Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 2699

www.rsc.org/dalton

PAPER

Reactions of a methylmercury zwitterionic thiolate complex [MeHg(Tab)]PF_6 with various donor ligands: relevance to methylmercury detoxification†

Ai-Xia Zheng,[a] Hong-Xi Li,[a] Kai-Peng Hou,[a] Jing Shi,[a] Hui-Fang Wang,[a] Zhi-Gang Ren[a] and Jian-Ping Lang*[a,b]

Received 19th November 2011, Accepted 4th December 2011
DOI: 10.1039/c2dt12219g

Reaction of MeHgI with Ag_2O in H_2O followed by addition of equimolar TabHPF_6 in MeCN gave rise to a methylmercury zwitterionic thiolate complex [MeHg(Tab)]PF_6 (**1**) (TabH = 4-(trimethylammonio) benzenethiol) in a high yield. Treatment of **1** with KI and KSCN afforded an anion exchange product [MeHg(Tab)]I·0.25H_2O (**2**·0.25H_2O) and [MeHg(Tab)]SCN (**3**), respectively, while that of **1** with equimolar Tab resulted in the formation of another MeHg/Tab compound [MeHg$(Tab)_2$]PF_6 (**4**). The cation of **2** or **3** shows an approximately linear structure in which the central Hg(II) is coordinated by one C atom of one CH_3 group and one S atom of a Tab ligand. The Hg(II) center of the cation of **4** is trigonally coordinated by one C atom of the CH_3 group and two S atoms of two Tab ligands. The analogous reaction of **1** with NH_4SCN led to the cleavage of the Hg–C bond of **1** and the formation of a known four-coordinated Hg(II)/Tab complex [Hg$(Tab)_2(SCN)_2$] (**5**). When **4** was treated with 4,6-Me_2pymSH or EtSH, another four-coordinated Hg(II)/Tab complex [Hg$(Tab)_4]_3(PF_6)_6$ (**6**) was generated in a high yield. The Hg(II) center of each cation of **6** is tetrahedrally coordinated by four S atoms of four Tab ligands. The results suggested that cleavage of the Hg–C bond in the methylmercury complex **1** could be completed by increasing the coordination number of its Hg(II) center by S-donor ligands and protonating the methyl group by weak acids.

Introduction

The high affinity of organomercurials for thiols and their lipophilic nature make them highly toxic to living organisms, causing irreversible damage to the central nervous system.[1] Owing to the relatively high stability of the Hg–CH_3 bond under physiological conditions,[2] the methylmercury ion, $MeHg^+$, is probably the most ubiquitous compound and one of most dangerous pollutant agents, which has the ability to bio-accumulate and bio-magnify in aquatic food webs.[3] As a result, fishes in numerous lakes worldwide contain ever-increasing MeHg concentrations.[4] For humans, the main pathway of exposure to MeHg is the consumption of fish and sea mammals.[5] For example, it has caused the death of almost 2000 people by Minamata disease.[6]

Therefore, it becomes critically important to find suitable approaches to detoxification of organomercury compounds. In nature, bacteria respond to the toxicity of the organomercurial compounds by developing two peculiar resistance mechanisms that involve the cleavage of the Hg–C bond and the reduction of the mercuric residues to elemental mercury, Hg(0). The relevant catalysts that perform the above reactions are MerB, organomercurial lyase, and MerA, mercuric ion reductase.[7,8] Much attention has been devoted, in the literature, to the study of the mechanism of the Hg–C cleavage.[9] Parkin *et al.* suggested that the Hg–C bonds of the mercury alkyl complexes are readily cleaved by a thiol which may be ascribed to the consequence of the mercury center of two-coordinate being able to access higher coordination numbers.[10] Barbaro *et al.* also have demonstrated that a higher coordination number of mercury can contribute to the activation of the Hg–C bonds.[11] Bencini *et al.* showed the mechanism of the Hg–C bond cleavage by halogenic acids *via* theoretical calculation.[12]

