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Note

Mono- and dinuclear Hg(II) complexes of bis-(*N*-heterocyclic carbene) bridged with calixarene fragments: Synthesis, structure and sensing behavior

Cai-Xia Lin [a], Lin Guo [b], Qing-Shan Li [b], Zheng-Zhi Zhang [b], Yao-Feng Yuan [a, b, *], Feng-Bo Xu [b, **]

[a] *Department of Chemistry, Fuzhou University, Fuzhou 350108, People's Republic of China*
[b] *State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China*

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ABSTRACT

Mono- and dinuclear Hg(II) complexes of bis-(*N*-heterocyclic carbene) bridged with calixarene fragments, [Hg**L**]$(PF_6)_2$ (**4a**, **4b**) and $[Hg_2\mathbf{L}_2](PF_6)_4$ (**5a**, **5b**), (**L** = bis{3-(*N*-1-naphthylmethyl-imidazol-2-ylidene)methyl-5-R-2-methoxyphenyl}methane, **a**: R = Me, **b**: R = *t*-Bu) were both obtained by treatment of corresponding bis-imidazolium salts with mercuric acetate. The structures of complexes **4a** and **5a** were established by X-ray diffraction. Mononuclear complex **4a** displays a small rigid cavity consisting of a mercury cation and a bis-NHC ligand. Dinuclear complex **5a** shows a 28-memebered metallamacrocycle formed by two mercury cations and two bis-NHC ligands. Short mercury–oxygen contacts are found between mercury cations and methoxy groups of ligands in **4a** and **5a**. Cation–π–arene interactions are present between mercury cations and naphthalene rings of ligands. Additionally, the fluorescent chemosensing behaviors of complex **5a** with large cavity to diphenylacetylene, (*E*)-azobenzene and (*E*)-4,4′-azobispyridine were investigated.

1. Introduction

N-heterocyclic carbenes (NHCs) are weak π-acceptors and strong σ-donors and they can form strong M-C bonds with transition metal centers [1–3]. The transition metal complexes of NHCs have attracted considerable interests for many decades and have been widely applied in structural [4–8], biological [9–11], and catalytical areas [12–14]. Although the Hg(II)–NHC complexes have been firstly prepared by Wanzlick and Schönherr since 1968 [15,16], compared with other transition metal–NHC complexes, they have received much less attention [17,18]. In recent years, Hg(II)–NHC complexes have been found as potential transmetallation reagents for synthesizing other types of transition metal–carbene complexes [19–21]. Owing to the potential applications as carbene transfer agents, the design and synthesis of Hg(II)–NHC complexes of diverse scaffolds is of great importance. Recently, some Hg(II)–bis(NHC) complexes containing interesting metallacycle frameworks linked by cyclophane [20], aryl chains [18,22–32] and ether chains [33,34] have been reported. And among the metallacycles, only a few are metallamacrocycles constructed by two mercury atoms sandwiched between two bis-NHC ligands bridged with aryl chains (Chart 1) [22,30–32,35]. Our group is interested in a kind of metallamacrocycles featuring metal bridged bidentate ligands containing half-calix [4]arene fragment scaffolds, which can be acted as molecular receptors for small organic molecule and anion [36–38]. In this paper, we would like to report Hg(II)–bis(NHC) complexes of new bis-imidazolium ligands $[H_2\mathbf{L}](PF_6)_2$ (**L** = bis{3-(*N*-1-naphthylmethylimidazol-2-ylidene)methyl-5-R-2-methoxyphenyl}methane) bridged with half-calix [4]arene fragments. Contrasting with those reported Hg(II)–bis(NHC) complexes bridged with aryl chains [18,23,25,39,40], mononuclear complex [Hg**L**]$(PF_6)_2$ and dinuclear complex $[Hg_2\mathbf{L}_2](PF_6)_4$were both obtained in the reaction of the corresponding bis-imidazolium salt with mercuric acetate.

