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Synthesis, Structures, and Luminescence Properties of Ternary Supramolecular Hydrogen-Bonded Complexes Involving $[(o\text{-}C_6F_4)Hg]_3$, Carbazole, and a Lewis Base

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ABSTRACT: *The interaction of trimeric perfluoro-*ortho*-phenylene mercury (**1**) with carbazole in dichloromethane, THF, and THF/NEt*$_3$ *leads to the crystallization of* $[\mathbf{1}\cdot C_{12}H_8NH]$ (**2**), $[\mathbf{1}\cdot(C_{12}H_8NH\cdot THF)]$ (**3**), *and* $[\mathbf{1}\cdot(C_{12}H_8NH\cdot NEt_3)]$ (**4**), *respectively. Adducts* **3** *and* **4** *have been characterized by elemental analysis, IR spectroscopy, and luminescence spectroscopy. The crystal structures of* **3** *and* **4** *have also been determined. Both adducts have extended structures that exhibit supramolecular binary stacks, where molecules of* **1** *and the carbazole–Lewis base complex alternate. Short Hg–C contacts involving molecules of* **1** *and carbazole indicate the presence of secondary Hg–π interactions. In addition, adducts* **3** *and* **4** *display hydrogen-bonding interactions between the acidic N—H moiety of carbazole and the heteroatom of the Lewis base. The presence of this hydrogen bond is also confirmed by IR spectroscopy, which shows that the* ν_{N-H} *of* **3** *and* **4** *is lower than that of* **2**. *The luminescence spectra of these adducts correspond to the phosphorescence of carbazole, which is induced by the mercury heavy atom effect. In the case of* **3** *and* **4**, *additional low-energy bands are observed at 578 and 567 nm.* Heteroatom Chem 18:195–201, 2007; DOI 10.1002/hc.20329

INTRODUCTION

Trimeric perfluoro-*ortho*-phenylene mercury (**1**) has been shown to interact with aromatic substrates to form supramolecular binary stacks, where molecules of **1** and the arene alternate [1–8]. In these adducts, as a result of the close proximity of three mercury centers, the arene experiences an intense spin orbit perturbation resulting in room temperature phosphorescence of the arene [1–4]. Although the photophysics of adducts involving **1** has been extensively studied, the chemical consequences of complexation with **1** requires more attention. In search of possible systems, we investigated the ability of **1** to increase the acidity of aromatic derivatives.

Bearing in mind that carbazole forms hydrogen-bonded complexes with various Lewis bases [9–11], we decided to determine if its hydrogen bond donor ability could be enhanced by cofacial complexation with **1**. Indeed, the π-acidic properties of **1** [2,12–14] might be expected to withdraw electron density from carbazole leading to an increase in the acidity and hydrogen bond donor character of the N—H functionality. The compounds discussed in this paper represent the first structurally characterized hydrogen-bonded complexes of carbazole and THF

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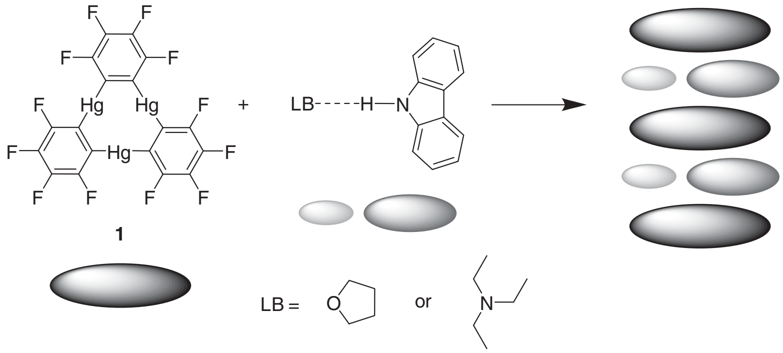

SCHEME 1

or triethylamine (Scheme 1). In addition to the structure and characterization of these supramolecules, unusual temperature-dependent luminescent properties are also presented.

EXPERIMENTAL

General

Because of the toxicity of the mercury compounds discussed, extra care was taken at all times to avoid contact with solid, solution, and air-borne particulate mercury compounds. The studies herein were carried out in a well-aerated fume hood. Atlantic Microlab, Inc. (Norcross, GA) performed the elemental analyses. All commercially available starting materials and solvents were purchased from Aldrich Chemical and VWR, Inc. (USA) and were used as received. Compound **1** was prepared according to the published procedure [15]. The luminescence spectra were recorded with a SLM/AMINCO model 8100 spectrofluorometer equipped with a xenon lamp. Low-temperature measurements were made in a cryogenic device of local design. Collodion was used to attach the powder samples to the holder. The collodion was scanned for a baseline subtraction. Liquid nitrogen was used to obtain the 77 K measurements. The solid-state IR spectroscopy was performed on a Perkin-Elmer spectrum 100 FTIR.