On the other hand, we are interested in the preparation of metal complexes of a zwitterionic thiolate, 4-(trimethylammonio)benzenethiol (TabH) which bears an ammonium group and a sulfhydryl group and to some extent is similar to cysteine.[13] As an extension of this study, we carried out the reaction of MeHgI with Ag_2O and TabHPF_6, and isolated a unique complex [MeHg(Tab)]PF_6 (**1**) in a high yield. In our previous reports, we employed [Hg$(Tab)_2]$$(PF_6)_2$ to react with donor ligands (inorganic anions, organic amines, nitrogen heterocyclic compounds and organic carboxylic acids). In most of these reactions, the linear coordination geometry of the Hg atom in [Hg$(Tab)_2]$$(PF_6)_2$ was further fulfilled by additional donor ligands. Do some donor

[a]*College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, P. R. China. E-mail: jplang@suda.edu.cn; Fax: 86-512-65880089*
[b]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China*

† Electronic supplementary information (ESI) available. CCDC reference numbers 853202–853205. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12219g

ligands such as I^-, SCN^-, Tab and other weak acids react with the Hg center of **1**? Does the introduction of these ligands change the linear structure of **1**? Can the methyl group be readily cleaved by these ligands? With these questions in mind, we carried out the reactions of **1** with KI, KSCN, Tab, NH_4SCN, 4,6-dimethylpyrimidine-2-thione (4,6-Me_2pymSH) or EtSH, and isolated two anion exchange products **2** and **3**, one three-coordinated MeHg/Tab complex **4**, and two methyl-free products **5** and **6**. These reactions along with the structural characterization of **2**, **3**, **4** and **6** may provide an interesting insight into detoxification of organomercury compounds, which will be described below.

Experimental

Materials and methods

TabHPF_6 and 4,6-Me_2pymSH were prepared according to the literature method.[14] Tab was obtained from reactions of TabHPF_6 with Et_3N in MeCN followed by filtration and dried in vacuo. Other chemicals and reagents were obtained from commercial sources and used as received. IR spectra were recorded on Varian Scamiter-1000 spectrometer (4000–400 cm^{-1}) as the KBr disk. The elemental analyses for C, H, N and S were performed on a Carlo-Erba CHNO-S microanalyzer. ^1H NMR spectra were recorded at ambient temperature on a Varian UNITY-400 spectrometer. Chemical shifts are quoted relative to the solvent signal in DMSO-d_6. UV-vis spectra in MeCN were measured on a Hitachi U-2810 spectrophotometer. ESI mass spectra were performed on a DECAX-30000 LCQ Deca XP mass spectrometer using MeCN as mobile phase.

Caution! *All mercury compounds are toxic and appropriate safety precautions must be taken in handling these compounds*.

Synthesis of [MeHg(Tab)]PF_6 (1). To a solution of MeHgI (116 mg, 0.2 mmol) in H_2O (5 mL) was added Ag_2O (23 mg, 0.1 mmol). The resulting mixture was stirred for 48 h to form a yellow precipitation of AgI and filtered. The resulting colorless solution was then treated with a solution containing TabHPF_6 (62 mg, 0.2 mmol) in MeCN and the mixture was stirred for 2 h, forming in a large amount of a white precipitate. The precipitate was dried *in vacuo* to give **1** as a white powder. Yield: 98 mg (92% based on Hg). Anal. Calcd. for $C_{10}H_{16}F_6HgNPS$: C, 22.75; H, 3.06; N, 2.65; S, 6.07. Found: C, 22.43; H, 3.27; N, 2.98; S, 6.25. IR (KBr disc): 2916 (w), 1586 (w), 1490 (m), 1417 (w), 1127 (w), 1010 (w), 956 (m), 840 (s), 746 (w), 558 (m) cm^{-1}. UV-Vis (MeCN; λ_{max}, nm (ε, M^{-1} cm^{-1})): 272 (74600). ^1H NMR (400 MHz, DMSO-d_6): δ 7.50–7.64 (m, 4H, Ph), 3.54 (s, 9H, NMe_3), 0.71 (s, 3H, MeHg).

