

Preparation of platinum complexes containing a thioamide-based SCS pincer ligand and their light emitting properties

Takaki Kanbara ^{a,*}, Keisuke Okada ^a, Takakazu Yamamoto ^{a,*}, Hiromitsu Ogawa ^b, Tetsuji Inoue ^b

^a Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^b TDK Corporation, Technical Center, 2-15-7 Higashi-Ohwada, Ichikawa-shi, Chiba 272-8558, Japan

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Abstract

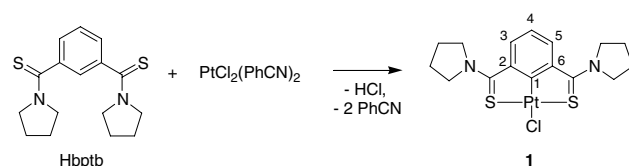
Reaction of 1,3-bis(1-pyrrolidinothiocarbonyl)benzene with $\text{PtCl}_2(\text{PhCN})_2$ afforded a platinum complex with $\eta^3\text{-S,C,S}$ type coordination. The molecular structure of the SCS-pincer platinum(II) complex was determined by X-ray analysis. Substitution of chloro ligand with anionic ligands such as iodo and acetylide was carried out. The complexes exhibit strong emission in a glassy frozen state as well as in the solid state. Light-emitting diodes based on the complexes displayed red electroluminescence. © 2004 Elsevier B.V. All rights reserved.

Keywords: Thioamide; Pincer ligand; Platinum; Luminescence; Light-emitting diode

1. Introduction

Recently, pincer ligands play an increasing role in coordination chemistry and catalysis [1]. One of their advantages comes from the possibility to finely tune the reactivity of the metal center by adjusting the electronic properties of the different pincer ligands. For example, NCN-pincer ligand ($\text{NCN} = [2,6\text{-(CH}_2\text{NMe}_2)_2\text{C}_6\text{H}_3]^-$) stabilizes unusual oxidation states of the metals such as Ni(III) intermediate in the Kharasch addition. These have led to the continuous interest that has been devoted to the synthesis of pincer ligands with various mixed systems incorporating different heteroatoms such as O, S, N, and P. However, much less attention has been paid to SCS-pincer ligands constituted of thioamide group (e.g. 1,3-bis(thiocarbamoyl)benzene) and their cyclometalated transition-metal complexes [2]. The thioamide-based SCS-pincer ligands also consist of mixed donor sets ($\eta^3\text{-S,C,S}$ coordination mode), and the thioamide group could exist as zwitterionic form. Therefore, they could be prospective anionic pincer li-

gands comparable to the 1,3-bis[(thioether)methyl]benzene and its derivatives, which have been recently investigated for a number of catalytic reactions extensively [1,3]. Nonoyama and coworkers [2] have investigated cyclopalladation of a series of thioamide-based aromatic ligands, and *ortho ortho*-cyclopalladation of 1,3-bis(thiocarbamoyl)benzenes has also been reported. On the other hand, tridentate cyclometalated platinum(II) complexes have also attracted considerable attention in recent years, mainly because of their interesting photoluminescence properties and their utilization [4]. We thus have prepared a thioamide-based new pincer platinum(II) complex with 1,3-bis(1-pyrrolidinothiocarbonyl)benzene (Hbptb). The molecular structure, substitution reactions, photoluminescence properties of the complexes, and its preliminary application in light-emitting diodes (LEDs) are also reported.



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* Corresponding authors. Tel.: +81459245222; fax: +81459245276.
E-mail address: tkanbara@res.titech.ac.jp (T. Kanbara).