*Synthesis of [**1**·$C_{12}H_8NH$] (**2**)*

Compound **1** (0.020 g, 0.019 mmol) was dissolved in CH_2Cl_2(5 mL). In a separate vial, a CH_2Cl_2solution of carbazole (0.003 g, 0.019 mmol) was prepared. The two solutions were mixed. Upon concentration by slow evaporation of the solvent, crystals of **2** formed in 96% yield (0.022 g, 0.018 mmol). mp 310°C (decomp). Anal. Calcd for $C_{34}H_8F_{12}Hg_3$: C, 32.77; H, 0.65. Found: C, 32.54; H, 0.54.

*Synthesis of [**1**·($C_{12}H_8NH{\cdot}THF$)] (**3**)*

Compound **1** (0.020 g, 0.019 mmol) was dissolved in THF (3 mL). In a separate vial, a THF solution of carbazole (0.003 g, 0.019 mmol) was prepared. The two solutions were mixed. Upon concentration by evaporation of the solvent, crystals of **3** formed in 83% yield (0.020 g, 0.016 mmol). Extended storage required contact with THF. mp 349°C (decomp). Anal. Calcd for $C_{34}H_{17}NOF_{12}Hg_3$: C, 31.82; H, 1.34. Found: C, 31.67; H, 1.24.

*Synthesis of [**1**·($C_{12}H_8NH{\cdot}NEt_3$)] (**4**)*

Compound **1** (0.020 g, 0.019 mmol) was dissolved in THF (3 mL). In a separate vial, a triethylamine solution (5 mL) of carbazole (0.003 g, 0.019 mmol) was prepared. The two solutions were mixed. Upon concentration by evaporation of the solution, crystals of **4** formed in 78% yield (0.020 g, 0.015 mmol). Extended storage required contact with triethylamine. mp 316°C (decomp). Anal. Calcd for $C_{36}H_{23}N_2F_{12}Hg_3$: C, 32.92; H, 1.84. Found: C, 32.74; H, 1.63.

Crystal Structure Determinations

X-ray data for **3** and **4** were collected on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation (=0.71073 Å). Specimens of suitable size and quality were selected and glued onto a glass fiber with freshly prepared epoxy resin. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

RESULTS AND DISCUSSION

Synthesis and Structure of the Adducts

Slow evaporation of CH_2Cl_2, THF, or THF/NEt_3 solution of **1** and carbazole at room temperature affords [**1**·$C_{12}H_8NH$] (**2**), [**1**·($C_{12}H_8NH$·THF)] (**3**), and [**1**·($C_{12}H_8NH$·NEt_3)] (**4**), respectively, which have been characterized by elemental analysis, IR spectroscopy, and luminescence spectroscopy. Although all three adducts are air stable and soluble in polar solvents such as acetone and THF, long-term storage of **3** and **4** requires contact with THF or NEt_3, respectively. While the solid-state structure of **2** has not been elucidated, the structures of adducts **3** and **4** have been determined using X-ray crystallography (Table 1). In both adducts, there are no unusual intramolecular bond distances or angles of the three components. The extended structures exhibit supramolecular stacks, where molecules of **1** and the carbazole-solvent hydrogen-bonded complex alternate (Fig. 1). It is important to note that crystallization of pure carbazole from THF or NEt_3 yields only crystalline carbazole as evidenced by unit cell determination.

Compound **3** crystallizes in the triclinic space group *P*-1 with one molecule of **1**, one molecule of carbazole, and one molecule of THF in the asymmetric unit (Fig. 2). The orientation of the carbazole component allows for the π-face of the heterocycle to be directly exposed to the trinuclear mercury core of **1**. The resulting Hg–C distances of 3.25–3.41 Å are within the sum of the van der Waals radii for Hg (1.7–2.0 Å) [16] and C_{aromatic}(1.5 Å) [17], suggesting the presence of secondary Hg–π interactions. The THF molecule does not engage in any close interactions with the mercury centers or the perfluoroaryl backbone of **1**. However, the short distance of 2.76 Å between N(1) of the carbazole molecule and O(1) of THF suggests the presence of a relatively strong hydrogen bond. The similarity of the C(27)–N(1)–O(1)