Synthesis of [MeHg(Tab)]I·0.25H_2O (2·0.25H_2O). To a solution of **1** (53 mg, 0.1 mmol) in MeCN (5 mL) was added KI (17 mg, 0.1 mmol) in MeOH (2 mL). The resulting mixture was stirred for 1 h to form a colorless solution and filtered. Diethyl ether (20 mL) was layered onto the filtrate to form colorless prisms of **2**·0.25H_2O in several days, which were collected by filtration, and washed with Et_2O and dried in *vacuo*. Yield: 44 mg (87% based on Hg). Anal. Calcd. for $C_{10}H_{16}HgINS$: C, 23.56; H, 3.16; N, 2.75; S, 6.29. Found: C, 23.87; H, 3.52; N, 2.41; S, 6.03. IR (KBr disc): 3012 (w), 2910 (w), 1587 (w), 1487 (s), 1411 (w), 1125 (m), 1009 (m), 966 (w), 822 (w), 551 (w) cm^{-1}. UV-Vis (MeCN; λ_{max}, nm (ε, M^{-1} cm^{-1})): 246 (74200), 270 (45000). ^1H NMR (400 MHz, DMSO-d_6): δ 7.57–7.68 (m, 4H, Ph), 3.55 (s, 9H, NMe_3), 0.71 (s, 3H, MeHg).

Synthesis of [MeHg(Tab)]SCN (3). Compound **3** was prepared as colorless blocks in a similar way to that described for the preparation of **2**, except KSCN (10 mg, 0.1 mmol) was used in place of KI. Yield: 36 mg (82% based on Hg). Anal. Calcd. for $C_{11}H_{16}HgN_2S_2$: C, 29.96; H, 3.66; N, 6.35; S, 14.54. Found: C, 29.58; H, 3.41; N, 6.72; S, 14.83. IR (KBr disc): 3024 (w), 2054 (s), 1582 (w), 1491 (m), 1413 (w), 1126 (w), 1009 (w), 958 (w), 833 (w), 738 (w), 555 (w) cm^{-1}. UV-Vis (MeCN; λ_{max}, nm (ε, M^{-1} cm^{-1})): 234 (67100), 272 (87200). ^1H NMR (400 MHz, DMSO-d_6): δ 7.55–7.70 (m, 4H, Ph), 3.54 (s, 9H, NMe_3), 0.70 (s, 3H, MeHg).

Synthesis of [MeHg(Tab)$_2$](PF_6) (4). Compound **4** was prepared as colorless flakes in a similar way to that described for the preparation of **2**, except Tab (34 mg, 0.2 mmol) was used in place of KI. Yield: 56 mg (80% based on Hg). Anal. Calcd. for $C_{19}H_{29}F_6HgN_2PS_2$: C, 32.82; H, 4.20; N, 4.03; S, 9.22. Found: C, 32.45; H, 4.42; N, 3.93; S, 9.47. IR (KBr disc): 2963 (w), 1579 (w), 1488 (m), 1416 (w), 1126 (w), 1009 (w), 959 (w), 853 (s), 746 (w), 559 (m) cm^{-1}. UV-Vis (MeCN; λ_{max}, nm (ε, M^{-1} cm^{-1})): 286 (48300). ^1H NMR (400 MHz, DMSO-d_6): δ 7.39–7.51 (m, 8H, Ph), 3.52 (s, 18H, NMe_3), 0.64 (s, 3H, CH_3).

Synthesis of [Hg(Tab)$_2$(SCN)$_2$] (5). Compound **5** was prepared as colorless blocks in a similar way to that described for the preparation of **2**, except NH_4SCN (10 mg, 0.2 mmol) was used in place of KI. Yield: 23 mg (35% based on Hg). Anal. Calcd. for $C_{20}H_{26}HgN_4S_4$: C, 36.88; H, 4.02; N, 8.60; S, 19.69. Found: C, 36.54; H, 4.25; N, 8.39; S, 19.92. IR (KBr disc): 2080 (s), 1581 (w), 1489 (m), 1126 (w), 1010 (w), 953 (m), 831 (s), 740 (w), 555 (m) cm^{-1}. UV-Vis (MeCN; λ_{max}, nm (ε, M^{-1} cm^{-1})): 271 (17400). ^1H NMR (400 MHz, DMSO-d_6): δ 7.51–7.63 (m, 4H, Ph), 3.58 (s, 9H, NMe_3).

