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Syntheses of a pyrene-based π-expanded ligand and the corresponding platinum(II) complex, bis[2-[(octylimino)methyl]-1-pyrenolato-*N*,*O*] platinum(II)

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ABSTRACT

A pyrene-based new ligand (**1**) attaching hydroxyl and imine group, *i.e.*, a salicylaldimine-style ligand based on pyrene, was designed and synthesized. The ligand was prepared from the commercially available pyrene in five steps. A treatment of this ligand **1** (L) with $Pt(II)Cl_2(PhCN)_2$ in the presence of AcONa in PhCl afforded the corresponding metal complex, $Pt(II)L_2$ (**2**) (80%). Single crystal diffraction study revealed that the complex is a square planar four-coordinated platinum(II) complex. The ligands bind to the metal in *trans*-manner. The coordination geometry, *i.e.*, bond distances and angles for the coordination site, is the typical of the reported platinum(II) salicylaldiminatos, *e.g.*, the mean Pt–N distance (*d*(Pt–N)): 2.011 and *d*(Pt–O): 1.994 Å, respectively. The expansion of the π-system of the ligand induces the bathochromic shift in absorption spectra. The lowest excitation energy of **2** was found at 520 nm. Theoretical studies suggest that this phenomenon is attributable to the narrowing intramolecular HOMO–LUMO gap of **2**.

1. Introduction

The chemistry of metal complexes with the ligands based on aromatic molecules (MArLs) has been attracting much attention since the beginning of the last century [1–3]. To obtain elaborated physical properties on MArLs, chemical modification of the ligand (ArLs) is one of the most promising strategies. Among these methods, the replacement of π-system of the ligand-nucleus to π-expanded aromatic molecules induces drastic change in the properties of the resultant complexes. This method was introduced by Calvin and coworkers in the middle of 1940s, as far as our best knowledge is concerned [2,4,5]. They replaced benzene moiety of salicylaldehyde (SA) to π-expanded naphthalene, *i.e.*, 1-hydroxy-2-naphthaldehyde, 2-hydroxy-1-naphthaldehyde, and 3-hydroxy-2-naphthaldehyde, and prepared a series of transition metal complexes. In these studies, they revealed the relationship between the stability constant of the complex and the delocalication of π-electrons [4]. After the pioneering work of Calvin, the research interest shifts to the development of advanced materials focusing on the physical properties induced by narrow HOMO–LUMO gap which is the typical achievement of the π-expansion. The field of the typical application is the development of light absorption–emitting materials including electroluminescent devices [6–8].

With an aim at opening a new coordination chemistry, the authors focused on pyrene for the nucleus of ArLs because of its rich sciences, *e.g.*, large in size, expanded delocalized π-electronic system, low oxidation potential, and long-lived excited state [9]. The ligand **1** was designed considering the vast coordination chemistry of *N*-alkylsalicylaldiminatos, *i.e.*, introducing hydroxyl and imine groups on 1- and 2-positions of pyrene, respectively [10]. Furthermore, we performed the metallation reaction of **1** with Pt(II) considering the future application of this complex, **2**, in the field of photochemistry [8].

Here we report the molecular design of the ligand **1**, the synthesis and basic properties of the corresponding Pt(II) complex **2**, and the single crystal diffraction study of **2**.

2. Result and discussion

2.1. Synthesis

The syntheses of the ligand (**1**) and the corresponding platinum(II) complex (**2**) are shown in Scheme 1. The important intermediate, **5**, was prepared according to the literatures from the commercially available pyrene in four steps [11]. A treatment of *n*-octylamine on **5** afforded **1** quantitatively as moderately soluble red solids.

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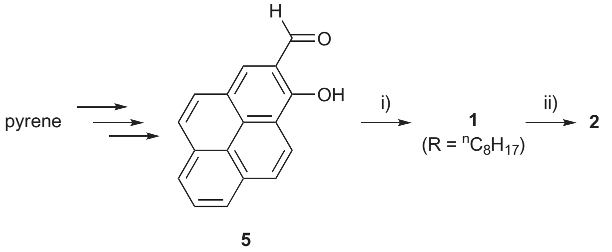
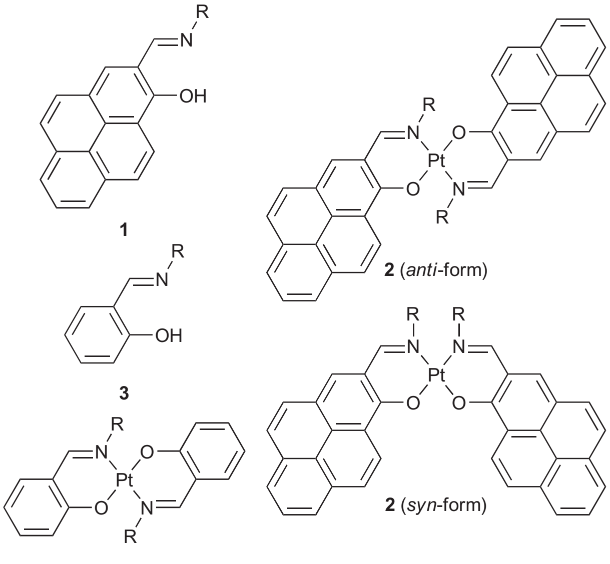


Scheme 1. Reagents and conditions: (i) *n*-octylamine/CH_2Cl_2/RT, (ii) $PtCl_2(PhCN)_2$/AcONa/PhCl/reflux.