2. Results and discussion

The SCS-pincer platinum complex (PtCl(bptb), **1**) was obtained in moderate yield (67%) from the reaction of Hbptb and an equimolar amount of dichlorobis(benzonitrile)platinum(II) (PtCl₂(PhCN)₂). Complex **1** is fairly stable to air and water. In the IR spectrum of **1**, a higher frequency shift of $\nu(\text{C}-\text{N})$ for the thioamide group (1503 cm⁻¹) is observed (1481 cm⁻¹ for Hbptb), indicating the S-coordination of the thioamide group and an increase in double bond character of the C–N bond in the coordination form. In the ¹H NMR spectrum of **1**, the ratios of peaks area of the aromatic proton signals are reduced by 1H and the methylene signals assignable to the pyrrolidino group is deshielded on complexation. In the ¹³C-spectrum of **1**, the *ortho-ortho*-platinated carbon (C(1)) is deshielded by 37 ppm (δ 128.3 for Hbptb). ¹⁹⁵Pt NMR spectrum of **1** shows a signal at δ -5281.

The molecular structures of Hbptb and **1** were confirmed by X-ray crystallography (Fig. 1). Complex **1** has a distorted square-planar geometry similar to [PdCl(bptb)] [2b]. The Pt(1)–C(1) and Pt(1)–Cl(1) bond lengths lie in

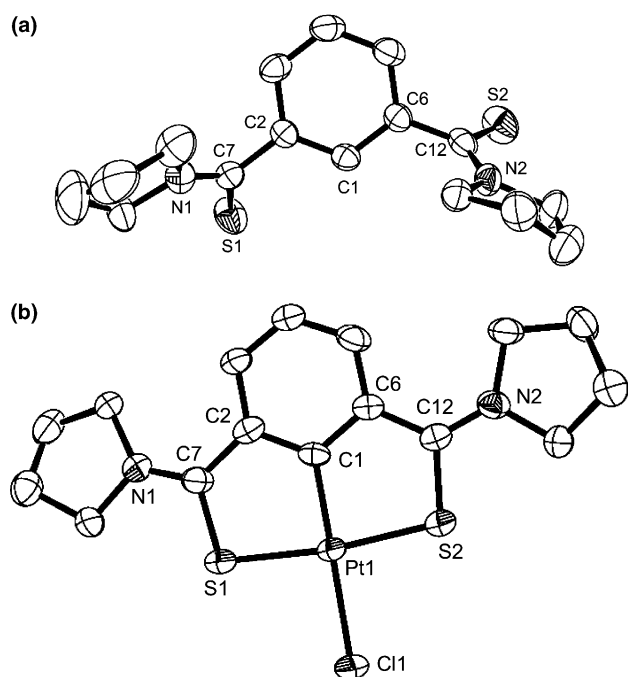
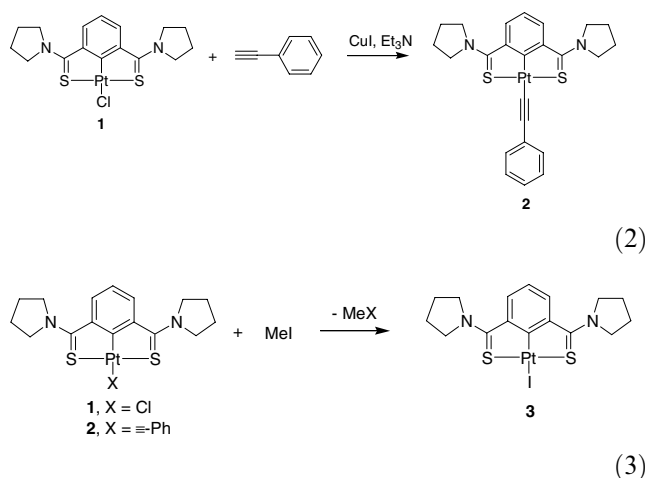


