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Notes

Preparation and Characterization of Luminescent SCS and NCN Pincer Platinum Complexes Derived from 3,5-Bis(anilinothiocarbonyl)toluene

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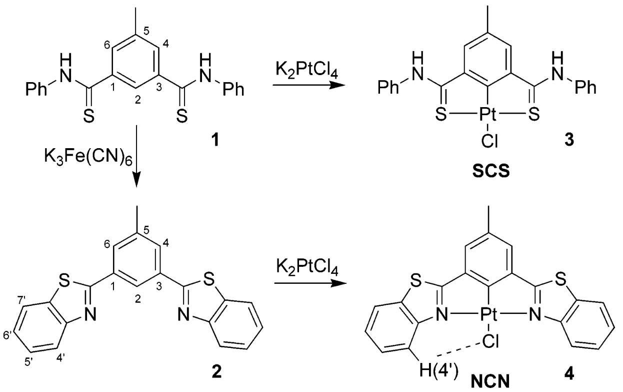
*Summary: Starting from 5-methyl-1,3-bis(anilinothiocarbonyl)-benzene (**1**), two types of luminescent pincer platinum complexes with κ^3S,C,S and κ^3N,C,N coordination modes were obtained. Reaction of **1** with K_2PtCl_4 afforded a pincer Pt(II) complex (**3**) with the κ^3S,C,S coordination mode, whereas oxidative cyclization of **1** yielded 5-methyl-1,3-bis(benzothiazol-2-yl)-benzene (**2**), which provided a pincer Pt(II) complex (**4**) with the κ^3N,C,N coordination mode. Molecular structures and photochemical properties of the complexes have been examined. The decay lifetimes of the emission from the complexes were in the range 10^{-5}−10^{-6} s, which were indicative of phosphorescent emission.*

Introduction

Square-planar cycloplatinated complexes are often light emissive,[1] and use of such light emissive metal complexes, especially phosphorescent metal complexes, as emitters in light-emitting diodes (LEDs) has attracted much attention.[2]

Scheme 1. New Pincer Pt(II) Complexes 3 and 4 Derived from 1



We previously reported that κ^3S,C,S pincer Pt(II) complexes containing tertiary thioamide-based pincer ligands exhibited strong phosphorescent emission in the glassy frozen state and in the solid state.[1q] We have extended the research and now report that the secondary thioamide compound **1** is a good starting material to afford the two new pincer Pt(II) complexes **3** and **4**.

Secondary thioamides have been used in the field of medical and organic chemistry,[3,4] and it is known that oxidative cyclization of secondary *N*-arylthioamides with $K_3[Fe(CN)_6]$ gives benzothiazole derivatives.[4] Such a cyclization reaction can proceed with bis(secondary thioamide)s, and **1** can be transformed into **2**; thus, from the ligands **1** and **2**, the new complexes **3** and **4** are obtained. Consequently, expansion of the complex synthesis exhibited in Scheme 1 by modifying the aromatic groups in **1** is expected to give various Pt complexes of the types **3** and **4**.

Cyclometalated κ^2C,N Ir(III) and Pt(II) complexes of 2-arylbenzothiazoles[1a,2c] and related κ^3N,N,N type metal complexes of neutral tridentate ligands such as 2,6-bis(benzothiazol-

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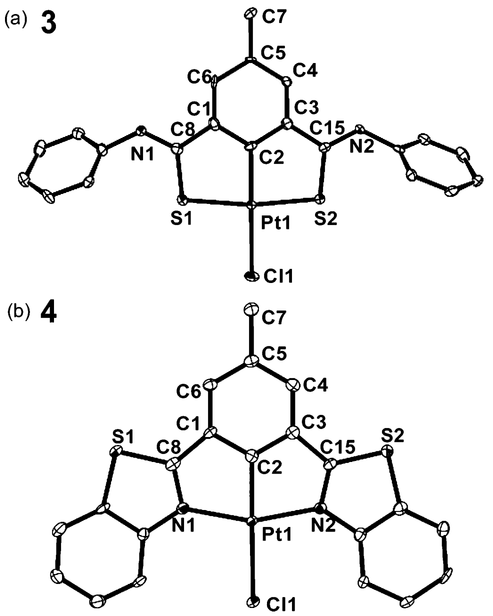

Figure 1. X-ray crystal structures of (a) **3** and (b) **4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvated molecules are omitted for simplicity.