2. Results and discussion

2.1. Synthesis and characterization of complexes

As shown in Scheme 1, bisimidazolium salts bridged by half-calix [4]arene fragments, $[H_2\mathbf{L}](Br)_2$ were prepared by reaction of

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[*] Corresponding author. Department of Chemistry, Fuzhou University, Fuzhou 350108, People's Republic of China. Tel./fax: +86 591 2286 6161.
[**] Corresponding author. Tel./fax: +86 22 2350 5927.
E-mail addresses: yaofeng_yuan@fzu.edu.cn (Y.-F. Yuan), xufb@nankai.edu.cn (F.-B. Xu).

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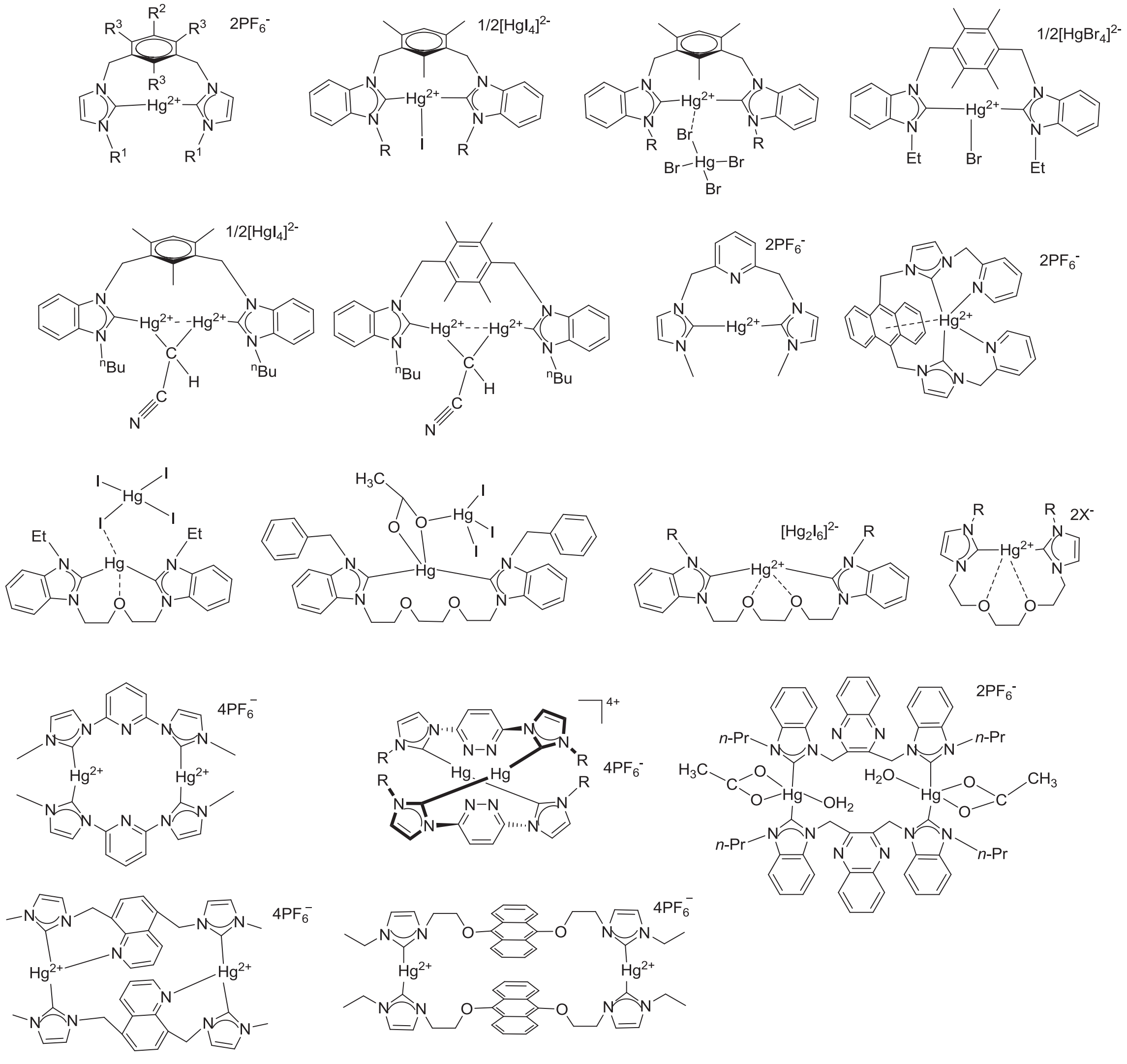