Synthesis of [Hg(Tab)$_4$]$_3$(PF_6)$_6$·MeOH·2MeCN (6·MeOH·2MeCN). A solution of 4,6-Me_2pymSH (14 mg, 0.1 mmol) in MeOH (2 mL) was treated with a solution of **4** (69 mg, 0.1 mmol) in MeCN (5 mL) to form a colorless solution. A workup similar to that used in the isolation of **2** afforded colorless flakes of **6**·MeOH·2MeCN. Yield: 45 mg (42% based on Hg). Anal. Calcd. for $C_{36}H_{52}F_{12}HgN_4P_2S_4$: C, 37.29; H, 4.52; N, 4.83; S, 11.06. Found: C, 37.42; H, 4.39; N, 4.68; S, 11.36. IR (KBr disc): 1580 (w), 1482 (s), 1127 (s), 1011 (m), 960 (w), 841 (s), 559 (s) cm^{-1}. UV-Vis (MeCN; λ_{max}, nm (ε, M^{-1} cm^{-1})): 284 (73500). ^1H NMR (400 MHz, DMSO-d_6): δ 7.57–7.72 (m, 4H, Ph), 3.52 (m, 9H, NMe_3).

X-ray crystallography

Single crystals of **2**·0.25H_2O, **3**, **4** and **6**·MeOH·2MeCN suitable for X-ray analysis were obtained directly from the above preparations. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Crystals of **2**·0.25H_2O, **3**, **4** and **6**·MeOH·2MeCN were mounted with grease at the top of a glass fiber and cooled at 223 K in a liquid nitrogen stream.

Diffraction data were collected at ω mode with a detector-to-crystal distance of 35 mm. Cell parameters were refined by using the program *Crystalclear* (Rigaku and MSc, Ver. 1.3, 2001) on all observed reflections. The collected data were reduced by using the program *CrystalClear* (Rigaku and MSc, version 3.6, 2004), and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **2**·0.25H_2O, **3**, **4** and **6**·MeOH·2MeCN were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with *SHELXTL-97* program.[15] Because of the partial evaporation of the solvent molecules, we could not locate any more solvent molecules in the potential solvent area of 156 Å^3 per unit cell (18.1% of the total cell volume calculated by the *Platon* program[15c]) in **6**·MeOH·2MeCN. For **6**·MeOH·2MeCN, the methyl groups of one Tab ligand were found to be disordered over two positions with an occupancy factor of 0.49/0.51 for C79–C82/C79A-C82A. All non-hydrogen atoms, except for those of the MeOH molecules (C113, C116, O1, O2) in **6**·MeOH·2MeCN were refined anisotropically. Hydrogen atoms of the disordered water molecule (O1) in **2**·0.25H_2O and the MeOH molecules (C116, O1, O2) in **6**·MeOH·2MeCN were not located. All other hydrogen atoms were placed in geometrically idealized positions (C–H = 0.98 Å for methyl groups; C–H = 0.95 Å for phenyl groups) and constrained to ride on their parent atoms with U_{iso}(H) = 1.5U_{eq} (C) for methyl groups and U_{iso}(H) = 1.2U_{eq}(C) for phenyl groups. Pertinent crystal data and collection and refinement parameters for **2**·0.25H_2O, **3**, **4** and **6**·MeOH·2MeCN are given in Table 1.

Results and discussion

Synthetic and spectral aspects

Treatment of MeHgI with excess silver oxide for 48 h in water developed a large amount of yellow solid (AgI), which was removed by filtration (Scheme 1). The resulting colorless solution was mixed with equimolar TabHPF_6, forming a large amount of colorless precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. The elemental analysis, the IR spectrum and the ^{1}H NMR spectrum of the white solid were all well consistent with the chemical formula [MeHg(Tab)]PF_6 (**1**). However, attempts to grow its single crystals always failed.

Since methylmercury(II) was regarded as an essentially unifunctional cation to give coordination number 2 for mercury(II), we tentatively assumed the Hg(II) center of **1** to be two-coordinate. Considering that access to geometries of the Hg(II) center with a coordination number greater than two is required for the efficient activity of MerB, the two-coordinated Hg atom of **1** may be further coordinated by other donor ligands such as halide or pseudohalide or Tab ligand to afford a three- or four-coordination environment. We thus carried out the reaction of **1** with equimolar KI in MeCN/MeOH. To our surprise, no expected product [MeHg(Tab)I], but an anion-exchanged product **2**·0.25H_2O, was isolated in 87% yield (Scheme 1). Compound **2**·0.25H_2O could be also prepared in a quantitative yield when MeHgI was treated with equimolar TabHPF_6 in the presence of Et_3N. An analogous reaction of **1** with one or more equivalents of KSCN also produced another anion-exchange product **3** in 82% yield (Scheme 1). When a solution of **1** was combined with a solution of Tab in a 1 : 1∼3 molar ratio, a unique three-coordinated MeHg/Tab complex **4** was isolated in various yields (Scheme 1). These results showed that, if any, the interaction between [MeHg(Tab)]$^+$ and PF_6^- was quite weak. In addition, **1** is readily soluble in MeCN, DMF and DMSO, which implies that **1** could be a two-coordinate complex, not a coordination polymer.