2-yl)pyridine have been reported.[5] However, a κ^3N,C,N pincer complex such as **4** constituted of the benzothiazole unit has not yet been reported to our knowledge. On this basis, we here report that **1** can give two luminescent pincer Pt(II) complexes, **3** and **4**, which are composed of different donor sets with κ^3S,C,S and κ^3N,C,N pincer coordination modes, respectively. Molecular structures and photochemical properties of the complexes are also described.

Results and Discussion

Preparation of **1** is described in the Experimental Section. The oxidative cyclization of **1** using $K_3[Fe(CN)_6]$ afforded **2**. Reactions of **1** and **2** with K_2PtCl_4 in acetic acid led to regioselective *ortho,ortho*-cycloplatination at the C-2 position of the centered benzene ring with Pt(II) and afforded the corresponding pincer complexes **3** and **4** in 63 and 51% yields, respectively.

3 and **4** were fairly stable to air and water and were thermally stable up to 300 °C. **3** showed good solubility in polar organic solvents such as MeOH, EtOH, DMF, and DMSO. **4** was less soluble and showed only low solubility in CH_2Cl_2 and $CHCl_3$. The ^1H NMR spectra of **3** and **4** shown in Figure S1 agree with their structures. In the ^{13}C NMR spectrum of **3**, the *ortho,ortho*-cycloplatinated carbon (C_{ipso}) was shifted to a higher magnetic field by 24 ppm according to the σ-bonding to Pt.

The ORTEP drawings of **3** and **4** are presented in Figure 1, and selected bond lengths and bond angles of **1**−**4** are summarized in Table 1. **3** and **4** have a distorted square-planar geometry similar to each other. As shown in Figure 1a, **3** has a κ^3S,C,S pincer complex strucrture, similar to previously reported thioamide-based pincer complexes.[1q,6] The Pt−C and Pt−Cl bond lengths are consistent with those of the reported thioamide-based pincer Pt(II) complexes. The C═S bond lengths are longer than those observed with **1**, and the C(S)−N bond lengths are somewhat shorter than those observed with **1**, indicating that the *S*-coordination to Pt decreases the double-bond character of the C═S bond. Two DMSO molecules in the crystal are hydrogen bonded to the N−H protons of **3** through the O of DMSO (N···O = 2.809 and 2.852 Å), in agreement with known hydrogen-bonding donor ability of the N−H hydrogen of the secondary thioamide.[7]

Table 1. Selected Bond Lengths and Bond Angles for 1−4

Bond Lengths (Å)

	1	3	2	4
Pt−C		1.957(7)		1.924(5)
Pt−Cl		2.389(2)		2.4254(14)
C−S	1.671(2)	1.700(7)	1.728(8)	1.712(5)
C−S		1.714(7)	1.768(6)	1.724(5)
C(S)-N	1.331(2)	1.31(1)	1.311(9)	1.349(7)
C(S)-N		1.32(1)	1.190(9)	1.327(7)

Bond Angles (deg)

	3	4
Cl−Pt−C	178.76(17)	177.72(16)
S−Pt−S	170.77(6)	
N−Pt−N		158.57(18)

As depicted in Figure 1b, **4** has a κ^3N,C,N coordination mode. The Pt−C bond length is shorter than those in **3** and related pincer Pt(II) complexes.[1e,8] The cycloplatination brings about a close contact between the H(4′) hydrogen of the benzothiazole ring and the Cl ligand in **4**, as depicted in Scheme 1, and distances of 2.66 and 2.70 Å are obtained for the distance between H(4′) and Cl by X-ray crystallography. The distance is smaller than the sum (2.95 Å) of the van der Waals radii of H and Cl, indicating the presence of an intramolecular hydrogen bonding interaction between H(4′) and Cl.[9] The two benzothiazole rings are nearly parallel to the center benzene ring. The intramolecular hydrogen-bonding interaction agrees with a ^1H NMR shift of the H(4′) hydrogen peak of **2** to a lower magnetic field by 1.77 ppm by the complexation with Pt, as shown in Figure S1.