TABLE 1 Crystal Data, Data Collection, and Structure Refinement for **3** and **4**

	3	**4**
	Crystal Data	
Formula	$C_{34}H_{17}F_{12}Hg_3NO$	$C_{36}H_{24}F_{12}Hg_3N_2$
M_r	1285.26	1314.34
Crystal size (mm^3)	0.18 × 0.09 × 0.04	0.24 × 0.17 × 0.08
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*P*2 (1)/*c*
a (Å)	7.7605 (16)	12.121 (2)
b (Å)	14.167 (3)	22.893 (5)
c (Å)	16.065 (3)	13.047 (3)
α (°)	113.83 (3)	
β(°)	96.00 (3)	112.74 (3)°
γ (°)	96.98 (3)	
V (Å^3)	1580.5 (6)	3338.9 (12)
Z	2	4
ρ_{calc} (g cm^{-3})	2.701	2.615
μ(Mo K_α) (mm^{-1})	14.637	13.859
F(000) (e)	1168	2408
	Data Collection	
T (K)	110 (2)	110 (2)
Scan mode	ω	ω
hkl range	−9 → 9, −16 → 16, −19 → 19	−13 → 13, −26 → 24, −14 → 14
Measured reflections	11,425	21,747
Unique reflections, [R_{int}]	5527, [0.0701]	5239, [0.1130]
Reflections used for refinement	5527	5239
Absorption correction	SADABS	SADABS
$T_{\text{min}}/T_{\text{max}}$	0.444896	0.382563
	Refinement	
Refined parameters	346	478
R1[a], wR2[b] [$I > 2\sigma(I)$]	0.0542, 0.1097	0.0538, 0.1245
ρ_{fin} (max/min) (eÅ^{-3})	2.361, −3.045	3.441, −1.740

[a] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$.

[b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0470$ (**3**), 0.0710 (**4**); $b = 0.0000$ (**3**), 0.0000 (**4**).

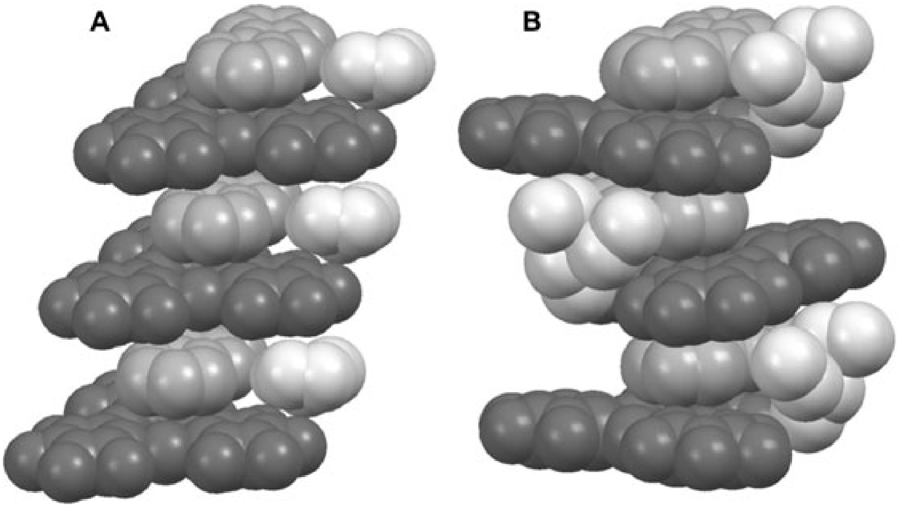

FIGURE 1 Space-filling view of (A) **3** and (B) **4**. Color code: **1**, dark grey; carbazole, medium grey; THF (A) and NEt_3 (B), light grey.

