Complexation of 4,4′-di(*tert*-butyl)-5-ethynyl-2,2′-bithiazole with mercury(II) ion: Synthesis, structures and analytical applications

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Abstract

Two new mononuclear mercury(II) alkynyl complexes containing substituted bithiazole unit [R–C≡C–HgMe] (**2**) and [R–C≡C–Hg–C≡C–R] (**3**) (R = 4,4′-di(*tert*-butyl)-2,2′-bithiazol-5-yl) were prepared in good yields by mercuration of 4,4′-di(*tert*-butyl)-5-ethynyl-2,2′-bithiazole (**1**) at room temperature via the dehydrohalogenation reaction of MeHgCl and HgCl$_2$ with terminal acetylene R–C≡CH. The structures of the title compounds were characterized by NMR and IR spectroscopy, FAB mass spectrometry, X-ray crystallography and luminescence spectra. A new protocol for derivatization of inorganic and organic mercury(II) ions to mono- and dialkynyl mercury(II) compounds followed by extraction into dichloromethane is suggested, which can be effectively analyzed by HPLC technique using UV detection. The proposed procedure can offer a new opportunity for the simultaneous determination of inorganic Hg(II) and MeHg(II) in aqueous solutions.
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1. Introduction

The realization that various forms of mercury such as monomethylmercury [MeHg]$^+$ is a potential threat to public health sparked our interest in their chemistry [1]. [MeHg]$^+$ has a rich coordination chemistry, forming complexes with a variety of organic and inorganic ligands. Yet its coordination chemistry is fascinatingly simple since it is known to link to coordinating groups to form mostly two-coordinate mercury(II) complexes [2]. Indeed, this simplicity forms the basis for its use as a highly selective reagent in biological systems [3]. Concern regarding anthropogenic and natural contamination by mercury continues the stimulation of the development of new methods of analysis [4]. Major efforts are currently devoted to the search for rapid, sensitive and reliable separation and detection procedures

for these mercury compounds. To address this problematic issue, different approaches have been reported in the literature. In most of the early cases, thiol ligands were employed since thiolate ions are known to form very strong bonds with MeHg and MeHg–thiol complexes are very stable thermodynamically [2]. As a recent alternative, derivatization procedures which convert Hg(II) and MeHg(II) species into organometallic acetylide derivatives suitable for chromatographic analysis have been shown to be effective measures with regards to the goal [5]. Upon derivatization followed by solvent extraction, the resulting complexes can be separated and analyzed by GC, HPLC, etc. HPLC has an advantage over GC in that formation of volatile derivatives is not necessary.

From a synthetic perspective, the preparation, structure and luminescence properties of transition metal complexes of alkynyl ligands have attracted enormous attention in the past two decades [6]. Metal alkynyls are common for many transition metals, particularly those of group 8–11 metals, and their chemistry has been developed extensively [6,7].

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In contrast to the large body of work on alkynylgold(I) compounds, the chemistry of d^{10} alkynylmercury(II) compounds has not been so thoroughly investigated, and related research work on the isoelectronic mercury(II) system is still in its infancy [8]. Indeed, mono- and dialkynyl mercury complexes have been demonstrated to be useful in the analysis of toxic mercury(II) species [5] and to be good building blocks for the synthesis of luminescent metallopolymers and supramolecular aggregates [8].

In the context of these important areas, a program is initiated to synthesize new mercury(II) alkynyl molecular systems that can be employed to develop a sensitive method for the detection of inorganic Hg(II) and MeHg(II) ions using suitable derivatization steps. Here, we describe the first synthesis, characterization, luminescence behavior of two novel mononuclear mercury(II) alkynyl complexes containing substituted bithiazole chromophore and their potential analytical applications using HPLC/UV analysis.

2. Results and discussion

2.1. Synthesis

4,4′-Di(*tert*-butyl)-2,2′-bithiazole was prepared in very good yield by the direct reaction of 1-bromopinacolone with dithiooxamide in refluxing EtOH [9]. Monobromination was effected by using one equivalent of N-bromosuccinimide (NBS) in DMF to give 5-bromo-4,4′-di(*tert*-butyl)-2,2′-bithiazole. The trimethylsilyl-protected ligand was obtained by the coupling of 5-bromo-4,4′-di(*tert*-butyl)-2,2′-bithiazole with trimethylsilylacetylene using the well-established palladium coupling method [10]. This ligand can then be protodesilylated to give **1**, using methanolic K_2CO_3. Yellow crystalline product of **1** was isolated in satisfactory yield after purification by column chromatography, and recrystallization from CH_2Cl_2/hexane. In contrast to the structurally related counterpart, viz. 5-ethynyl-2,2′-

bithiophene [11], the new terminal acetylene **1** is stable as solid or on exposure to light for long periods. Two new Hg(II) alkynyl complexes **2** and **3** were obtained in good yields by the general reaction routes described in Scheme 1. Reactions of **1** with MeHgCl and $HgCl_2$ take place readily in an excess of NaOMe in MeOH to furnish new mercury complexes **2** and **3**, respectively, which can be precipitated from the solution mixture directly as yellow powders. The feed mole ratios of the Hg(II) chloride precursors and the derivatizing alkyne **1** were 1:1 and 1:2 for **2** and **3**, respectively. Both metal complexes are air-stable and can be stored without demanding any special precautions. They generally exhibit good solubility in chlorocarbons such as CH_2Cl_2 and $CHCl_3$, but are insoluble in hydrocarbons.