The crystal-packing diagrams of **3** and **4** exhibit that the complexes are stacked in a head-to-tail fashion with interplanar distances of 3.56 and 3.40 Å for **3** and **4**, respectively, as depicted in Figure S4. The molecular planes are slipped and the Pt···Pt distances between Pt in the upper complex and Pt in the lower complex are 6.00 and 5.51 Å for **3** and **4**, respectively. These data indicate that there is no significant d^8−d^8 interaction.

Electrochemical Response. Redox behavior of **3** and **4** has been investigated by cyclic voltammetry, and the data are given in Table 2. Electrochemical reduction of **3** occurs at −1.78 V vs Cp_2Fe^+/Cp_2Fe, which is considered to occur mainly at the ligand. The reduction peak is located at a higher potential than that of **1** ($E_p^{red} = -2.38$ V), presumably due to bonding to

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Table 2. Photochemical, Electrochemical, and Thermal Data of 3 and 4

	3	4
absorption[a] (UV−vis)	294 (25 300)	321 (23 800)
λ_{max}/nm	383 (5900)	388 (5900)
(ϵ, M^{-1} cm^{-1})	425 (6400)	425(8300)
	478 (11 100)	449 (12 800)
	544 (1300)	
emission (PL) λ_{max}/nm[b]	631	550, 597, 649, 717sh
λ_{max}/nm[c]		550, 597, 649, 718sh
λ_{max}/nm[d]	741	702
ϕ_f[e]	0.08	0.33
τ/μs[f]	3.7	9.4 (4.1)
E_p^{red}/V[g]	−1.78	−1.98
E_p^{ox}/V[g]	0.64	
T_{d10}/°C[h]	331	326

[a] In THF. The values in the parentheses are molar absorption coefficients. [b] In a CH_2Cl_2−THF (3:2) matrix at 77 K. [c] In a CH_2Cl_2−THF (3:2) solution at 298 K. [d] For a microcrystalline sample at 298 K. [e] Quantum yield in a CH_2Cl_2−THF (3:2) matrix at 77 K. *fac*-Tris(2-phenylpyridine)iridium (ϕ_f = 0.4 ± 0.1) was used as a reference.[13] [f] Emission decay lifetime at 77 K and that at 298 K in parentheses. [g] Electrochemical oxidation and reduction peak current potentials vs Cp_2Fe^+/Cp_2Fe. Measured in a THF solution of $[(n\text{-}Bu)_4N][BF_4]$ (0.10 M). [h] Temperature for 10% weight loss under N_2.

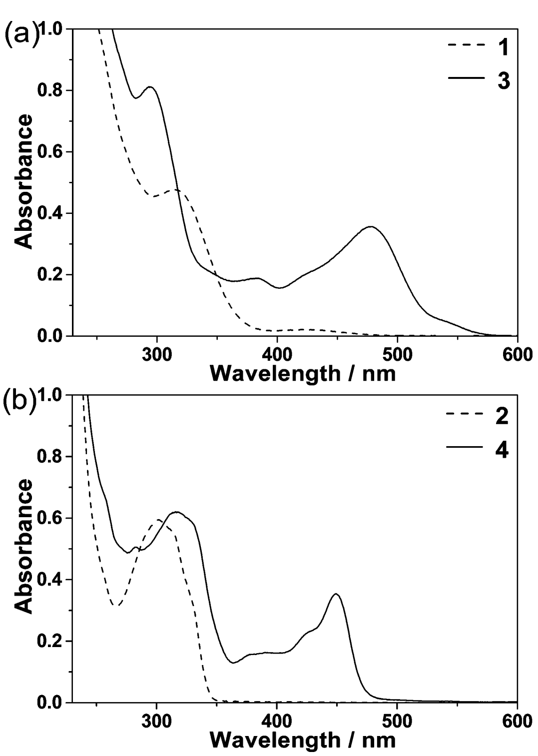

Figure 2. UV−vis spectra of the ligands and the complexes in THF at room temperature: (a) **1** and **3**; (b) **2** and **4**.

