

Note

Luminescent palladium complexes containing thioamide-based SCS pincer ligands

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Abstract

Thioamide-based tridentate ligands, 1,3-benzenedicarbothioamides (**1a–c**), were used to afford pincer palladium(II) complexes (Pd(**1–H**)Cl, **2a–c**) with η^3 -S,C,S type coordination. The complexes exhibit strong emission in a glassy frozen state as well as in the solid state. The decay lifetime of the emission from the complexes is in a range of $8\text{--}9 \times 10^{-5}$ s, which is indicative of phosphorescent emission.

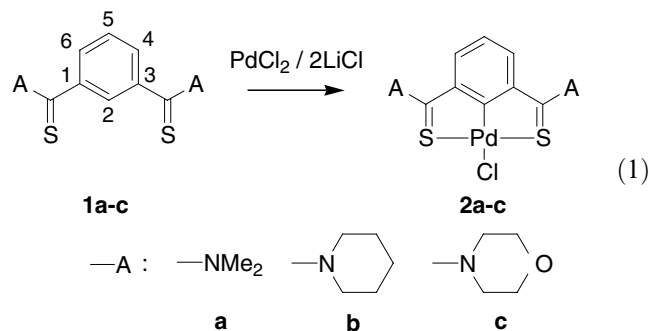
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Keywords: Palladium; Pincer ligand; Thioamide; Luminescence

1. Introduction

Recently, cyclometalated platinum(II) complexes have represented an important class of complexes particularly from the point of view of their luminescent properties, and using the phosphorescent complexes as emitters in the light-emitting diodes (LEDs) has attracted much attention from both researches in institutions and industrial sectors [1]. Luminescent cyclopalladated complexes are also potential candidates for luminescent devices [2]. However, there are not many reports on solid state luminescence at room temperature for the cyclopalladated complexes [2a,2i]. We have recently investigated luminescent pincer platinum complexes having thioamide-based SCS-pincer ligands [3]. Related pincer palladium complexes have previously been reported by Nonoyama et al. [4], however, photo-physical properties of the complexes have not been described. To further explore the luminescent pincer complexes, this work is concerned with the pincer Pd(II)

complexes containing thioamide-based SCS-pincer ligands. We here present the Pd(II) complexes which are luminescent in the solid state.



2. Results and discussion

The thioamide-based pincer ligands, 1,3-benzenedicarbothioamides (**1a–c**), were prepared by the Willgerodt–Kindler reaction according to the previous reports [3–5]. The reported Pd(II) complexes (**2a**) was prepared as described previously [4]. The *ortho,ortho*-

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Table 1
Photophysical properties and thermal property of the pincer palladium complexes **2a–c**

Complex	$\lambda_{\text{max}}^{\text{a}(\text{b})}$ [nm (M ⁻¹ cm ⁻¹)]	$\lambda_{\text{em}}(\text{solid})^{\text{c}}$ [nm]	$\lambda_{\text{em}}(\text{glass})^{\text{d}}$ [nm]	$\phi_{\text{r}}^{\text{e}}$	τ^{f} [μs]	$T_{\text{d}10}^{\text{g}}$ [°C]
2a	275 (25 500), 341 (9000), 400 (8600), 450 ^h (3100)	713	570 ^h , 713	0.08	85	327
2b	281 (22 500), 344 (9600), 409 (9000), 460 ^h (3400)	690, 715 ^h	575 ^h , 713	0.12	89	303
2c	285 (21 400), 345 (8600), 412 (8700), 460 ^h (3200)	735	585 ^h , 711	0.10	83	316

^a Absorption maxima in CH₂Cl₂ at room temperature.

^b Molecular absorption coefficient.

^c Emission maximum of a microcrystalline sample.

^d Emission maximum in CH₂Cl₂–THF (3:2) matrix at 77 K (ca. 1.2 × 10⁻⁵ M).

^e Photoluminescence quantum yield compared with that of *fac*-tris(2-phenylpyridine)iridium ($\phi_{\text{r}} = 0.4 \pm 0.1$) [11].

^f Emission decay lifetime at 700 nm.

^g Temperature for 10% weight loss of the sample under nitrogen.

^h Shoulder peak.

cyclopalladation of **1b,c**, according to the literature method [3,4], gave the corresponding SCS-pincer palladium(II) complexes (Pd(**1–H**)Cl, **2b,c**) in good yields. In contrast, a related OCO-pincer ligand (1,3-bis(1-piperidinocarbonyl)benzene) [6] did not afford the corresponding pincer complex, suggesting that the S-coordination ability of thioamide groups toward Pd(II) was a crucial factor for the *ortho,ortho*-cyclopalladation.