Fig. 1. X-ray crystal structure of Hbptb (a) and **1** (b) with thermal ellipsoids drawn at the 50% probability level. One of the two crystallographically independent molecules of **1** is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): (a) S(1)–C(7), 1.678(4); S(2)–C(12), 1.676(5); N(1)–C(7), 1.316(5); N(2)–C(12), 1.319(5); S(1)–C(7)–C(2), 118.5(3); S(1)–C(7)–N(1), 122.4(3); S(2)–C(12)–C(6), 119.6(3); S(2)–C(12)–N(2), 123.0(3). (b) Pt(1)–C(1), 1.945(7); Pt(1)–Cl(1), 2.388(2); Pt(1)–S(1), 2.265(3); Pt(1)–S(2), 2.255(2); S(1)–C(7), 1.716(8); S(2)–C(12), 1.721(7); N(1)–C(7), 1.31(1); N(2)–C(12), 1.32(1); S(1)–Pt(1)–S(2), 172.56(7); Cl(1)–Pt(1)–C(1), 179.2(2); S(1)–C(7)–C(2), 116.5(6); S(1)–C(7)–N(1), 118.0(6); S(2)–C(12)–C(6), 116.9(6); S(2)–C(12)–N(2), 116.5(5).

the range observed for the pincer Pt complexes [1a, 1b, 4, 5]. The C=S bond lengths are longer than those of free Hbptb, whereas the C–N bond lengths of thioamide group are not significantly altered upon coordination of the thioamide groups. The C=S and C–N bond lengths lie in the range of lengths found in [PdCl(bptb)] [2b].

Reaction of **1** with phenylacetylene in the presence of CuI and triethylamine easily led to a transmetalation to form a phenylacetylide complex (Pt(C≡CPh)(bptb), **2**) in good yield. Treatment of **1** and **2** with an excess of CH₃I gave iodo complex (PtI(bptb), **3**), respectively. ¹H NMR spectra of **1** and **2** after the reaction with an excess of CH₃I showed the signals assigned to **3** and chloromethane (for the reaction of **1**), and 1-phenyl-1-propyne (for the reaction of **2**). Several arenium–platinum complexes have been prepared and isolated from reactions of the pincer-type platinum complexes with CH₃I, which would be formed via S_N2-type nucleophilic substitution of the halide by the metal nucleophile followed by a 1,2-methyl migration between Pt and the *ortho,ortho*-platinated carbon of the aryl ligand [1a, 1c, 5, 6]. The iodo complex **3** was also obtained from the reaction of **1** with AgBF₄ and NaI.



The complexes **1** and **2** are not light-emissive in solution at room temperature, whereas strong photoluminescence was observed in the glassy frozen state as well as in the solid state. The iodo complex **3** is not light-emissive in solution and in the solid state. The absorption spectral data and emission data of the complexes **1** and **2** are summarized in Table 1. The lifetime of the complexes in the frozen state is about 10 μs, indicating phosphorescent emission. Fig. 2 shows emission spectra of **1** and **2** in the solid state and in the glassy frozen state. Not large difference in energy between the solid state and the glassy emission suggests the same electronic origins of the emitting states. Solid state d⁸–d⁸ and ligand–ligand interactions of the photoluminescent cyclometalated platinum(II) complexes have been investigated [4a–4d]. In the present case, however, X-ray diffraction analysis of **1** confirms that the Pt···Pt distance between adjacent

Table 1
Photophysical properties of **1** and **2**

	$\lambda_{\text{max}}^{\text{a}}$ (nm) (ϵ^{b} , $\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}}^{\text{c}}$ (nm)	$\lambda_{\text{em}}^{\text{d}}$ (nm)	$\phi_{\text{f}}^{\text{e}}$	τ^{f} (μs)
1	255 (33 000), 345 (10 400), 440 (4500)	630	595	0.11	11.0
2	247 (32 000), 340 (10 300), 445 (1400)	640	600	0.24	8.3

^a Absorption maxima in CH_2Cl_2 at room temperature.

^b Molecular absorption coefficient.

^c Emission maximum of a microcrystalline sample.

^d Emission maximum in a mixture of CH_2Cl_2 , ethanol, and methanol matrix at 77 K.

^e Fluorescence quantum yield compared with that of *fac*-tris(2-phenylpyridine)iridium ($\phi_{\text{f}} = 0.4 \pm 0.1$) [9].

^f Emission decay lifetime.