electron-donating Pt. The oxidation of **3** with E_p^{ox} of 0.64 V is considered to take place mainly at Pt, because **1** is oxidized at a considerably higher positive potential (E_p^{ox} = 1.01 V). **4** exhibits a reduction peak at −1.98 V, and the reduction potential is also at a higher potential than that of **2** (E_p^{red} = −2.49 V). However, oxidation of **2** and **4** was not observed up to 1.2 V.

Optical Data. Figure 2 shows absorption spectra of **1**−**4**. The strong absorption bands around 300 nm are attributed to a π−π^* transition in the ligands. **1** exhibits a tail absorption in the range 380−500 nm, which is assigned to an n−π^* transition in the thioamide group.[10,11] Absorption spectra of **3** and **4** show overlapped absorption bands in the region 400−500 nm, and the shape of the spectra in the region is similar to that of reported cycloplatinated complexes.[1j,s,11] Absorption bands of similar Pt complexes in this region have been assigned to metal-to-ligand charge-transfer (MLCT) transitions.[1q,t] The position of the UV−vis peak of **3** roughly agrees with the difference between the electrochemical oxidation and reduction potentials of **3** (0.64 − (−1.98) = 2.62 V or 21 000 cm^{-1}) and supports the assignment of the UV−vis band to the MLCT band. The UV−vis peak of **3** at about 470 nm exhibits solvatochromism, as shown in Table S1; such solvatochromism is often observed for charge-transfer bands and gives additional support for the assignment to the MLCT band.[12]

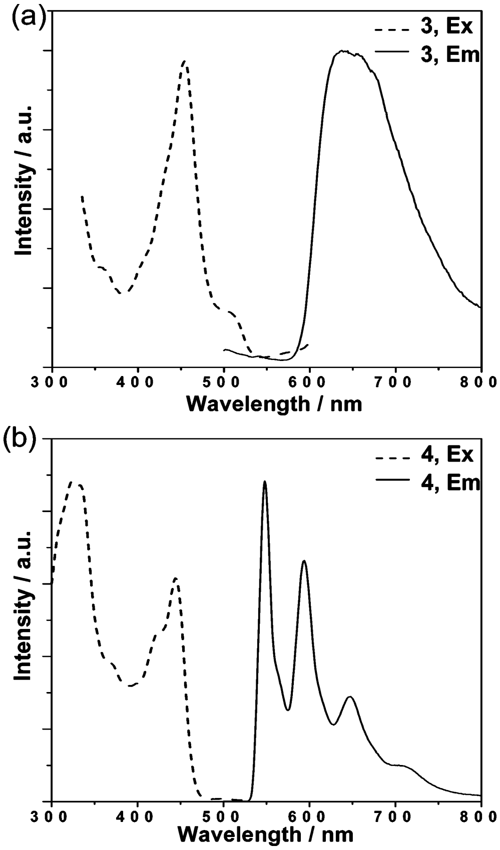

Figure 3. Excitation and emission spectra of (a) **3** and (b) **4** in a frozen matrix of CH_2Cl_2−THF (3:2) at 77 K.