The complexes **2a–c** are fairly stable to air and water, and are thermally stable up to 300 °C (see Table 1). The complexes **2b,c** show good solubility in organic solvents such as CH₂Cl₂, CHCl₃, DMF, and DMSO, whereas **2a** is soluble in DMF and DMSO, however, is slightly soluble in CH₂Cl₂ and CHCl₃. Structures of the complexes were confirmed by NMR, FAB-mas, and elemental analysis. In ¹H NMR spectra of the complexes, the signal assigned to H at the 2-position of the centered benzene ring disappears, and a downfield shift of the C-2 carbon resonance in the ¹³C NMR spectrum is observed, in consistent with the cyclopalladation at the C-2 position [2,7].

The molecular structures of **1b** and **2b** are presented in Fig. 1. The geometry around the Pd center is a distorted square plane similar to that of the reported **2a** [4a]. The plane of coordination in **2b** somewhat bends out of the centered benzene ring, as indicated by the dihedral angle (20.41°) of the SCS plane and the benzene ring. The Pd–C and Pd–Cl bond lengths lie in the range of lengths found in related palladium complexes [2,4,7]. The C=S bond lengths are somewhat longer than those of free ligand **1b**. In the crystal lattice, neither intercomponent π -stacking interaction of the centered benzene ring nor intermolecular $d^{\delta-}-d^{\delta-}$ interaction is observed with a Pd···Pd separation distances of 5.54 Å. Similar structural feature was observed with **2a**, **2c**, and related platinum complexes [3].

The complexes **2a–c** are not light-emissive in solutions at room temperature, whereas strong photoluminescence (PL) was observed in a glassy frozen state as well as in the solid state at room temperature. The UV–Vis absorption data and PL data of the complexes are summarized in Table 1. The complexes **2a–c** show broad overlapped absorption bands in a region of

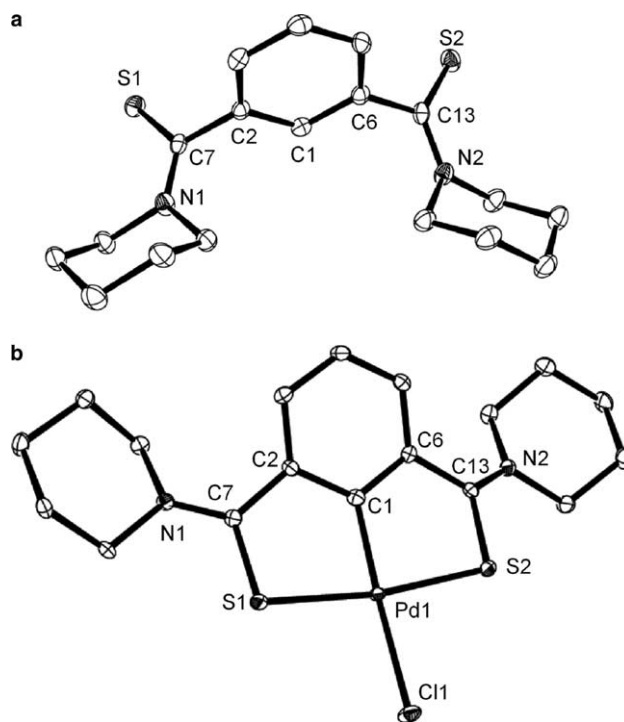


Fig. 1. X-ray crystal structures of **1b** (a) and **2b** (b) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for simplicity. Selected bond lengths (Å) and angles (°): (a) S(1)–C(7), 1.676(2); S(2)–C(13), 1.675(2); N(1)–C(7), 1.324(3); N(2)–C(13), 1.336(3). (b) Pd(1)–C(1), 1.961(2); Pd(1)–Cl(1), 2.3973(5); Pd(1)–S(1), 2.2939(5); Pd(1)–S(2), 2.2984(4); S(1)–C(7), 1.720(2); S(2)–C(13), 1.723(2); N(1)–C(7), 1.324(2); N(2)–C(13), 1.327(2); S(1)–Pd(1)–S(2), 170.84(2); Cl(1)–Pd(1)–C(1), 176.83(5).