Chart 1. Hg(II)–bis(NHC) complexes.

bis(3-bromomethyl-5-*R*-2-methoxyphenyl)methane (**1**) with *N*-1-naphthylmethylimidazole (**2**) in refluxing THF. Anion exchange of the $[H_2\mathbf{L}](Br)_2$ with NH_4PF_6 in methanol afforded $[H_2\mathbf{L}](PF_6)_2$ (**3**). Treatment of ligand (**3**) with 1.1 mol eq. mercuric acetate in refluxing acetonitrile for 48 h afforded mono- and dinuclear mercury complexes **4** and **5**. In the preparation of the Hg(II)–NHC complexes, the concentration of the reactant **3** dominates the contribution of the main two products. A high concentration of **3** gives mononuclear complex **4** as main product, and a dilute solution of **3** gives dinuclear complex **5**. The produced complex **4** or **5** can be purified by recrystallization with acetone and ethyl acetate after reaction.

The ^1H NMR and ^{13}C NMR spectra of all new compounds were obtained in d_6-DMSO at room temperature (Figs. S1–S6). In the ^1H NMR spectra of precursors **3a**–**b**, the characteristic resonances for imidazolium acidic protons C^6–*H* appear at 9.35 and 9.38 ppm and the ^{13}C NMR signals display at 136.82 and 136.37 ppm (Table 1), which are consistent with those of reported imidazolium salts [41].

In the ^1H NMR spectra of complexes **4** and **5**, the characteristic resonances for the acidic protons disappeared compared with that in **3a**–**b**, which confirmed the formation of Hg–C_{NHC} bonds. There are some proton signals shifted upfield in the ^1H NMR spectra of complexes **4** compared with that of relative precursors **3**. Compared the ^1H NMR spectrum of **4a** with that of its precursor **3a**, the signals of two protons in NHC rings of **4a** shifted downfield from 7.81 ppm to 8.27 ppm, which could be attributed to the deshielding effect of naphthalene ring. And the proton signals of methoxy groups shifted upfield from 3.56 ppm to 2.68 ppm, which could be attributed to the shielding effect of naphthalene rings. The proton signals of methylene groups in **4a** between NHC rings and naphthalene rings are also affected by the shielding effect of naphthalene ring shifting upfield from 5.39 ppm to 4.99 ppm. However, the methylene groups between NHC rings and benzene rings in **4a** showed slight difference compared with that of **3a**, appearing at 5.99 ppm. The ^1H NMR spectrum of complex **4b** is very similar to that of **4a**. Comparably, there is no apparent shift of the proton signal in the ^1H NMR spectrum of complex **5a** comparing to that of precursor **3a**. And the ^1H NMR spectrum of complex **5b** is approximate to that of **5a**. However, there are no much difference for the ^{13}C NMR spectra of complexes **4** and **5**, the signals of the carbene carbons located in the range of 173.0–174.7 ppm, which are similar to the values for reported Hg(II)–NHC complexes [18,25,27–29,39].

2.2. Crystal structure of complexes

A single crystal of $\mathbf{4a}\cdot CH_3COOC_2H_5$ was grown by diffusion of ethyl acetate into its acetone solution. A single crystal of $\mathbf{5a}\cdot 2C_3H_6O\cdot 2C_2H_6O\cdot H_2O$ was obtained by slow evaporation of its