3 and **4** were photoluminescent in a glassy frozen state and in the solid; **4** was light emissive even in solutions at room temperature. The photoluminescence data of **3** and **4** are included in Table 2, and Figure 3 shows photoluminescence spectra of **3** and **4**. As seen from Figure 3a, **3** shows a broad emission band at about 630 nm when excited with 455 nm light in the glassy frozen state at 77 K. The emission peak is located at a longer wavelength than the onset position of the UV−vis absorption band at about 580 nm, and the emission gives a decay lifetime (τ) of 3.7 μs in the glassy state. These data are indicative of phosphorescent emission. The emission spectrum and lifetime τ of **3** are similar to those of reported tertiary thioamide-based pincer Pt(II) complexes,[1q] and the reported emission of the Pt(II) complexes has been assigned to the emission occurring from a ^{3}MLCT excited state. A microcrystalline sample of **3** exhibited

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a weak emission at about 740 nm at room temperature, which was significantly red-shifted from that observed in the glassy frozen state, suggesting stabilization of the excited state by formation of excimer-like adduct(s) in the solid.[14] The layer-to-layer packed structure of **3** seems to be suited for the formation of such an adduct in the solid.

As shown in Figure 3b, **4** in the glassy frozen state exhibits a vibronic-structured emission band in the range 530−750 nm, with a spacing of about 1400 ± 60 cm^{-1}, which corresponds to skeletal vibrational frequencies of the benzothiazole ligand.[1a,i,j] Essentially the same emission spectrum was obtained at room temperature, as depicted in Figure S5. The emission peak of **4** also deviates from the onset position of the UV−vis absorption band. **4** gave long lifetimes of 9.4 and 4.1 μs in the glassy frozen state and in a 3:2 mixture of CH_2Cl_2 and THF at room temperature, respectively. The large Stokes shift and the relatively long lifetime suggest that the emission of **4** is also a phosphorescent emission. With reference to previous spectroscopic studies on related pincer Pt(II) complexes such as [5-methyl-1,3-di(2-pyridyl)phenyl-*C*^{2},*N*,*N′*]chloroplatinum(II) (**5**),[1j] the emission from **4** would be assigned to a ligand-centered $^3(\pi^*\pi)$ transition. The excitation and emission peaks of **4** were observed in a lower energy region by about 1620 cm^{-1} than those of **5**, suggesting that the expansion of the aromatic system in the ligand resulted in the reduction of the band gap. In the solid state, the emission peak of **4** was red-shifted to about 700 nm, which was also related to the layer-to-layer stacking of the complex in the solid.

Conclusion and Scope

S-Coordinating and oxidative cyclization ability of **1** provided two phosphorescent pincer Pt(II) complexes, **3** and **4**, with different κ^3S,C,S and κ^3N,C,N coordination systems. The electrochemical, UV−vis, and photoluminescence data support a notion that the emission from **3** originates from the ^{3}MLCT excited state. On the other hand, the emission from **4** is considered to originate from $^3(\pi^*\pi)$ emission. By modifying the structure of the starting material **1**, various new Pt complexes of the types **3** and **4** are considered to be obtained, and the chemistry of the luminescent pincer complexes is expected to be expanded.

Experimental Section

Synthesis of 5-Methyl-1,3-bis(anilinothiocarbonyl)benzene (1). To magnesium powder (255 mg, 10.5 mmol) was added dropwise a THF (5 mL) solution of 3,5-dibromotoluene (1.25 g, 5 mmol). The reaction mixture was refluxed under N_2 for 12 h. The resulting mixture was allowed to cool at 0 °C, and a THF (5 mL) solution of phenylisothiocyanate (1.35 g, 10 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. After water was added, the resulting yellow precipitate was collected by filtration. The precipitate was washed with chloroform and ether (543 mg, 30% yield).

FAB-mass: *m/z* 363 $[M + H]^+$. ^{1}H NMR (400 MHz in DMSO-d_6): δ 11.83 (s, 2H), 8.03 (s, 1H), 7.81−7.80 (m, 6H), 7.44 (t, $J = 7.2$ Hz, 4H), 7.28 (t, $J = 7.2$ Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz in DMSO-d_6): δ 196.7, 142.2, 140.0, 137.3, 130.3, 128.5, 126.4, 124.2, 123.5, 21.0. Anal. Calcd for $C_{21}H_{18}N_2S_2$: C, 69.58; H, 5.00; N, 7.73; S, 17.69. Found: C, 69.55; H, 4.85; N, 7.57; S, 17.42.