320–480 nm. The ligands **1a–c** only absorb weakly in the region and exhibit an $n-\pi^*$ transition peak with $\epsilon < 600 \text{ M}^{-1} \text{ cm}^{-1}$ at about 390 nm [8]. These data indicate involvement of the Pd center in electronic transitions for the overlapped absorption bands observed in the range of 320–480 nm. Metal-to-ligand charge-transfer (MLCT) and ligand-to-metal charge-transfer (LMCT) transitions are considered to occur in the region [1,2]. The decay lifetime of the emission from the complexes in the glassy state is in a range of $8-9 \times 10^{-5} \text{ s}$; the relatively long life time is indicative

of phosphorescent emission. We tentatively assign that the emission of the complexes occurs from a triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) excited states, similar to the case of related pincer platinum complexes [1,2]. The PL peak usually appears near the onset position of UV–Vis absorption bands for non-metallated organic compounds. However, for the complexes **2a–c**, the PL peak position is apparently shifted to a longer wavelength from the onset position of the UV–Vis band. The photoexcited Pd-complexes seem to be stabilized to a triplet state (presumably to a $^3\text{MLCT}$ state) to give PL with the relatively long life time. The possibility of the emission originates from a metal-centered ligand field (^3LF) excited state may also be suggested [1n,1o]. As shown in Fig. 2, the emission from the complex seems to be comprised of two parts. Their positions did not depend on the excitation wavelength (e.g., 400 and 450 nm). However, the microcrystalline sample at room temperature and the complex in the glassy frozen matrix give the main PL peak at the similar position. The data suggests that the shift of the PL peak from the onset position of the UV–Vis band is not attributed to the formation of excimeric species. Although solid state intermolecular $d^{\delta}-d^{\delta}$ and ligand–ligand interactions of the photoluminescent cycloplatinated complexes have been reported [1], occurrence of such an intermolecular interactions seems to be less plausible for mononuclear square planar palladium complexes [2a,9], which is also supported by the X-ray crystallographic analysis of **2b,c**.

As described above, phosphorescent Pd(II) pincer complexes have been obtained from *ortho,ortho*-cycloplatinated thioamide-based SCS-pincer ligands. Since thermally and chemically stable light-emissive Pd(II) complexes are rare compared to analogous Pt(II) complexes, the present results should broaden the scope

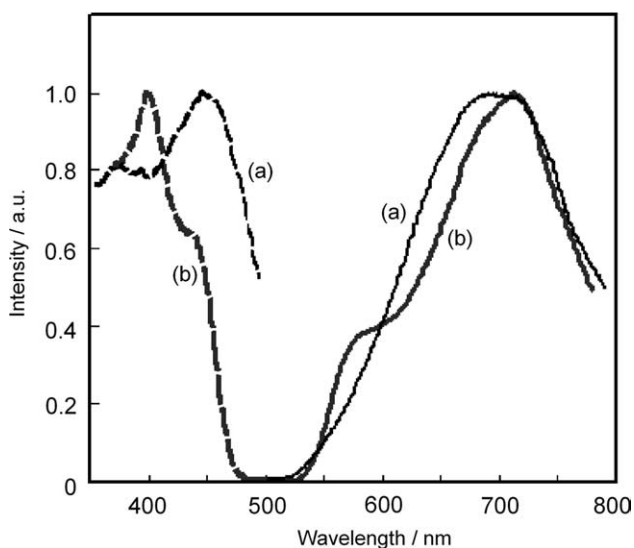


Fig. 2. Emission spectra (solid line) and excitation spectra (broken line) of **2b**: (a) for a microcrystalline sample at room temperature and (b) in frozen CH_2Cl_2 –THF (3:2) matrix (77 K).

of luminophores for optical and electroluminescence devices.

3. Experimental

3.1. General procedures and materials

All reactions were carried out under N_2 . Solvents for the reactions were dried and distilled prior to use. The neutral ligands (**1a,c**) and the Pd(II) complex (**2a**) were prepared as described previously [4,6,10]. The ligand **1b** was prepared by the Willgerodt–Kindler reaction according to the literatures (99% yield) [3–5].

1b. FAB-mas: m/z 333 $[\text{M} + \text{H}]^+$. Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{S}_2$: C, 65.01; H, 7.27; N, 8.42; S, 19.29. Found: C, 64.09; H, 7.22; N, 8.15; S, 18.35%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.38 (t, 1H, $J = 7.6$ Hz), 7.20 (dd, 2H, $J = 7.6, 1.6$ Hz), 7.07 (s-br, 1H), 4.25 (s-br, 4H), 3.48 (t, 4H, $J = 5.6$ Hz), 1.67 (m-br, 8H), 1.50 (s-br, 4H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 196.2, 142.7, 128.1, 124.8, 121.7, 52.5, 49.7, 26.2, 25.0, 23.3.