2.2. Spectroscopic properties

The ligand and the mercury(II) complexes were fully characterized by common spectroscopic techniques such as infrared, ^1H and ^{13}C NMR spectroscopies and FAB mass spectrometry which agree with their chemical structures (see Section 4). The solution IR spectra of **2** and **3** are each characterized by a single sharp $\nu(C\equiv C)$ absorption band at ca. 2124–2141 cm^{-1}, which are in line with the linear arrangement in such Hg(II) system. Compared with the IR spectrum of **1**, no band in the range of 3200–3300 cm^{-1} typical for the $\equiv C$–H stretching vibration was observed for **2** and **3**, confirming that the free alkyne **1** is bonded to the metal group via σ bonds. ^1H NMR resonances arising from the protons of the organic moieties were noted for **2** and **3**, and their good solubilities in chlorocarbons allow complete ^{13}C NMR spectra to be interpreted. Notably, two distinct ^{13}C NMR signals for the individual sp alkyne carbon atoms in **2** and **3** were observed, in accord with their formulations, and they are shifted downfield with respect to **1** [12]. The formulas of all the new compounds were successfully established by
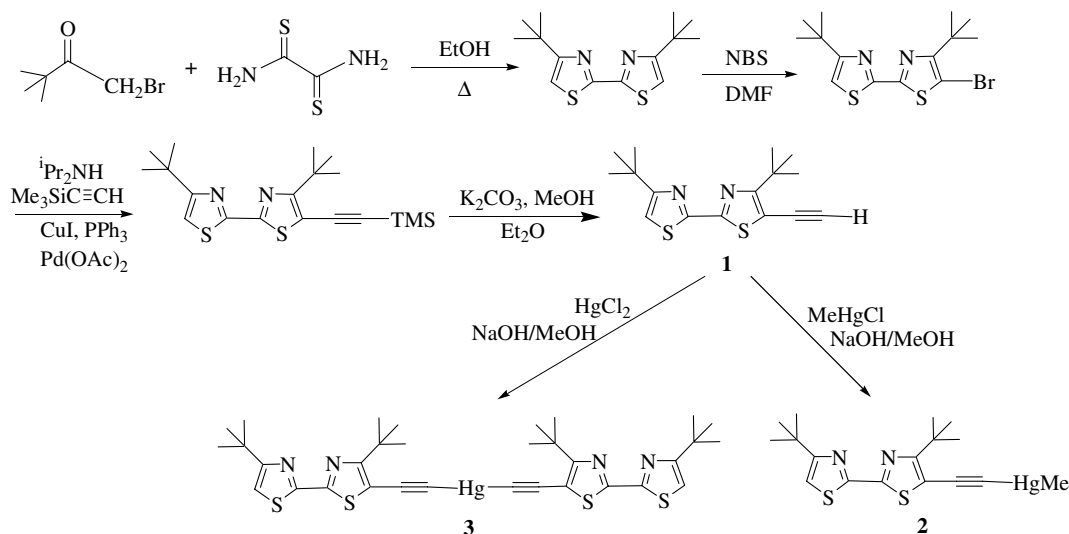
Scheme 1.

the presence of intense molecular ion peaks in their respective positive FAB mass spectra.

2.3. Crystal structure analyses

The molecular structures of **1** and **2** were ascertained by X-ray crystallography. Perspective views of their structures are shown in Figs. 1 and 2, respectively. Pertinent bond distances and angles are summarized in Table 1. In Fig. 1, the C≡C bond is at 1.160(6) Å which appears to be shorter than that in **2** (1.184(6) Å) due to the libration effect [13]. The two thiazole rings are planar and in a *trans* disposition to each other so that the repulsion between the two *tert*-butyl groups and between the two lone pairs on the sulfur atoms can be minimized. Electronic factor also plays a key role here. As shown from the resonance structures in Chart 1 for both isomers in which the nitrogen atom is more electronegative than the sulfur atom, the two negative charges on N atoms and the two positive charges on S atoms will destabilize the resonance hybrid in the *cis* geometry. However, the corresponding canonical form for the

Table 1
Selected bond lengths (Å) and angles (°) for **1** and **2**

	1	**2**
S(1)–C(sp^2) (average)	1.713(4)	1.718(4)
S(2)–C(sp^2) (average)	1.727(4)	1.727(4)
N(1)–C(7)	1.315(4)	1.312(5)
N(2)–C(8)	1.309(4)	1.313(5)
C(15)–C(16)	1.160(6)	1.184(6)
Hg(1)–C(16)		2.034(4)
Hg(1)–C(17)		2.077(6)
C(sp^2)–C(15)–C(16)	175.4(5)	177.2(5)
C(sp^2)–S(1)–C(sp^2)	88.67(19)	88.86(19)
C(sp^2)–S(2)–C(sp^2)	88.96(17)	88.91(18)
C(16)–Hg(1)–C(17)		179.6(4)
Hg(1)–C(16)–C(15)		179.5(7)

trans isomer will be stabilized by the presence of two unequal charges on each side of the bithiazole moiety.