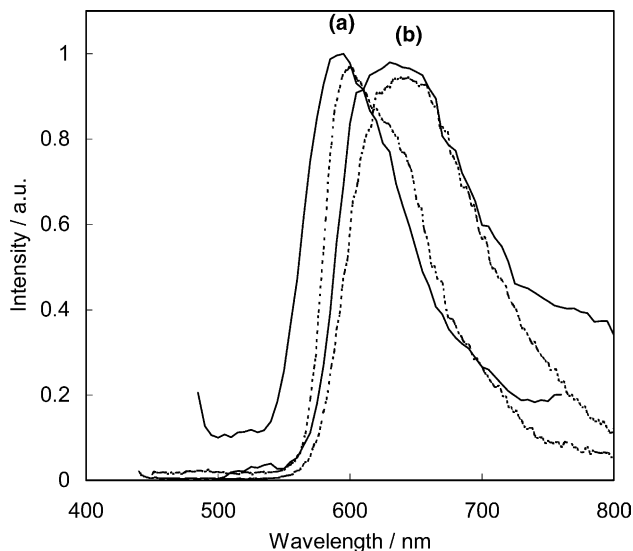


Fig. 2. Emission spectra of **1** (—) and **2** (---): (a) microcrystalline sample at room temperature, (b) in frozen CH_2Cl_2 -MeOH-EtOH matrix (77 K).

complexes is 6.59 Å, indicating there is no d^8 - d^8 interaction, while the intermolecular plane separation between the two ligand planes (about 7.2 Å) would not allow overlap of the π orbitals. We tentatively assigned that the emissive excited state of the complexes is related to $^3\text{MLCT}$ formed by intersystem crossing between singlet and triplet states. A similar photoluminescent feature was recently observed with a platinum complex containing phosphine sulfide-based SCS pincer ligand [4e].

Based on the photoluminescence properties, preliminary application of **1** and **2** as light-emitting materials in the LEDs has been examined. Fig. 3 shows electroluminescence spectra of the LEDs (the LEDs fabricated in the present study were illustrated in the inset of Fig. 3). Red (**1**) or reddish orange (**2**) electroluminescence was observed. The electroluminescence spectra of the LEDs essentially agreed with the photoluminescence spectra of the complexes, revealing that the electroluminescence emission occurred at the complexes. The sub-peak at about 430 nm was attributable to the emission from poly(9-vinylcarbazole) matrix. The present LEDs using **1** and **2** have emission intensities of

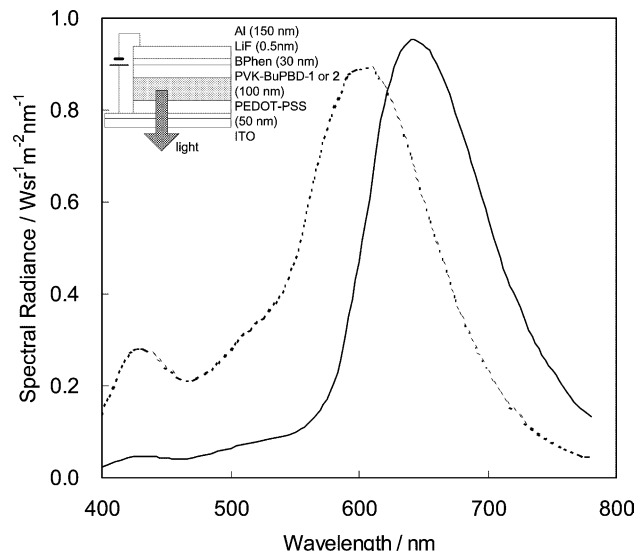


Fig. 3. Electroluminescence spectra of the LEDs for **1** (—) and **2** (---) (inset: multilayer configuration of LED).

180 cd m^{-2} (0.20% efficiency) and 422 cd m^{-2} (0.20%) at 100 mA cm^{-2} , respectively. In order to make practicable LEDs, further optimization should be required.