3.2. Pd(I–H)Cl (**2b,c**)

2b. A mixture of dilithium tetrachloropalladate, prepared in situ from PdCl_2 (2.5 mmol, 440 mg) and LiCl (5.0 mmol, 210 mg), and **1b** (3.0 mmol, 1000 mg) in methanol (200 mL) was refluxed under N_2 for 2 h to yield a yellow precipitate. The precipitate was filtered off, washed with methanol and dried in vacuo to give **2b** as a yellow solid (1065 mg, 90% yield). FAB-mas: m/z 437 $[\text{M} - \text{Cl} + \text{H}]^+$. Anal. Calc. for $\text{C}_{18}\text{H}_{23}\text{ClN}_2\text{PdS}_2$: C, 45.67; H, 4.90; N, 5.92; Cl, 7.49; S, 13.55. Found: C, 45.46; H, 4.93; N, 5.97; Cl, 7.49; S, 13.28%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.40 (d, 2H, $J = 7.6$ Hz), 7.11 (t, 1H, $J = 7.6$ Hz), 4.13 (s-br, 8H), 1.79 (m-br, 12H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 199.0, 168.7, 145.6, 129.3, 120.3, 55.4, 53.0, 26.5, 25.0, 22.7.

2c. **2c** was prepared analogously (99% yield). FAB-mas: m/z 441 $[\text{M} - \text{Cl} + \text{H}]^+$. Anal. Calc. for $\text{C}_{16}\text{H}_{19}\text{ClN}_2\text{O}_2\text{PdS}_2$: C, 40.26; H, 4.01; N, 5.87; Cl, 7.43; S, 13.44. Found: C, 40.15; H, 3.97; N, 5.89; Cl, 7.64; S, 13.82%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.47 (d, 2H, $J = 8.0$ Hz), 7.12 (t, 1H, $J = 8.0$ Hz), 4.24 (t, 8H, $J = 4.4$ Hz), 3.90 (s-br, 4H), 3.77 (s-br, 4H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 199.9, 169.3, 145.4, 129.9, 120.5, 66.1, 65.3, 55.1, 51.8.

3.3. Crystal data for **1b**, **2b** and **2c**

The diffraction data were collected with a Rigaku Saturn CCD area detector with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71070 \text{ \AA}$) at -160°C . The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.

The structure was solved by direct methods (SIR 92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters.

Crystallographic data for **1b**: $C_{18}H_{24}N_2S_2$, $M = 332.52$, triclinic, space group $P\bar{1}$, $a = 8.215(5)$ Å, $b = 9.386(6)$ Å, $c = 12.056(8)$ Å, $\alpha = 108.079(13)^\circ$, $\beta = 101.409(9)^\circ$, $\gamma = 88.904(4)^\circ$, $V = 865.4(10)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.276$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 3.06$ cm⁻¹, $T = 113$ K, $F(000) = 356$, 12958 reflections measured, 3699 unique, 2607 observed ($I > 3\sigma(I)$), 199 variables, $R_1 = 0.038$, $R_w = 0.048$, GOF = 0.916.

Crystallographic data for **2b**: $C_{18}H_{23}ClN_2PdS_2$, $M = 473.37$, monoclinic, space group $P2_1/c$, $a = 11.940(1)$ Å, $b = 10.7153(9)$ Å, $c = 14.487(2)$ Å, $\beta = 99.603(4)^\circ$, $V = 1827.5(3)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.720$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 13.93$ cm⁻¹, $T = 113$ K, $F(000) = 960$, 24672 reflections measured, 4099 unique, 3514 observed ($I > 3\sigma(I)$), 217 variables, $R_1 = 0.023$, $R_w = 0.037$, GOF = 0.877.

Crystallographic data for **2c**·CHCl₃: $C_{17}H_{20}Cl_4N_2O_2PdS_2$, $M = 596.69$, monoclinic, space group $P2_1/n$, $a = 10.5997(4)$ Å, $b = 16.3942(5)$ Å, $c = 12.5241(5)$ Å, $\beta = 98.170(2)^\circ$, $V = 2154.3(1)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.840$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 15.68$ cm⁻¹, $T = 113$ K, $F(000) = 1192$, 29440 reflections measured, 4799 unique, 4203 observed ($I > 3\sigma(I)$), 253 variables, $R_1 = 0.019$, $R_w = 0.031$, GOF = 0.870.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center; publication numbers CCDC 266568 (**1b**), 266569 (**2b**), and 266570 (**2c**).

Acknowledgments

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