text{C}\cdots\text{H}\cdots\text{O}$ and $\text{C}\cdots\text{H}\cdots\pi$ contacts (Table S3) is revealed (Fig. 2).

The crystal packing of complex $[\text{AgL2NO}_3]$ (Fig. 3) revealed the presence of numerous $\text{C}\cdots\text{H}\cdots\text{O}$ contacts established by two of oxygen atoms from the coordinated nitrate anion and the two oxygen atoms of nitro group of **L2** as well as off-set $\pi\cdots\pi$ stacking between

the aromatic rings of **L2** (with distances centroid-centroid of 3.55 and 3.93 Å).

2.3. UV–visible absorption spectroscopy

Fig. 4 shows the normalized UV–visible absorption spectra of ligands **L1–L4** that were recorded in dichloromethane solution ($\sim 2 \times 10^{-5}$ M) at room temperature. Ligands **L1** and **L3** exhibit two strong electronic absorption bands at $\lambda = 266$ nm and 438 nm for **L1**

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