Synthesis and characterization of luminescent zinc(II) complexes with a N,N-bidentate 1-pyridylimidazo[1,5-a]pyridine ligand

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ABSTRACT

Ligand 2-(1-(pyridin-2-yl)imidazo[1,5-a]pyridin-3-yl)phenol (**L**) has been reacted in a 2:1 molar ratio with different $Zn(Y)_2 n H_2O$ salts, where Y represents a polyatomic anion (Y = ClO_4^-, NO_3^-, BF_4^-, PF_6^-). The X-ray structural analysis performed on two of the derivatives obtained, namely $[Zn(\mathbf{L})_2(ClO_4)](ClO_4) \cdot H_2O$ (**1**) and $[Zn(\mathbf{L})_2(CH_3CN)_2](BF_4)_2$ (**6**), proves that as expected ligand **L** binds in a *N,N*-bidentate mode via the pyridine ring (N_{py}) and the pyridine-like nitrogen of the imidazo[1,5-a]pyridine skeleton (N_{im}). A spectroscopic investigation (including infrared, elemental analysis, ^{1}H and ^{31}P NMR, thermogravimetric analysis) has been performed on these species, allowing complete characterizations. A preliminary survey on their photophysical properties in the solid state was carried out: the complexes showing intense luminescence when excited with UV light (λ_{exc} = 421–469 nm) with λ_{max} of emission in the blue-green range (468–500 nm) and moderate absolute photoluminescence quantum yields (PLQYs).

1. Introduction

Transition metals based luminescent compounds are receiving increasing attention due to their applications for solid state optical devices, such as organic light emitting diodes (OLEDs) [1] and dye sensitized solar cells (DSSCs) [2] or for fluorescence sensing [3]. Most of the complexes used so far are based on heavy second- or third-row transition metals, such as Pt(II) [4], Ir(III) [5], Ru(II) [6] or Re(I) [7]. Unfortunately, these metals are quite rare and expensive, and consequently a crucial aim in this field is the synthesis of luminescent compounds based on less expensive and more abundant transition metals. Among other metal centers, those with d^{10} configuration proved to satisfy this goal [8] and reports on OLEDs based on M(I) (M = Cu, Ag, Au) [9] or M(II) (M = Zn, Cd) [10] already appeared in the literature. In this regard, Group 12 metals including both mononuclear [11] and polynuclear [12] compounds have revealed high luminescent performances and especially compounds containing neutral N-based ligands have showed great promises. Relevant examples of M(N∩N)X$_2$ systems (M = Zn, Cd; N∩N = bidentate nitrogen ligand; X = halide) with luminescent properties have been published. Wang has coordinated substituted 2,2′-bipyrimidines [13] and 2,2′-dipyridylamino derived ligands [14] to ZnCl$_2$. Other functionalized dipyridylamines

have been recently used by Song [15] and Schindler [16]. Similarly, Ghosh [17] reported on the structure and photoluminescence behavior of Zn(II) and Cd(II) atropisomers with unsymmetrical diimines, while very recently Larionov synthesized luminescent Zn(II) and Cd(II) complexes containing pyridophenazine derivatives [18]. In addition, the luminescent properties of bi- and tri-substituted $[Zn(N-N)_n]^{2+}$ compounds (n = 2, 3) have been deeply investigated, with N-N being phenanthroline [19,20], 2,2′-bipyridyl [21], pyridyl-imidazole [22] or functionalized terpyridine [23].

In the past, we widely explored the coordination chemistry of N-based multidentate ligands [24], with special attention to pyrazole and its analogs (imidazole, triazole) both in their neutral [25] and anionic azolate forms [26]. The corresponding transition-metal complexes have found applications in catalysis, material science or in the synthesis of polynuclear systems. Continuing our investigation on N-based ligands, we lately conducted a study on the photophysical properties of zinc(II) compounds with 3-aryl-substituted 1-pyridylimidazo[1,5-a]pyridine ligands. Heterocycles having the imidazo[1,5-a]pyridine skeleton are known to possess unique photophysical properties [27] with potential applications in the field of OLEDs [28] and organic thin-layer field effect transistors (FET) [29]. Moreover, different 1-pyridylimidazo[1,5-a]pyridines have been coordinated to transition metals giving rise to highly luminescent coordination compounds based on Re(I) [30], Zn(II) or Cd(II) [31] and Ru(II) or Os(II) [32] metal centers. In a recent paper, we reported on the blue emission of Zn(II) complexes obtained via coordination of two 1-(pyridin-2-yl)imidazo[1,5-a]pyridinyl