The X-ray structure of **2** shows a mononuclear mercury complex in which the mercury atom adopts a linear geometry with sp hybridization around the metal and acetylenic carbon. To our knowledge, structurally characterized examples of metallaynes bearing bithiazole derivatives are very rare in the literature [14]. The angles of Hg(1)–C(16)–C(15) and C(16)–Hg(1)–C(17) in **2** are 179.5(7)° and 179.6(4)° which are close to linearity. The Hg–C(alkyne) bond length (2.034(4) Å) is comparable to those in other known Hg(II) acetylide species [8a–e]. The two thiazole rings are arranged in a *trans* configuration as in **1** (vide supra). Attachment of the MeHg unit in **2** does not have a great influence on the bond parameters of the ligand chromophore. The lattice of **2** is highlighted by the presence of weak Hg···S interaction in a 3D network. The closest intermolecular non-bonded Hg···S contact is due to the two types of Hg(1)···S(1) interaction (3.813 and 3.801 Å). In contrast to the dimercury(II) bis(alkynyl) complexes described previously [8b,8d–f], there is no apparent mercuriophilic interactions between adjacent molecules in this case, presumably attributed to the presence of two bulky *tert*-butyl groups on the organic unit of the molecule to prevent their close approach.

2.4. Electronic absorption and luminescence spectra

The photophysical data of the new compounds **1–3** are shown in Table 2. Both mercury(II) complexes display similarly structured absorption bands in the near-UV region (Figs. 3 and 4). With reference to previous spectroscopic data in other similar systems, we can tentatively assign the absorption features to ligand-centered π–π* transitions, possibly with some admixture of metal d orbitals [8d,14]. As compared with the ligand precursor **1**, we note a red-shift in the lowest energy absorption bands of the metal complexes with reduced optical gaps (E_g) after the inclusion of mercury atom, which signifies that π-conjugation is preserved through the metal site by mixing of the frontier orbitals of metal and the ligand due to metal to ligand back-donation to π*(C≡CR). Thus, a red-shift of ca.
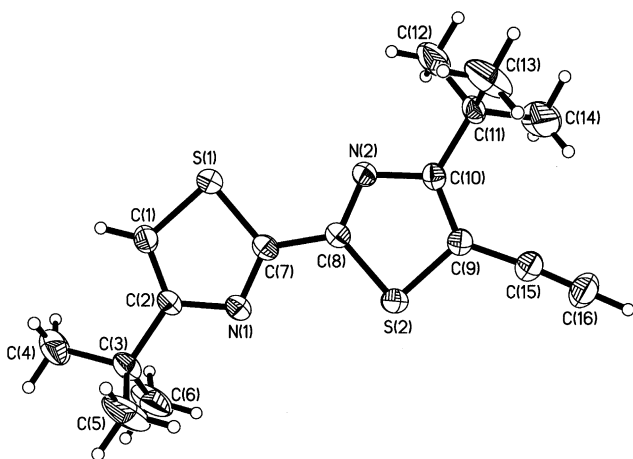

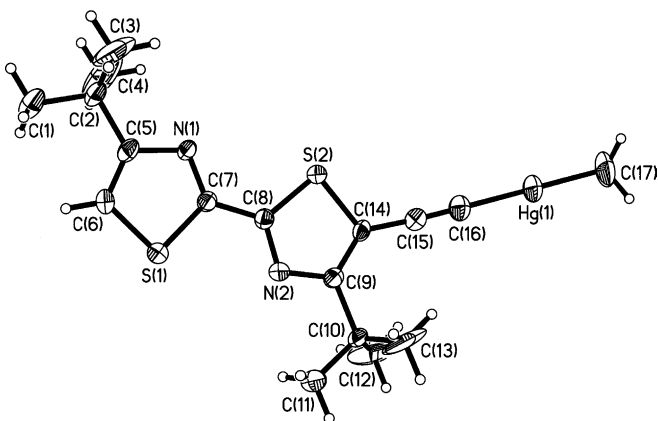Fig. 1. A perspective drawing of **1** with the thermal ellipsoids drawn at the 25% probability level.

Fig. 2. A perspective drawing of **2** with the thermal ellipsoids drawn at the 25% probability level.
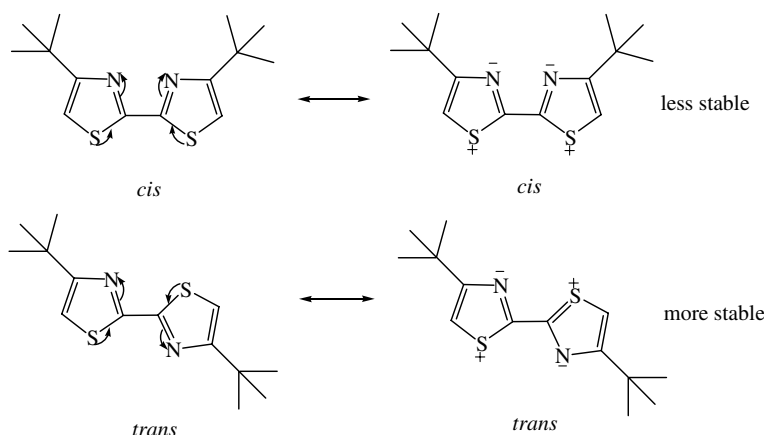
Chart 1.

