Synthesis and Optical Properties of Pincer Palladium and Platinum Complexes having Thioamide Units

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Pd and Pt complexes having a pincer ligand with thioamide units were prepared and investigated for photoluminescent material. The intensity of photoluminescence depends on a choice of a ligand on the metal center and structure of the pincer ligand. Light-emitting diodes using the complexes as an emitting layer showed red or reddish orange electroluminescence.

Keywords: pincer complex, photoluminescence, thioamide

1. Introduction

Pincer complex is a stable organometallic compound having a mono-anionic trident ligand. Electron density of a metal center can be controlled by a choice of a donating group (E), a substituent on an aromatic group (R), and a ligand on the metal center (X) (cf. A in Scheme 1).[1][2] Therefore, there have been many studies on molecular design of pincer complexes which serve as catalyst, emitting material, and a building block of supramolecular compounds. Pincer complexes with a cyclometalated Pt(II) center show interesting photoluminescent properties and can be utilized to electroluminescence devices.[3][4] These photoluminescent complexes generally have ligated C and N atoms on a pincer ligand like 1,3-dipyriddylenzene, which is described as NCN ligand.[5] This situation has led continuous interest that has been devoted to the synthesis of new pincer ligands with various heteroatoms such as P, O, and S.

[Diagram of Scheme 1: Structures of A, B, and C]

We have developed syntheses of pincer platinum and palladium complexes containing SCS ligands with thioamides and phosphine-sulfides as ancillary ligands (B and C in Scheme 1). Although the coordination chemistry of thioamides and phosphine-sulfides is well known, only little attention has been paid to the SCS-pincer ligands consisted of thioamides and phosphine-sulfides. Nonoyama’s group [6][7] and Bowman-James’s group [8][9] have reported syntheses and catalytic activity of thioamide-based pincer Pt(II) and Pd(II) complexes. However, photophysical properties of the complexes have not been described. To further explore the photoluminescent pincer complexes, our group focuses on photoluminescence of Pt(II) and Pd(II) complexes with thioamide and phosphine-sulfide groups. This review describes the syntheses of the pincer complexes, their photophysical properties, and a preliminary application in light-emitting diodes (LEDs).

2. Results

2.1 Synthesis of thioamide-based pincer complex

Thioamide-based pincer ligands, 1,3-benzenedicarbothioamide derivatives, were prepared by the Willgerodt-Kindler reaction from isophthalaldehyde, secondary amine (HA), and sulfur according to previous reports (Scheme 2).[10-12]

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Reactions of the 1,3-benzenedicarbothioamide derivatives with PtCl₃(PhCN)₂ and with a mixture of PdCl₂ and LiCl gave Pt and Pd pincer complexes (1-4) in moderate to good yields (Scheme 2).[13][14] In contrast to smooth formation of κ¹-SCS-pincer complexes, OCO-pincer ligand, 1,3-bis(1-piperidinocarbonyl)benzene, did not afford the corresponding complex. This result indicates that the strong coordination ability of thioamide groups to metal centers is necessary for metalation to a central benzene unit. Similar N-metalation of 1H-pyrrole-2,5-dicarbothioamide also provided corresponding κ¹-SNS-pincer complexes.[15]

2.2 Substitution reactions of anionic ligand

From the view point of photophysical properties of the pincer complexes of group 10 metals, a choice of an anionic ligand on a metal center is an important factor. Therefore, substitution reactions of the anionic ligand were carried out (Scheme 3).[13] The reaction of 1 with phenylacetylene in the presence of CuI and triethylamine resulted in a formation of a phenylacetylide complex 5 in good yield. Treatment of 1 and 5 with excess amount of CH₃I gave an iodo complex 6 accompanied by liberation of CH₃Cl and CH₃C=CHPh, respectively.

2.3 Secondary thioamide based pincer complex

Starting from a reactive secondary thioamide ligand, two types of pincer complexes with different SCS and NCN coordination modes were obtained.[16] The reaction of 5-methyl-1,3-bis(anilinothiocarbonyl)benzene with K₂PtCl₄ gave a SCS-pincer complex 7 having secondary thioamide groups (Scheme 4). Since a secondary thioamide group can be converted to benzothiazole derivatives via an oxidative cyclization with K₃[Fe(CN)₆], the pincer ligand is transformed into 5-methyl-1,3-bis(benzothiazol-2-yl)benzene. This product reacts with K₂PtCl₄ to give a NCN-pincer complex 8.[16]

2.4 Phosphine-sulfide-based pincer complex

5-Methyl-1,3-bis(diphenylphosphinoothiol)benzene was prepared via Pd-catalyzed aryl phosphination reaction of 5-methyl-1,3-dibromobenzene and subsequent sulfurization on diphenylphosphine groups (Scheme 5).[17][18]
Metalation reactions of the ligand with Pt and Pd metal precursors smoothly proceed to give SCS-pincer Pt (9) and Pd (10) complexes. To our best knowledge, this procedure is the first synthetic method of a phosphine-sulfide-based pincer complex.[19][20] In order to create a new function of a pincer complex, the central phenylene unit was replaced by a pyridine unit having a reacting and coordinating imine nitrogen (N_Py). The Pd complexes with 3,5-bis(diphenylphosphinothiyl) pyridine unit (12 and 13) react with alkyl halides to afford N_Py-quaternized pyridinium complexes (14-16) (Scheme 6).[21]

result in formation of heterobimetallic complexes, 17 and 18, respectively (Scheme 7). Single-crystal X-ray diffraction studies reveal piano-stool conformation of the Ru center in 17 and square planar geometry around the Pt center in 18[21].