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ligands, namely 1-(pyridin-2-yl)-3-*o*-tolylimidazo[1,5-*a*]pyridine and 2-(1-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-3-yl)phenol, to ZnX$_2$ fragments (X = Cl, Br, I) [33]. Herein, we reacted ligand 2-(1-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-3-yl)phenol (**L**) with Zn(Y)$_2$ salts, where Y represents a polyatomic anion (Y = ClO$_4^-$, NO$_3^-$, BF$_4^-$, PF$_6^-$). The synthesis and spectroscopic characterization of these compounds are reported and show the zinc center surrounded by two molecules of ligand **L**. A preliminary exploration of the photoluminescent properties of these species in the solid state was also performed: a bathochromic shift with respect to free ligand is observed for all the derivatives investigated, intra-ligand $\pi-\pi^*$ transitions being responsible for fluorescence, as expected for a *N*,*N*-chelating ligand coordinated to a closed shell Zn^{2+} ion.
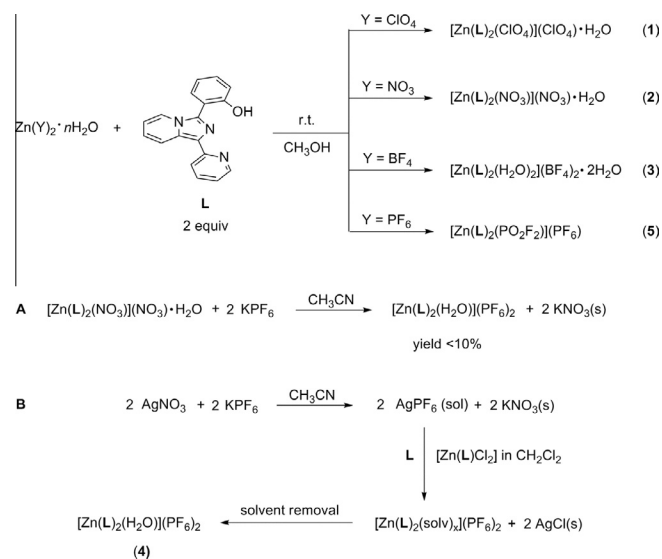
2. Results and discussion

2.1. Syntheses and spectroscopic characterization

2-(1-(Pyridin-2-yl)imidazo[1,5-*a*]pyridin-3-yl)phenol (**L**) was obtained as a light yellow powder according to a published procedure [34] and its purity was assessed by ^{1}H, ^{13}C{^{1}H} NMR and elemental analysis. Complexes **1**, **2** and **3** have been prepared following similar procedures (Scheme 1), by reacting ligand **L** with the corresponding zinc(II) salt, namely Zn(ClO$_4$)$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O and Zn(BF$_4$)$_2$·*n*H$_2$O, in a 2:1 ligand:metal ratio, in methanol, at room temperature. They all are yellow crystalline powders and have been characterized by elemental analysis, infrared spectroscopy and thermogravimetric analysis (TGA). They are formulated respectively as [Zn(**L**)$_2$(ClO$_4$)](ClO$_4$)·H$_2$O (**1**), [Zn(**L**)$_2$(NO$_3$)](NO$_3$)·H$_2$O (**2**) and [Zn(**L**)$_2$(H$_2$O)$_2$](BF$_4$)$_2$·2H$_2$O (**3**).

On the contrary, the direct reaction of Zn(PF$_6$)$_2$·*n*H$_2$O (prepared as described in the experimental) with two equivalents of **L**, following the aforementioned procedure, did not generate complex [Zn(**L**)$_2$(H$_2$O)](PF$_6$)$_2$ (**4**). Actually, the product isolated after workup was later formulated as [Zn(**L**)$_2$(PO$_2$F$_2$)](PF$_6$) (**5**) in accordance with the elemental analysis and ^{31}P{^{1}H} NMR evidences (Scheme 1). The water molecules in the starting zinc(II) hexafluorophosphate salt caused partial hydrolysis of the PF$_6^-$ to PO$_2$F$_2^-$ [35]. Consequently, a different approach was followed to prepare pure [Zn(**L**)$_2$(H$_2$O)](PF$_6$)$_2$ (**4**): first, a metathetic exchange reaction was performed (Scheme 1, **A**) by treating a suspension of complex [Zn(**L**)$_2$(NO$_3$)](NO$_3$)·H$_2$O (**2**) in acetonitrile with two equivalents of KPF$_6$. Unfortunately, incomplete NO$_3^-$/PF$_6^-$ substitution occurred, and compound **4** was recovered in very low yield (<10%). Thus, despite silver hexafluorophosphate being known to undergo partial hydrolysis, a reaction involving AgPF$_6$ was attempted (Scheme 1, **B**). This salt was added to a dichloromethane solution of compound [Zn(**L**)Cl$_2$] (prepared as described in Ref. [33]), resulting in the formation of insoluble AgCl and a solution of **4**, which was isolated as a yellow powder after removal of the solvent and recovery with diethylether.