Table 2
Photophysical data for **1**–**3**

Compound	λ_{max} (nm)[a]		E_g (eV) [b]	λ_{em} (nm)	
	CH$_2$Cl$_2$	Film		CH$_2$Cl$_2$ (290 K)	Φ (%)[c]
1	292 (0.7)	297	3.63	317	57.5
	304 (0.5)	309		331	
	317 (0.8)	317			
2	271 (0.4)	376	2.94	397	4.37
	363 (2.9)	393		400	
				420	
3	275 (1.0)	383	2.91	399	7.52
	368 (5.2)	405		422	

[a] Extinction coefficients $(\varepsilon \times 10^{-4}\, dm^3\, mol^{-1}\, cm^{-1})$ are shown in parentheses.
[b] Estimated from the onset wavelength of the solid-state optical absorption.
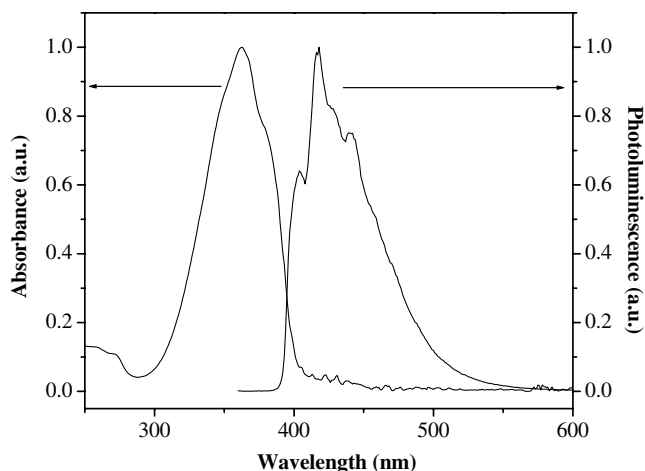[c] Fluorescence quantum yield relative to anthracene $(\Phi = 0.27)$.

Fig. 4. Absorption and emission spectra of **3** in CH$_2$Cl$_2$ at 290 K.

Fig. 3. Absorption and emission spectra of **2** in CH$_2$Cl$_2$ at 290 K.

46 nm is observed from **1** to **2**, whereas the shift is 51 nm from **1** to **3**. Introduction of the mercury(II) segment in **2** and **3** is also found to increase the absorption intensity, signaling an enhancement in the extent of π-delocalization through the metal group. While there is an increase in the molar extinction coefficients from **2** to **3** that is caused
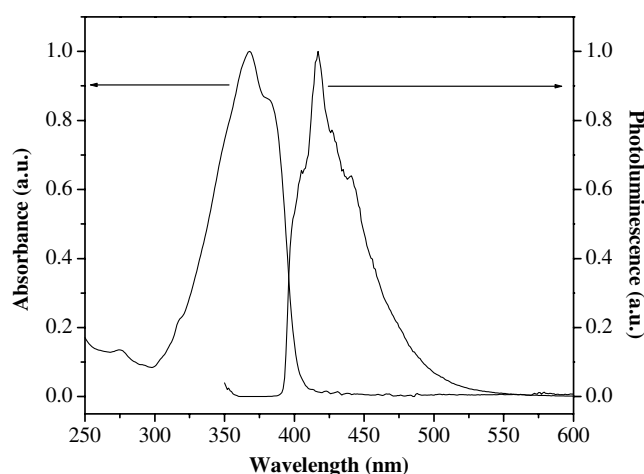
by the presence of one additional bithiazole absorbing chromophore in the dialkynylated complex, we also note a slight bathochromic shift in the lowest energy absorption peak from **2** to **3**.

Compounds **1**–**3** are all emissive at room temperature. In dilute CH$_2$Cl$_2$ solutions at 290 K, we observe an intense $^1(\pi–\pi^*)$ emission peak in the range of 397–421 nm for **2** and **3** due to the ligand-based fluorescence emission (Figs. 3 and 4). The featureless luminescence spectra are independent of the excitation wavelength used, suggesting that a single emissive state or multiple states in equilibrium is (are) responsible for the observed emission. The emission band was shown to shift to the lower energies on going from the ligand to the metal complexes but it does not vary much between **2** and **3**. There is a decrease in the emission quantum yield by about one order of magnitude in going from **1** to **2** and **3**. The quenching observed may be the result of the heavy-atom effect induced by the mercury ion, in which the heavy metal catalyzes the nonradiative deactivation of the singlet excited states of the chromophore [15]. In our case here, there is no evidence of observing the phosphorescence of organic luminophore upon the covalent attachment with a mercury ion, in contrast to the

recent reports by Gabbai et al. in which the heavy-atom effect of mercury has led to the enhancement of ligand phosphorescence rather than a quenching effect alone [16].

2.5. Analytical application in the speciation of mercury

Alkyne-mercury coordination chemistry has previously been exploited in an environmental profitable way for mercury speciation in water [5]. The method is based on the reactivity of monosubstituted 1-alkynes with inorganic Hg(II) and MeHg(II) ions in alkaline aqueous conditions, in analogy to the known chemistry of Hg(II) species towards acetylenes. To this purpose, we envisioned alkyne **1** as an attractive candidate, since it carries an auxiliary group which is photophysically active in the UV–Vis region, and, as a further advantage, the synthesis was straightforward and required simple routine chemistry. Moreover, the ligand itself can react smoothly with MeHgCl and HgCl$_2$ in dichloromethane/water solution to give mononuclear Hg(II) complexes on a preparative scale. The photophysical properties of these Hg(II) complexes have been studied in CH$_2$Cl$_2$ (vide supra). The unique photophysical features of **2** and **3** appear to be appropriate for analytical detection. This was clearly confirmed by preliminary HPLC measurements.

We found that stirring a two-phase system of aqueous HgCl$_2$ and MeHgCl containing NaOH and NaCl and a dichloromethane solution of ligand **1** for 2 h affords mercury(II) complexes almost quantitatively, which is directly extracted into the organic phase. Moreover, the high extinction coefficient makes both mercury complexes suitable for HPLC analysis using UV detection below.