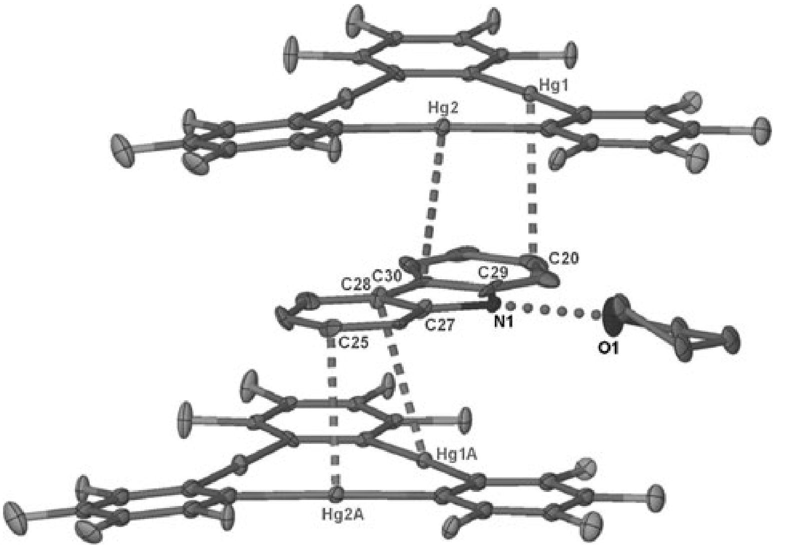

FIGURE 2 Structure of **3**. ORTEP view (50% ellipsoid) with H atoms omitted for clarity. Representative intermolecular distances (Å): N(1)–O(1) 2.760, Hg(1)–C(20) 3.328, Hg(1A)–C(28) 3.357, Hg(2)–C(30) 3.408, Hg(2A)–C(25) 3.251.

and C(29)–N(1)–O(1) angles (127° and 125°, respectively) indicates that the N—H···O interaction is virtually linear, as typically observed in strong hydrogen-bonding interactions [18–21].

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of **1**, one molecule of carbazole, and one molecule of NEt_3 in the asymmetric unit (Fig. 3). As in the case of **3**, the carbon atoms of the carbazole component engage in secondary Hg–π interactions with the mercury centers of **1** as evidenced by the short Hg–C distances (3.25–3.43 Å). Furthermore, there is a short Hg–N interaction of 3.38 Å between Hg(3A) and N(1). As with **3**, the NEt_3 molecule does not interact with the mercury centers or the perfluoroaryl backbone of **1**. The short N(1)···N(2) distance of 2.94 Å suggests a hydrogen bond between the NEt_3 nitrogen atom and the carbazole N—H moiety. In addition, the C(27)–N(1)–O(1) and C(29)–N(1)–O(1) angles (136° and 114°, respectively) indicate that the N—H···N interaction is nearly linear. Typical N···N distances attributed to hydrogen-bonding interactions typically range from

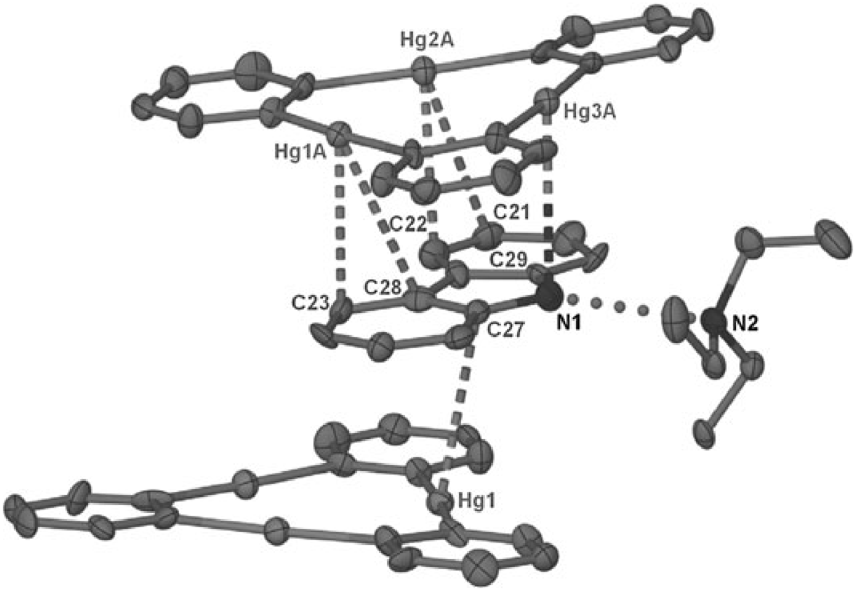

FIGURE 3 Structure of **4**. ORTEP view (50% ellipsoid) with H and F atoms omitted for clarity. Representative intermolecular distances (Å): N(1)–N(2) 2.940, Hg(1)–C(27) 3.432, Hg(1A)–C(23) 3.141, Hg(1A)–C(28) 3.362, Hg(2A)–C(21) 3.432, Hg(2A)–C(22) 3.207, Hg(3A)–N(1) 3.375.