In their infrared spectrum (nujol mull, Figs. S1–S5 in Supporting information) all zinc derivatives show the typical pattern of the ligand, with sharp and intense stretching bands in the region 1614–1516 cm^{-1} and an additional band of medium intensity around 1640 cm^{-1} ($\nu_{C=N}$). Furthermore, the infrared spectra of compounds **1**–**5** show a very broad band at about 3300 cm^{-1} due to the OH vibration, and a broad stretching in the region 1300–1000 cm^{-1} attributable to the counteranions.

The ^{1}H NMR spectra (CD$_3$C(O)CD$_3$, 25 °C, Figs. S6–S10 Supporting information) of complexes **1**–**5** show the expected pattern of ligand **L**, with some shifts due to the *N*,*N*-coordination to the metal center. Low-intensity additional peaks associated to free ligand are also detected, thus suggesting a possible lability for these complexes, with ligand **L** partially dissociated in solution. The ^{31}P{^{1}H} NMR

Scheme 1. Syntheses of compounds **1**–**5**.

spectrum of compound [Zn(**L**)$_2$(H$_2$O)](PF$_6$)$_2$ (**4**) (Fig. S11, top) shows the expected septet ($^1J_{PF}$ = 708 Hz) due to uncoordinated hexafluorophosphate. As previously mentioned, treatment of Zn(PF$_6$)$_2$ hydrate with two equivalents of ligand **L** afforded the complex [Zn(**L**)$_2$(PO$_2$F$_2$)](PF$_6$)$_2$ (**5**), which showed a different ^{31}P NMR pattern. Actually, in accordance with other PF$_6^-$–PO$_2$F$_2^-$ containing transition metals compounds [35], the spectrum recorded for **5** consists of two sets of distinct sharp signals, respectively centered at −17.9 ppm and −144.4 ppm (Fig. S11, bottom). The upper field signal appears as a septet ($^1J_{PF}$ = 706 Hz) and is associated to uncoordinated PF$_6^-$, whereas the lower field signal is a triplet ($^1J_{PF}$ = 950 Hz) and attributed to μ-PO$_2$F$_2^-$.

The presence of water molecules in the complexes have been confirmed by thermogravimetric analysis (TGA, Figs. S12–S15 in Supporting information). In the TGA plot recorded for [Zn(**L**)$_2$(ClO$_4$)](ClO$_4$)·H$_2$O (**1**) (Fig. S12) a weight loss of 1.95% is detected at about 60 °C and associated to the presence of one water molecule (calculated m/m loss = 2.10%) in the crystal packing of **1**. This feature was eventually confirmed by single crystal X-ray analysis performed on **1**. For compound [Zn(**L**)$_2$(H$_2$O)$_2$](BF$_4$)$_2$·2H$_2$O (**3**), the TGA trace (Fig. S14) shows two consecutive and distinct losses (4.12%), respectively at about 100 °C and 260 °C, associated to the presence of four water molecules (in accordance to elemental analysis). Most probably, two different kind of water molecules interact with the complex: the first two molecules, lost at 100 °C (calculated m/m loss = 4.06%) likely belong to the outer coordination sphere of [Zn(**L**)$_2$(H$_2$O)$_2$](BF$_4$)$_2$·2H$_2$O. It is then necessary to heat the sample up to 260 °C [36–38] to lose the two remaining water molecules in the first, inner coordination sphere around the metal center (calculated m/m loss = 4.23%). Also for compounds [Zn(**L**)$_2$(NO$_3$)](NO$_3$)·H$_2$O (**2**) (drop: −2.47% (experimental) versus −2.30% (calculated), Fig. S13) and [Zn(**L**)$_2$(H$_2$O)](PF$_6$)$_2$ (**4**) (drop: −1.99% (experimental) versus −1.90% (calculated), Fig. S15) the experimental data are in good agreement with the expected values.

2.2. X-ray crystal structures

Complex [Zn(**L**)$_2$(ClO$_4$)](ClO$_4$)·H$_2$O (**1**) was characterized via single-crystal X-ray diffraction analysis (Fig. 1). In **1**, the zinc center shows a penta-coordination, with a N$_4$O environment deriving from two molecules of ligand **L**, each binding in a *N*,*N*-bidentate