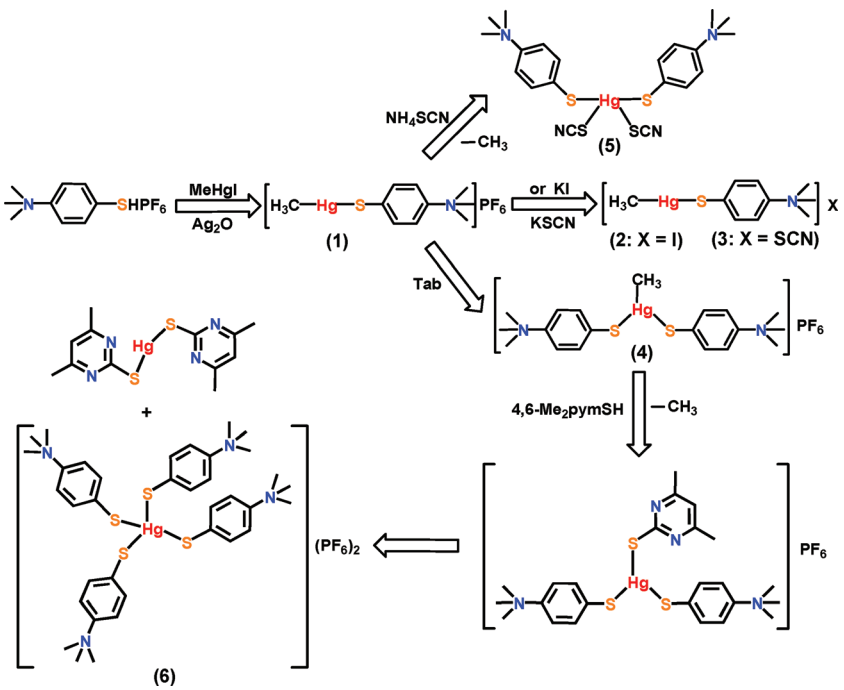
On the other hand, similar reaction of **1** with 2 equiv. of NH_4SCN did not yield the expected [MeHg(Tab)(SCN)] or the anion-exchange product **3** but generated a four-coordinate Hg/Tab complex **5** in 35% yield (Scheme 1). The crystal structure of **5** is the same as that of the previously reported one.[13a] In this case, the methyl group of **1** was protonated by the weak acid, NH_4^+, and the whole structure may be decomposed. The remaining species such as Hg^{2+}, Tab, and NCS^- in the solution might re-organize into compound **5**. The reason for the decomposition of **1** and the formation of **5** may be attributed to the weak acidity of NH_4^+ ions. This is in accordance with the fact that the Hg–C bond of the RHgX compounds could be broken by the acids.[12a] We also attempted the analogous reactions of **1** with NH_4Cl, NH_4Br or NH_4I, but the cleavage of Hg–C bond of **1** and the formation of the similar compounds like **2** did not occur. Such a phenomena may be ascribed to the fact that the Hg–C bond of the mercury alkyl complexes are readily cleaved by S-donor ligands and the formation of three- or four-coordinated Hg(II) complexes of S-donor ligands.[9a,10] According to the literature,[10b] cleavage of the Hg–C bonds of both PhSHgEt and {LHgEt}[BF_4] by PhSH could be promoted by addition of L (L = 2-mercapto-1-*t*-butylimidazole). Parks *et al.* also suggested that coordination of R–Hg(II) by two equivalents of cysteine thiolate is necessary and sufficient to activate the Hg–C bond toward protonolysis.[9a] Thus we carried out the reaction of **4** with 4,6-Me_2pymSH and isolated another Hg(II)/Tab product [Hg(Tab)$_4$]$_3$(PF_6)$_6$ (**6**) (Scheme 1). In this reaction, the methyl group of **4** might be acidified by 4,6-Me_2pymSH and subsequently eliminated. The initial mercury product was assumed to be [Hg(Tab)$_2$(4,6-Me_2pymS)]PF_6 (Scheme 1). This complex could not be isolated because it may quickly disproportionate into **6** and a known Hg(II)/thiolate complex [Hg(4,6-Me_2pymS)$_2$].[16] The later complex was identified by ESI mass spectrometry (m/z = 480.0 {M + 1}$^+$) (Fig. 1a). Both products were also observed when **4** was treated with EtSH. We attempted the direct reactions of **1**, **2**, or **3** with 4,6-Me_2pymSH, EtSH and other thiols, but no evident Hg–Me cleaving reactions were taking place, and only the starting complexes were recovered. It is evident that the Hg–C bond of the trigonally-coordinated complex **4** might be more readily activated than those of the linear coordinated complexes **1–3**.