HPLC chromatograms of working solutions obtained by derivatization show the expected peak, the corresponding UV spectrum being identical to that of the standard compound **2**. Peaks of compounds **1** (retention time $t_R = 16.9$ min) and **2** ($t_R = 17.4$ min) are very symmetrical and fully separated (Fig. 5) using a C-8 reversed phase column, and eluting with THF/water that is linearly changing within 18 min. Detection was set at 363 nm. The eluent flow was 0.6 mL/min. Column temperature was maintained at 34 °C. Dose–response curve for complex **2** was measured, and a good proportionality exists between the amount of analyte injected and peak areas. Calibration graph based on peak areas is shown in Fig. 6 and is linear over 0.5–54.0 mg/L for **2** over two orders of magnitude with a correlation coefficient of 0.9998; the excellent fit and linearity indicate that this method is suitable for quantitative analysis. The detection limit, expressed as the absolute amount of analyte injected to give a signal three times higher than the signal noise, was found to be ~0.5 ng injected Hg for **2**.

Likewise, symmetric peaks of **1** (retention time $t_R = 14.3$ min) and **3** ($t_R = 15.9$ min) are also well separated (Fig. 7) using a C-8 reversed phase column, and eluting with THF/water that is linearly changing within 16 min. Detection was set at 368 nm. The eluent flow was
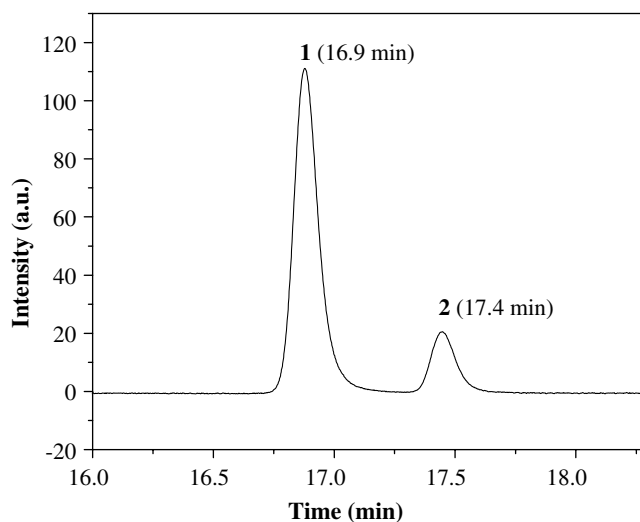
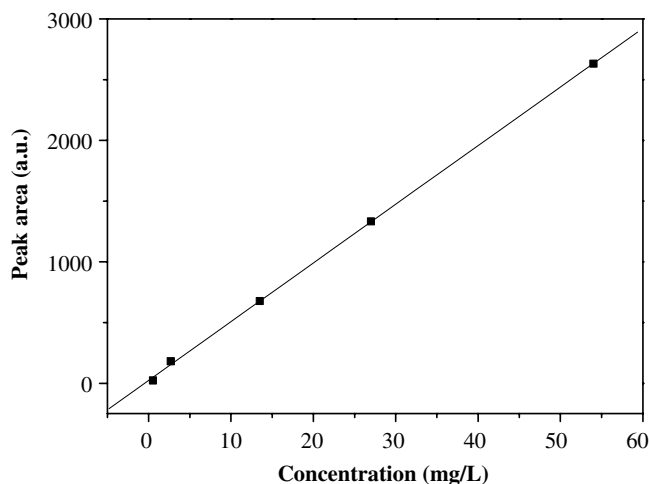Fig. 5. Chromatographic peaks of **1** and **2**.
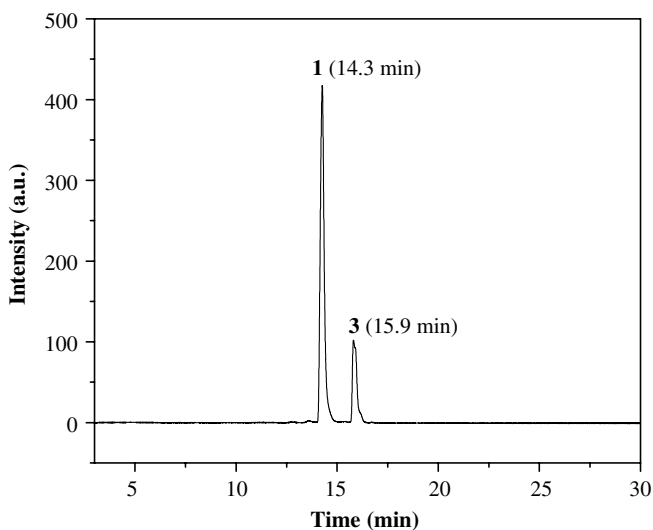
Fig. 6. Calibration graph for analyte **2**.

Fig. 7. Chromatographic peaks of **1** and **3**.

0.8 mL/min. The corresponding calibration graph based on peak areas is linear over 2.7–84.0 mg/L for **3** with a correlation coefficient of 0.9970 (Fig. 8). The limit of detection was measured to be ~0.3 ng injected Hg for **3**, and the lower value is in line with its larger extinction coefficient than that for **2** (see Table 2).