Synthesis of 5-Methyl-1,3-bis(2-benzothiazolyl)benzene (2). To a suspension of **1** (181 mg, 0.5 mmol) in ethanol (1 mL) was added a 30% solution of aqueous NaOH (1 mL). The solution was added dropwise to freshly prepared aqueous potassium ferricyanide (1.317 g, 4.0 mmol) at 80 °C, and the reaction mixture was stirred at 80 °C for 30 min. After cooling to room temperature, the precipitate was washed thoroughly with water to give a pale yellow powder of **2** (116 mg, 65% yield).

FAB-mass: *m/z* 359 $[M + H]^+$. ^{1}H NMR (400 MHz in $CDCl_3$): δ 8.55 (s, 1H), 8.11 (d, $J = 7.6$ Hz, 2H), 8.07 (s, 2H), 7.94 (d, $J = 7.2$ Hz, 2H), 7.52 (s, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz in $CDCl_3$): δ 167.1, 154.0, 139.8, 135.1, 134.4, 130.3, 126.4, 125.3, 123.3, 121.6, 21.6. Anal. Calcd for $C_{21}H_{14}N_2S_2$: C, 70.36; H, 3.98; N, 7.81; S, 17.89. Found: C, 70.49; H, 3.94; N, 7.46; S, 17.39.

Synthesis of [5-Methyl-1,3-bis(anilinothiocarbonyl)phenyl-*C*^{2},*S*,*S′*]chloroplatinum(II) (3). A mixture of **1** (36 mg, 0.1 mmol) and K_2PtCl_4 (41 mg, 0.1 mmol) in acetic acid (3 mL) was refluxed for 72 h under N_2. The resulting orange precipitate was filtered and washed with methanol and water to give a bright reddish powder of **3** (38 mg, 63% yield).

FAB-mass: *m/z* 556 $[M - Cl]^+$. ^{1}H NMR (400 MHz in DMSO-d_6): δ 12.09 (s, 2H), 8.04 (s, 2H), 7.46−7.63 (m, 10H), 2.34 (s, 3H). ^{13}C NMR (100 MHz in DMSO-d_6): δ 202.2, 161.2, 153.9, 143.2, 137.4, 129.2, 129.1, 128.2, 125.6, 20.5. Anal. Calcd for $C_{21}H_{17}ClN_2PtS_2$: C, 42.60; H, 2.89; N, 4.73; Cl, 5.99; S, 10.83. Found: C, 42.03; H, 2.89; N, 4.40; Cl, 5.96; S, 11.17.

Synthesis of [5-Methyl-1,3-bis(2-benzothiazolyl)phenyl-*C*^{2},*N*,*N′*]-chloroplatinum(II) (4). Preparation of **4** was carried out in analogy with that of **3** using **2** to afford a yellow powder of **4** (51% yield).

FAB-mass: *m/z* 587 $[M + H]^+$, 552 $[M - Cl]^+$. ^{1}H NMR (400 MHz in $CDCl_3$): δ 9.88 (d, $J = 8.8$ Hz, 2H), 7.83 (d, $J = 8.0$ Hz, 2H), 7.66 (t, $J = 8.0$ Hz, 2H), 7.47 (t, $J = 8.8$ Hz, 2H), 7.39 (s, 2H), 2.36 (s, 3H). Anal. Calcd for $C_{21}H_{13}ClN_2PtS_2$: C, 42.90; H, 2.23; N, 4.76; Cl, 6.03; S, 10.91. Found: C, 42.91; H, 2.51; N, 4.42; Cl, 6.23; S, 10.23.

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Supporting Information Available: General procedures, X-ray crystallographic data, ^{1}H NMR spectra, and UV−vis and photoluminescence data. This material is available free of charge via the Internet at http://pubs.acs.org.

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