To demonstrate the potential of **1**, we chose platinum(II) for the complex formation reaction of **1** considering the stability of platinum(II) salicylaldiminato (**4**) under ambient condition. Although the syntheses of the most of Pt(II) *N*-alkylsalicylaldiminatos use K_2PtCl_4 [12–14] and/or more specific Pt reagents,[15] $PtCl_2(PhCN)_2$ was used in our study considering the solubility of the metal source in PhCl, which is the suitable solvent to dissolve **1**. Initially, a treatment of a half equivalent of $PtCl_2(PhCN)_2$ only gave a complex mixture. The addition of base, AcONa, resolved this problem. Sparingly soluble **2** was obtained from the reaction mixture as the red solid (80%). It should be mentioned that the new complex **2** is stable under ambient condition and/or toward the usual manipulations such as silica-gel chromatography and recrystallization from hot solvents, *e.g.*, boiling toluene, under the air and room light. The reference complex **4** was prepared according to the literature reported for the similar complex having another alkyl group [16–19].

2.2. Diffraction study

Considering the behaviors of other platinum(II) *N*-alkylsalicylaldiminatos, two configurations are possible for the structure of **2**, *anti*- and *syn*-forms (Formula) [12–14]. The structure of **2** was determined to be *anti*-form straightforwardly by single crystal diffraction study. Theoretical studies also suggest the *anti*-form is more stable than the *syn*-form, 12.53 kcal mol^{-1} (*vide infra* and Electronic supplementary materials (ESM)-#3, pp. 30–32).



Alkyl group of **1** ~ **4**: R = $^nC_8H_{17}$

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The crystal of **2** is made up crystallographically independent two complexes, *Complex #1* and *Complex #2* and the structure of *Complex #1* is represented in Fig. 1. The figures of *Complex #2* and the detailed bond distances and angles of the both are summarized in ESM-#2. As clear from this figure, **2** holds square planar four-coordinate platinum(II). The mean bond distances for Pt–N and Pt–O of **2** are 2.011, and 1.994 Å, respectively. Fernández-G and coworkers proposed that the former bond distance, metal-N bond, correlates with the electron delocalization of the ligand in their studies on Ni(II) salicylaldiminatos and the imines of hydroxynapthaldehydes [20]. The mean distance of **2**, 2.011 Å, is in the range of reported values for structurally similar Pt(II) complexes, *e.g.*, *N*-alkylsalicylaldiminatos: 2.001–2.02 Å or 1.945–2.009 for *N,N′*-ethylenebis(salicylimine) (see pp. 13–15 of ESM-#2). In addition, other values which characterize the coordination chemistry of **2** including Pt–O bond distances and bond angles for N–Pt–O are also similar to those of the reported Pt(II) complexes. Therefore, the effects of expansion and/or delocalization of π-electrons on the coordination geometry are still unclear in the scope of our study.

Although the coordination motif of **2** is capable of being classified into square-planar coordination, the complex is distorted in the crystal. Mean planes were fitted by 11 atoms of coordination moiety and/or 41 atoms of the complexes (*Plane #1* and *Plane* #2 in ESM-#2). The deviations of the individual atoms from theses mean planes are less than 1.2 Å (see ESM-#2). The planarity was estimated by the root-mean square out-of-plane displacement, Δ, and the values are 86×10^{-3} and 29×10^{-3} Å for Complex #1 and #2 to *Plane #1*, respectively. These nonplanarities were also observed for **4**. The Δs of **4** are 56×10^{-3} and 82×10^{-3} Å for two distinct complexes in the crystal. Consideration based on the values derived from the plane defined by all atoms of the complex is similar. Therefore, we might conclude the ligand **1** and the corresponding metal complex **2** have moderate flexibility in crystal.

These complexes pack in herringbone manner (Fig. 1(c)). There is no short intermolecular Pt–Pt interaction in the crystal lattice of **2**, in contrast to the reported structure for *N,N′*-disalicylalethylenediamine Pt(II) complex, Pt–Pt: 3.277(1) Å [21].

2.3. Spectroscopic studies: IR, ^1H NMR, and absorption spectra

Spectroscopic behaviors are also informative to determine the structure of **2**. Along with the reasonable ^1H NMR spectra of **1** and **2**[1], the characteristic behavior was observed in IR spectra, *i.e.*, the lower-frequency shift of the imine C=N stretching mode (ν_{CN}) attributable to the complex formation [22–24]. The intense ν_{CN} signal of **1**, 1623 cm^{-1}, was shifted to lower frequency region in **2**, 1615 cm^{-1}. π-Expansion only influences the ν_{CN} of **1** as the lower frequency shift [25]. The value of the parent ligand **3** is 1634 cm^{-1}. The complex **4** shows the similar value, 1616 cm^{-1}, with that of **2**. Reflecting the pyrene nucleus of **1** and **2**, several strong absorptions attributable to C–H out-of-plane vibrations of pyrene, γ_{CH}, were observed in the frequency range of 850–680 cm^{-1} [26].

Expansion of the π-system of the ligand induces the significant bathochromic shift in absorption spectra.[2] Absorption spectrum of

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[1] In platinum(II) salicylaldiminato and related complexes, the long-range spin coupling between ^{195}Pt and imine hydrogen was reported [15]. However, it was too difficult to observe such phenomena in our system not only for **2** but also **4** by our hands.

[2] Complex **2** shows emission, phosphorescence, at 648 nm (excitation: 530 nm, in CH_2Cl_2 at room temperature). The detailed behavior including quantum yield and phosphorescence life time will be reported in elsewhere.