Hg(II) concentrations of the working solutions are calculated from the calibration graph and the values together with the percent recovery are reported in Tables 3 and 4. Our results show that the Hg concentrations determined according to the proposed procedure match quite well the expected values (recovery >82% for derivatization time of 2 h) and reflect the nearly quantitative yield of the reaction and extraction step in several cases (entries 2 and 4 in Table 3, entry 1 in Table 4). Short derivatization time (ca. 0.5 h) still afforded a reasonably good percent recovery (entry 3 in Table 3). However, it is worth noting that a much lower conversion was observed after 2 h under our present experimental conditions if the solution only contained a very low Hg concentration (entry 1 in Table 3), and so this is yet to be improved and optimized for practical applications. We believe that such study should represent a promising starting point for the development of a rapid and sensitive method for the analysis of Hg(II) ion.
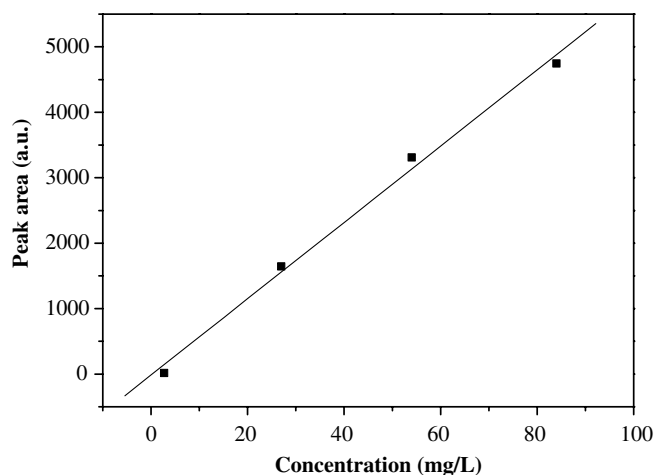

Fig. 8. Calibration graph for analyte **3**.

Table 3
Determination of inorganic mercury as **2** in THF[a]

Hg concentration (mg/L)	Found Hg concentration (mg/L)	Recovery (%)
0.647	0.130	20.1
1.940	1.804	93.0
1.940[b]	1.527	78.7
3.880	3.562	91.8
7.760	6.348	81.8

[a] Working solution, 50 mL; [NaOH] = 0.20 M; [NaCl] = 0.25 M. All experiments refer to three replicate analyses of working solution.
[b] Derivatization time is ca. 0.5 h.

Table 4
Determination of organic monomethylmercury as **3** in THF[a]

Hg concentration (mg/L)	Found Hg concentration (mg/L)	Recovery (%)
2.186	2.053	93.9
4.372	3.616	82.7
8.744	6.943	79.4

[a] Working solution, 50 mL; [NaOH] = 0.20 M; [NaCl] = 0.25 M. All experiments refer to three replicate analyses of working solution.

3. Concluding remarks

This paper reports a new way of converting dissolved inorganic mercury(II) and organic monomethylmercury(II) into stable mercury(II) acetylide derivatives functionalized with the bithiazole unit which can show interesting photophysical properties. In our study, a simple procedure for the speciation of mercury in water was developed based on such transformation and mercury detection can simply be obtained by HPLC analysis of these two organometallic species using a UV detector. Preliminary studies show that HgCl$_2$ and MeHgCl dissolved in alkaline aqueous solution is being trapped by the ethynylbithiazole ligand and converted into mercury acetylides in high derivatization yields which can easily be extracted into organic solvents. The development of such analytical protocols for the fast and cheap control of environmental pollutants represents a main goal of analytical green chemistry that is certainly worthy of further investigations. Future work will be focused on the effect of other interfering agents and matrix components in the Hg(II) determination and the applicability of this methodology to real biological and environmental samples such as wastewater, tissues and sediments collected in a contaminated area.

4. Experimental

4.1. General procedures

All the reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Analytical grade solvents were purified by distillation over appropriate drying agent under an inert nitrogen atmosphere prior to use. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. *Caution!* Organomercurials are extremely toxic, and all experimentation involving these reagents should be carried out in a well-vented hood. Glasswares were oven-dried at about 120 °C. Separation or purification of products were achieved by column chromatography over silica gel or preparative thin-layer chromatography (TLC) on glass plates (20 cm × 20 cm), pre-coated with Merck Kieselgel 60GF$_{254}$ prepared in our laboratory (0.7 mm).

The positive-ion fast atom bombardment (FAB) mass spectra were obtained using Finnigan-MAT SSQ710 mass

spectrometer. Infrared spectra were recorded on a Perkin–Elmer FT-IR 550 spectrometer, using CaF_2 cells with a 0.5 cm path length. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 FT-NMR system or a VARIAN 400 MHz NMR spectrometer, using deuterated solvents as the lock and reference. Chemical shifts were reported in ppm relative to $SiMe_4$. Electronic absorption spectra were obtained with a Hewlett–Packard 8453 or a Cary 100 UV–Vis spectrometer. The solution emission spectra were measured on a PTI Fluorescence Master Series QM1 spectrophotometer. The fluorescence quantum yields were determined in dichloromethane at 290 K against the anthracene standard ($\Phi = 0.27$). The HPLC system was a Hewlett–Packard 1050 instrument equipped with a UV–Vis detector. A reverse-phase column (Eclipse XDB-C8, 150×4.6 mm ID; 5 μm diameter particles) was used.