As described above, new platinum complexes having the thioamide-based SCS-pincer ligand have been prepared. The pincer complexes exhibit interesting photoluminescent properties and stability in air, making them good prospects for use in optoelectronic devices and sensors. Substitution of the chloro ligand of **1** with various neutral and anionic ligands was possible. Attempts to tune their photoluminescent properties of the platinum complexes and to prepare other transition-metal complexes with the thioamide-based SCS-pincer ligands are being undertaken.

3. Experimental

3.1. General procedures

All solvents were dried and distilled prior to use. $\text{PtCl}_2(\text{PhCN})_2$ was prepared as described previously [7].

Hbptb was prepared by the Willgerodt–Kindler reaction according to the literatures [2,8].

IR and NMR spectra were recorded on a JASCO FTIR-460Plus spectrometer, and JEOL JNM-EX-400 and La-500 NMR spectrometer, respectively. Elemental analyses were carried out with a Yanaco CHN Corder MT-5 and a Yanaco SX-Elements Micro Analyzer YS-10. UV–Vis. absorption spectra and emission spectra were recorded on a Shimadzu UV-3100PC spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Emission lifetime measurements were performed with a Hamamatsu Photonics C4780 picosecond fluorescence lifetime measurement system.

3.2. *PtCl(bptb)* (**1**)

An CH_3CN solution (25 ml) of Hbptb (30 mg, 0.1 mmol) was added to a chloroform solution (5 ml) of $\text{PtCl}_2(\text{PhCN})_2$ (47 mg, 0.1 mmol), and the reaction mixture was stirred at 65 °C for 15 h. The resulting precipitate was filtered and washed with CH_3CN and dried in vacuo to give **1** as an orange solid (36 mg, 67% yield).

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.76 (d, 2H, $J = 8.3$ Hz), 7.16 (t, 1H, $J = 7.9$ Hz), 4.29 (t-br, 4H), 3.97 (t-br, 4H), 2.08 (m-br, 8H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 198.2, 165.3 ($^1J(\text{Pt})$ was not resolved), 143.0 ($^2J(\text{Pt}) = 76.8$ Hz), 129.8 ($^3J(\text{Pt}) = 54.9$ Hz), 119.1, 55.8, 54.8, 25.9, 22.9. ^{195}Pt NMR (107 MHz, $\text{DMSO}-d_6$, referenced to H_2PtCl_6): δ -5281. Anal. Found C, 35.53; H, 3.83; N, 5.49; Cl, 6.74; S, 11.85. Calc. for $\text{C}_{16}\text{H}_{19}\text{ClN}_2\text{PtS}_2$: C, 35.99; H, 3.59; N, 5.25; Cl, 6.64; S, 12.01%.

3.3. *Pt(C≡CPh)(bptb)* (**2**)

To a DMF solution (1 ml) of **1** (27 mg, 0.05 mmol) was added phenylacetylene (92 mg, 0.9 mmol) and CuI (4 mg, 0.02 mmol) and triethylamine (1 ml). The reaction mixture was stirred at room temperature for 5 days. The resulting precipitate was filtered and washed with DMF and dried under vacuum to give **2** as an orange solid (25 mg, 82% yield).

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.86 (d, 2H, $J = 7.3$ Hz), 7.16 (m, 5H), 7.06 (t, 1H, $J = 7.2$ Hz), 4.32 (t-br, 4H), 4.03 (t-br, 4H), 2.09 (m-br, 8H). ^{195}Pt NMR (107 MHz, $\text{DMSO}-d_6$, referenced to H_2PtCl_6): δ -5521. Anal. Found: C, 47.78; H, 4.63; N, 4.44; S, 9.83. Calc. for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{PtS}_2$: C, 48.07; H, 4.03; N, 4.67; S, 10.69%.

3.4. *PtI(bptb)* (**3**)

3.4.1. Procedure A

To a CH_2Cl_2 solution (15 ml) of **1** (16 mg, 0.03 mmol) was added an excess MeI (0.1 ml). The solution was stirred at room temperature for 8 days. The solvent was

evaporated, and the crude product was washed with CH_3CN and dried under vacuum to give **3** as a red solid (12 mg, 65% yield).