2.8 to 3.0 Å [22]. Because of the increased crowding induced by the NEt_3 component, the planes of molecules of **1** and carbazole are not parallel. In fact, the planes of the mercury core of **1** containing Hg(1) and of the carbazole would intersect at a 6.1° dihedral angle.

In order to confirm the presence of a hydrogen-bonding interaction between the carbazole N—H group and the solvent molecules, we analyzed the adducts by IR spectroscopy. The N—H stretching bands appear at 3460 cm^{-1} for **2**, 3419 cm^{-1} for **3**, and 3417 cm^{-1} for **4**. The vibrational frequency shifts ($\Delta\nu$) between the isolated carbazole in **2** and the hydrogen-bonded complexes **3** and **4** are 41 cm^{-1} and 43 cm^{-1}, respectively. This weakening of the N—H stretch in **3** and **4** is in agreement with the presence of a hydrogen bond interaction, an effect which has been previously discussed for other hydrogen-bonded systems [23].

Solid-State Luminescence

At both room temperature and 77 K adduct, **2** emits blue light (Fig. 4). Examination of its emission spectra recorded at both temperatures indicates that the observed luminescence corresponds to the phosphorescence of carbazole [24]. As previously proposed for the *N*-methylcarbazole adduct of **1** [3], the observed phosphorescence is a direct result of the external mercury heavy atom effect which promotes intersystem spin crossing from the S_1 to the T_1 state of the carbazole. At low temperature (77 K), adducts **3** and **4** also emit blue light with emission spectra which also corresponds to the triplet emission of carbazole (Figs. 5a and 5b). In both spectra, however, weak bands are observed at 578 and 567 nm. Remarkably, elevation of the temperature leads to a drastic increase in the intensity of these bands, which results in a change of the color of the emission from blue to orange in the case of **3** and from blue to yellow in the case of **4**. The exact origin of these low-energy bands cannot be confirmed at this time.

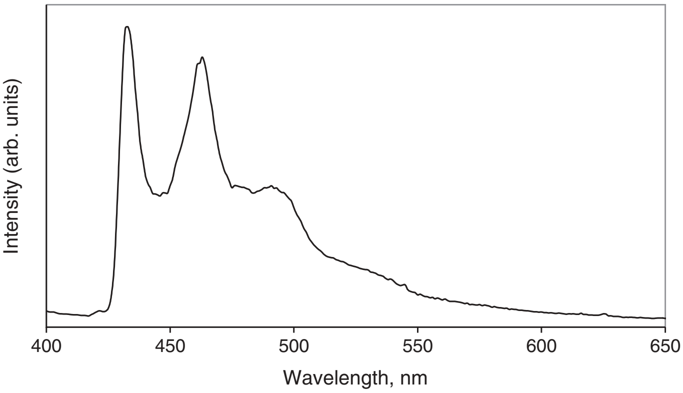

FIGURE 4 Emission spectra of **2** at 77 K.

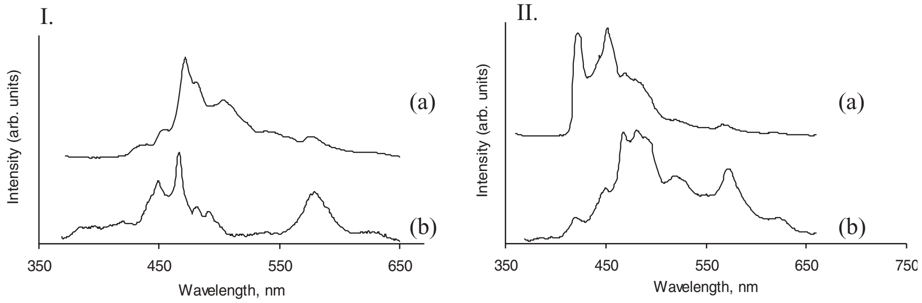

FIGURE 5 Emission spectra of (I) **3** and (II) **4** at (a) 77 K and (b) RT.

CONCLUSIONS

This report describes the first structurally characterized hydrogen-bonded complex of carbazole with coordinating solvents, specifically THF and NEt_3, which suggests that complexation to **1** allows for increasing the acidity of the carbazole substrate. Both adducts **3** and **4** are brightly luminescent indicating that the Lewis bases do not quench the excited state of the chromophores [9,25].

SUPPLEMENTARY INFORMATION

CCDC 622457 and 622458 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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