4.2. Preparation of compounds

4.2.1. Synthesis of 5-bromo-4,4′-di(tert-butyl)-2,2′-bithiazole

In the absence of light, NBS (0.32 g, 1.80 mmol) was added portionwise at $-20\,°C$ to a solution of 4,4′-di(tert-butyl)-2,2′-bithiazole (0.48 g, 1.80 mmol) in DMF (15 mL) and the mixture was stirred overnight. The reaction mixture was poured onto ice and extracted several times with CH_2Cl_2. The organic phases were combined, washed with water and dried over Na_2SO_4. Evaporation of solvent and separation by TLC using hexane afforded the product as a white solid (0.36 g, 56%). ^1H NMR (CDCl$_3$): δ 6.94 (s, 1H, Ar), 1.50 (s, 9H, CH$_3$) and 1.35 (s, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 167.78, 161.34, 159.90, 159.12, 112.14, 103.48 (Ar), 35.99, 34.95 (C(CH$_3$)$_3$) and 30.07, 29.81 (CH$_3$). FAB-MS: m/z 359 [M$^+$]. Anal. Calc. for C$_{14}$H$_{19}$N$_2$BrS$_2$: C, 46.79; H, 5.33; N, 7.80. Found: C, 46.55; H, 5.01; N, 7.53%.

4.2.2. Synthesis of 4,4′-di(tert-butyl)-5-(trimethylsilylethynyl)-2,2′-bithiazole

To an ice-cooled mixture of 5-bromo-4,4′-di(tert-butyl)-2,2′-bithiazole (0.70 g, 2.03 mmol) in freshly distilled diisopropylamine (40 mL) under N$_2$, CuI (0.51 g, 0.03 mmol), PPh$_3$ (0.015 g, 0.06 mmol) and Pd(OAc)$_2$ (0.005 g, 0.02 mmol) were added to the solution and the mixture was stirred for 20 min. After that, Me$_3$SiC≡CH (0.50 g, 5.08 mmol) was added to the mixture and the suspension was stirred for 30 min in an ice-bath before being warmed to room temperature. Then the mixture was stirred for another 30 min at room temperature. Finally, it was heated at 85 °C overnight. The solution was allowed to cool down to room temperature, Et$_2$O (20 mL) was added and the precipitate was filtered off. The brown filtrate was evaporated to dryness. This residue was redissolved in Et$_2$O and washed sequentially with 10% HCl (3×15 mL), water (3×15 mL) and NaHCO$_3$ (3×15 mL). The resulting organic solution was then dried with anhydrous MgSO$_4$. The solvent was removed and the brown residue chromato-

graphed over a silica gel column eluting with hexane. 4,4′-Di(tert-butyl)-5-(trimethylsilylethynyl)-2,2′-bithiazole was obtained as a yellow solid in 68% yield (0.52 g). IR (CH$_2$Cl$_2$): v(C≡C) 2141 cm^{-1}. ^1H NMR (CDCl$_3$): δ 6.96 (s, 1H, Ar), 1.49 (s, 9H, CH$_3$), 1.36 (s, 9H, CH$_3$) and 0.25 (s, 9H, TMS). ^{13}C NMR (CDCl$_3$): δ 169.35, 168.20, 160.27, 158.11, 113.57, 112.77 (Ar), 106.29, 96.26 (C≡C), 36.79, 35.26 (C(CH$_3$)$_3$) and 30.39, 30.25 (CH$_3$). FAB-MS: m/z 573 [M$^+$]. Anal. Calc. for C$_{19}$H$_{28}$N$_2$S$_2$Si: C, 60.59; H, 7.49; N, 7.44. Found: C, 60.33; H, 7.35; N, 7.20%.

4.2.3. Synthesis of 4,4′-di(tert-butyl)-5-ethynyl-2,2′-bithiazole (1)

4,4′-Di(tert-butyl)-5-(trimethylsilylethynyl)-2,2′-bithiazole (0.23 g, 0.63 mmol) was reacted with K$_2$CO$_3$ (0.08 g, 0.63 mmol) in a mixture of MeOH (10 mL) and diethyl ether (10 mL) and the mixture was stirred overnight at room temperature. The resultant solution was filtered and evaporated. The desired product 1 was isolated as a yellow solid in 87% yield (0.17 g). IR (CH$_2$Cl$_2$): v(C≡C) 2099 and v(≡C–H) 3301 cm^{-1}. ^1H NMR (CDCl$_3$): δ 6.96 (s, 1H, Ar), 3.65 (s, 1H, C≡CH), 1.50 (s, 9H, CH$_3$) and 1.36 (s, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 169.35, 167.94, 159.85, 158.29, 112.61, 112.03 (Ar), 87.89, 75.28 (C≡C), 36.49, 34.95 (C(CH$_3$)$_3$) and 30.07, 30.03 (CH$_3$). FAB-MS: m/z 305 [M$^+$]. Anal. Calc. for C$_{16}$H$_{20}$N$_2$S$_2$: C, 63.12; H, 6.62; N, 9.20. Found: C, 63.02; H, 6.43; N, 9.04%.