3.4.2. Procedure B

1 (16 mg, 0.03 mmol) was suspended in acetone (5 ml), and AgBF_4 (6 mg, 0.03 mmol) was added. After the dissolution of the starting complex, water (1 ml) was added. The precipitated silver chloride was filtered off. The addition of NaI (15 mg, 0.1 mmol) and water (5 ml) to the filtrate gave a red precipitate. The precipitate was filtered and washed with water and methanol and dried under vacuum to give **3** as a red solid (7 mg, 39% yield).

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.85 (d, 2H, $J = 8.4$ Hz), 7.24 (t, 1H, $J = 8.2$ Hz), 4.29 (t-br, 4H), 3.97 (t-br, 4H), 2.08 (m-br, 8H). Anal. Found: C, 31.00; H, 3.05; N, 4.91; I, 20.09; S, 9.34. Calc. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{IPtS}_2$: C, 30.73; H, 3.06; N, 4.48; I, 20.29; S, 10.25%.

3.5. Crystal data for Hbptb and **1**

The diffraction data were collected with a Rigaku AFC5R diffractometer with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71070$ Å) at room temperature. 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) or heavy-atom Patterson methods, 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.

Hbptb: $\text{C}_{16}\text{H}_{20}\text{N}_2\text{S}_2$, $M = 304.47$, orthorhombic, space group $P2_12_12_1$, $a = 12.012(9)$, $b = 17.707(9)$, $c = 7.492(7)$ Å, $Z = 4$, $D_{\text{calc}} = 1.269$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 3.26$ cm^{-1} , $T = 296$ K, $F(000) = 648$. A total of 2126 reflections were measured, 2103 unique. The final cycle of full-matrix least squares refinement on F was based on 1306 observed reflections ($I > 2\sigma(I)$), 181 valuable parameters) with factors of $R_1 = 0.037$, $R_w = 0.048$, GOF = 0.85.

1: $\text{C}_{16}\text{H}_{19}\text{ClN}_2\text{PtS}_2$, $M = 534.00$, triclinic, space group $P\bar{1}$, $a = 12.327(4)$, $b = 12.559(7)$, $c = 12.085(5)$ Å, $\alpha = 101.81(3)$, $\beta = 105.45(3)$, $\gamma = 102.30(4)^\circ$, $Z = 4$, $D_{\text{calc}} = 2.095$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 86.57$ cm^{-1} , $T = 296$ K, $F(000) = 1024$. A total of 8128 reflections were measured, 7771 unique. The final cycle of full-matrix least squares refinement on F was based on 4983 observed reflections ($I > 3\sigma(I)$), 397 valuable parameters) with factors of $R_1 = 0.030$, $R_w = 0.042$, GOF = 0.93.

3.6. Preparation and measurement of LEDs

LEDs consisted of the ITO electrode, the hole injection layer of poly[3,4-(ethylenedioxy)thiophene]-

poly(styrenesulfonic acid) (PEDOT-PSS), the emitting layer, the electron transporting layer of 4,7-diphenyl-1,10-phenanthroline (Bathophenanthroline, VPT), the electron injection layer of LiF, and the Al electrode. In all cases, the ITO anode was overcoated with PEDOT-PSS (about 50 nm). Thin films of the emitting materials (about 100 nm) were prepared by spin-casting from a mixture of chloroform–toluene (1:2) solution of a mixture of poly(9-vinylcarbazole), 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, and the platinum complex (PVK-*tert*-BuPBD-**1** or **2**). The thin layers of VPT (about 30 nm) and LiF (about 0.5 nm), and the Al cathode (about 150 nm) were prepared by vacuum deposition. Electroluminescence spectra and light-intensity characteristics of the LEDs were measured by using a monochromator with photodiode-array and luminance meter (light meter). All the measurements were done under vacuum (about 10^{-1} Pa) or argon atmosphere at room temperature.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center; publication numbers CCDC 220725 (Hbptb) and 220726 (**1**).

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