2.5 Photoluminescent property of pincer complex

The Pt complex 1 is not light emissive in solution at room temperature, whereas strong photoluminescence is observed in the glassy frozen state as well as in the solid state. Photoluminescence quantum yield is 0.11.[13] Detailed photoluminescence data are summarized in Table 1. It is noted that the Pd complexes (2-4) also show photoluminescence in the glassy frozen state and in the solid state at room temperature (entries 2-4).[14] This is a rare example of thermally and chemically stable light-emissive Pd(II) complex. The Pd phenylacetylide complex 5 shows stronger photoluminescence than that of the Pt-Cl complex 1 (entries 1 and 5). In contrast, the Pt-I complex 6 does not show photoluminescence, which indicates that iodo ligand on the Pt center has an effect to diminish photoluminescence. Fig. 1 shows emission spectra of 1 and 5 in the solid state and in the frozen state at 77 K.

The coordinating ability of N_Py allows the binding to another metal center. The reactions of 11 with [RuCl_3(η^6-C_6H_6)]_2 and [PdCl_2(PhCN)_2]

Fig. 1. Emission spectra of 1(—) and 5(---): (a) microcrystalline sample at room temperature, (b) in a frozen CH_2Cl_2-MeOH-EtOH matrix (77 K).

Table 1 Photoluminescent properties of the pincer complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>λ_em^a (solid state) (nm)</th>
<th>λ_em^b (glassy frozen state at 77 K)(nm)</th>
<th>Φ_em^c</th>
<th>τ^d (μs)</th>
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<tr>
<td>1</td>
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<td>630</td>
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<tr>
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<td>85</td>
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<td>690, 715^f</td>
<td>575^f, 713</td>
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<td>585^f, 711</td>
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<tr>
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<td>9</td>
<td>580</td>
<td>540</td>
<td>0.24</td>
<td>110</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>n.d.</td>
<td>580</td>
<td>0.14</td>
<td>240</td>
</tr>
</tbody>
</table>

^aEmission maximum of a microcrystalline sample. ^bEmission maximum in a glassy frozen state at 77 K.
^cPhotoluminescence quantum yield compared with that of fac-tris(2-phenylpyridine)iridium (Φ = 0.4 ± 0.1).[22] ^dEmission decay lifetime. ^eShoulder peak
Based on the photoluminescent properties, preliminary application of the complexes as light-emitting materials in the LEDs has been examined. The present LEDs using 1 and 5 have emission intensities of 180 cd m\(^{-2}\) and 422 cd m\(^{-2}\) at 100 mA cm\(^{-2}\), respectively (Fig. 2).[13]

Fig. 2. Electroluminescence spectra of the LEDs for 1(--->) and 5(--->). (inset: multilayer configuration of LED).

The Pt complexes 7 and 8, which are obtained from the same starting material, exhibit different photoluminescent properties (entries 6 and 7).[16] SCS-pincer-complex 7 shows a broad emission band at around 630 nm in the glassy frozen state at 77 K (Fig. 3). On the other hand, NCN-pincer-complex 8 shows relatively sharp three bands with spacing of 1400±60 cm\(^{-1}\) in range of 530-750 nm. The spacing corresponds to vibrational frequencies of the benzothiazole ligand. From the view point of emission intensity, complex 8 shows stronger emission (\(\Phi_e = 0.33\)) compared to that of complex 7 (\(\Phi_e = 0.08\)). The phosphine-sulfide-based pincer complexes 9 and 10 show photoluminescence in the frozen state at 77 K (entries 8 and 9).[18] In the case of the Pt complex 9, room temperature emission is also observed in the solid state. Replacement of central unit from benzene to pyridine strongly affects photoluminescent properties. The pincer complexes 11-13 having pyridine central unit shows almost no emission even in the frozen state. The quaterization and coordination reactions of complex 11 did not improve the emission ability.[21]

Fig. 3. Excitation and emission spectra of (a) 7 and 8 in a frozen matrix of CH\(_2\)Cl\(_2\)-THF (3:2) at 77K.

3. Discussion
The emission lifetime of the SCS-pincer complexes in the frozen state is 3.7-240 μs (Table 1). The results indicate that the emission from the complexes is phosphorescent emission. We tentatively assigned that the emissive exited state of the complexes is related to \(^3\)MLCT formed by intersystem crossing between singlet and triplet states. As shown in Figure 1, complexes 1 and 5 do not show large difference in \(\lambda_{em}\) between the solid state and the glassy frozen state. This phenomenon indicates the same electronic origin of the emitting states in the both state. On the other hand, \(\lambda_{em}\) of complex 7 in solid state (741 nm) is considerably different from that in the glassy frozen state (631 nm). The red-shifted emission in the solid state is presumably due to stabilization of the excited state by formation of eximer-like adduct. Since the crystal-packing diagram of 7 exhibits interplanar stacking distance of 3.56 Å, formation of the eximer-like adduct is reasonable in the solid state.
4. Conclusion

Emission intensity of thioamide- and phosphine-sulfide-based pincer complexes depends on the structure of the central aromatic unit and coordinating mode. The pincer complex with secondary thioamide groups shows red-shifted emission in the solid state compared to that in the glassy frozen state presumably due to formation of eximer-like adduct. We recently have achieved control of molecular arrangement of the secondary thioamide-based pincer complexes in the crystal state by using intermolecular hydrogen bonds.[23] Since the molecular packing would affect probability of the eximer formation, modulation of emission wavelength will be possible by the control of molecular arrangement in the solid state.

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Reference