4.2.4. Synthesis of complex 2

Compound 1 (79.2 mg, 0.26 mmol) in MeOH (5 mL) was first combined with MeHgCl (77.8 mg, 0.31 mmol) in MeOH (5 mL) and the NaOMe solution (0.36 mmol) was subsequently added as the base to give a brown suspension. The solvent was then decanted after 2 h and the yellow solid of 2 was washed with MeOH (2×20 mL) and air-dried (114.7 mg, 85%). IR (CH$_2$Cl$_2$): v(C≡C) 2124 cm^{-1}. ^1H NMR (CDCl$_3$): δ 6.94 (s, 1H, Ar), 1.51 (s, 9H, CH$_3$), 1.35 (s, 9H, CH$_3$) and 0.72 (s, $^2J_{Hg–H} = 148$ Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 168.14, 167.84, 160.18, 156.99, 156.15, 112.28 (Ar), 113.72, 96.17 (C≡C), 36.40, 34.95, (C(CH$_3$)$_3$), 30.10, 30.04 (CH$_3$) and 7.18 (HgMe). FAB-MS: m/z 519 [M$^+$]. Anal. Calc. for C$_{17}$H$_{22}$N$_2$HgS$_2$: C, 39.34; H, 4.27; N, 5.40. Found: C, 39.02; H, 4.10; N, 5.15%.

4.2.5. Synthesis of complex 3

A solution of HgCl$_2$ (40.7 mg, 0.15 mmol) in MeOH (5 mL) was mixed with 1 (109.7 mg, 0.36 mmol) in MeOH (5 mL). To this mixture, 5 mL of NaOMe solution (0.63 mmol) was added. Within a few minutes, a yellow solid precipitated from the homogeneous solution. The solid was then collected by filtration after stirring for 2 h, washed with MeOH (2×20 mL), and air-dried to furnish a yellow solid of the title complex in 90% yield (109.0 mg). IR (CH$_2$Cl$_2$): v(C≡C) 2124 and 2141 cm^{-1}. ^1H NMR (CDCl$_3$): δ 6.97 (s, 2H, Ar), 1.52 (s, 18H, CH$_3$) and 1.36 (s, 18H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 169.27, 167.86, 159.83, 157.79, 132.52, 122.50 (Ar), 122.37, 97.02

$(C\equiv C)$, 36.44, 34.86 ($C(CH_3)_3$) and 30.03, 29.98 (CH_3). FAB-MS: m/z 808 [M^+]. Anal. Calc. for $C_{32}H_{38}N_4HgS_4$: C, 47.60; H, 4.74; N, 6.94. Found: C, 47.38; H, 4.53; N, 6.65%.

4.3. General derivatization procedure

AR grade dichloromethane and HPLC grade THF were used. Stock standard solutions of $HgCl_2$ and MeHgCl were prepared in water and dichloromethane, respectively. Pure reference samples of **2** and **3** were synthesized. Solutions of known concentration of the reference samples in THF used for calibration are freshly prepared from a stock solution (300 mg/L) which can be stored for 2 weeks at room temperature without detectable decomposition by HPLC.

A solution of ligand **1** in dichloromethane (10 mL) was added to an aqueous $HgCl_2$ (or MeHgCl) working solution (50 mL), followed by the addition of 0.20 M NaOH and 0.25 M NaCl solutions. The reaction mixture was vigorously stirred at 20 °C for 2 h. The organic layer was separated and the aqueous phase was twice extracted with dichloromethane (10 mL). After solvent evaporation, the residue was diluted to 10 mL with THF and directly analyzed by HPLC. In each case, the data were obtained from three replicates of sample injection.

5. Crystallography

Single crystals of **1** and **2** suitable for X-ray crystallographic analyses were grown by slow evaporation of their respective solutions in dichloromethane/hexane at room temperature. The crystals were chosen and mounted on a glass fiber using epoxy resin. Crystal data, data collection parameters and refinement results of the analyses are listed in Table 5. The diffraction experiments were carried out at 293 K on a Bruker AXS SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The raw intensity data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm [17]. Corrections for Lorentz and polarization effects were also applied by SAINT. For each analysis, an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS [18]. The structures were solved by direct methods, and expanded by difference Fourier syntheses using the software SHELXTL [19]. Structure refinements were made on F^2 by the full-matrix least-squares technique. In each case, all the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their ideal positions but not refined.

Acknowledgements

Table 5
Summary of crystal structure data for complexes **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{16}H_{20}N_2S_2$	$C_{17}H_{22}N_2S_2Hg$
Molecular weight	304.46	519.08
Crystal size (mm)	$0.20 \times 0.10 \times 0.08$	$0.32 \times 0.08 \times 0.07$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a (Å)	24.371(4)	16.3900(15)
b (Å)	5.9079(9)	7.0102(6)
c (Å)	24.579(4)	16.9152(15)
α (°)	90	90
β (°)	105.768(3)	92.712(2)
γ (°)	90	90
V (Å^3)	3405.7(9)	1941.3(3)
μ (Mo Kα) (mm^{-1})	0.305	8.141
D_{calc} (g cm^{-3})	1.188	1.776
Z	8	4
$F(000)$	1296	1000
θ Range (°)	2.09–25.00	1.77–28.36
Reflections collected	7829	11 108
Unique reflections	2959	4460
R_{int}	0.0362	0.0340
Observed reflections [$I > 2\sigma(I)$]	1769	1782
Number of parameters	181	200
R_1, wR_2 [$I > 2\sigma(I)$]	0.0582, 0.1571	0.0358, 0.0888
R_1, wR_2 (all data)	0.1041, 0.1840	0.0930, 0.1147
Goodness-of-fit on F^2	1.034	0.933
Residual extreme in final difference map (e Å^{-3})	0.421/−0.317	0.914/−0.460

Appendix A. Supplementary material

Crystallographic data (comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analysis have been deposited with the Cambridge Crystallographic Centre (Deposition Nos. 286979 and 286980 for **1** and **2**, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.11.014.

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