Solids **2–6** are relatively stable toward oxygen and moisture and readily soluble in MeCN, DMF and DMSO but almost insoluble in MeOH, EtOH, CH_2Cl_2, benzene and H_2O. The elemental analyses of **1–6** were consistent with their chemical formulas. The IR spectra of **1**, **4**, and **6** showed the characteristic P–F stretching vibrations of PF_6^- at 840 and 559 cm^{-1}. The peak at 2054 cm^{-1} for **3** and 2080 cm^{-1} for **5** in the IR spectrum indicated the presence of the SCN^- anion. The ^{1}H NMR spectra of **1–6** in DMSO-d_6 at room temperature featured multiplets in the region of 7.39–7.72 ppm for phenyl groups and a singlet at

Table 1 Crystal data and structure refinement parameters for **2**·0.25H_2O, **3**, **4** and **6**·MeOH·2MeCN

Compounds	**2**·0.25H_2O	**3**	**4**	**6**·MeOH·2MeCN
Formula	$C_{40}H_{66}Hg_4I_4N_4OS_4$	$C_{11}H_{16}HgN_2S_2$	$C_{19}H_{29}F_6HgN_2PS_2$	$C_{113}H_{166}F_{36}Hg_3N_{14}OP_6S_{12}$
Formula weight	2057.21	440.99	695.12	3592.91
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pc
a/Å	14.339(3)	6.9713(14)	17.975(4)	27.196(5)
b/Å	7.3906(15)	21.564(4)	11.308(2)	12.152(2)
c/Å	28.086(8)	10.158(4)	12.905(3)	23.754(5)
β/°	109.38(3)	113.92(2)	105.36(3)	99.35(3)
V/Å^3	2807.7(11)	1395.9(7)	2529.3(9)	7746(3)
D_c/g cm^{-3}	2.433	2.098	1.825	1.540
Z	2	4	4	2
μ(Mo-Kα)/mm^{-1}	13.282	11.302	6.367	3.279
F(000)	1876	832	1352	3592
Total reflections	12787	7765	14147	47515
Unique reflection	6388 (R_{int} = 0.0526)	3116 (R_{int} = 0.0496)	5770 (R_{int} = 0.0499)	28302 (R_{int} = 0.0569)
No. observations	4858 [$I > 2.00\ \sigma(I)$]	2877 [$I > 2.00\ \sigma(I)$]	4153 [$I > 2.00\ \sigma(I)$]	23614 [$I > 2.00\ \sigma(I)$]
No. parameters	272	151	282	1711
R^a	0.0411	0.0457	0.0653	0.0688
wR^b	0.0927	0.1298	0.1787	0.1750
GOF^c	0.924	1.142	1.075	1.049

^{a} $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. ^{b} $wR = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. ^{c} GOF $= \{\Sigma w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.



Scheme 1

3.54 ppm for the methyl protons of the NMe_3 unit of the Tab ligands. The peak related to the methyl protons of MeHg was observed at 0.70 ppm for **1**–**4**.

In order to gain more insight into the behaviors of **1**–**4** and **6** in solution, their positive-ion ESI mass spectra were examined. The assignments were made through the inspection of peak positions and isotopic distributions. The positive-ion ESI-MS of **1**–**3** in MeCN exhibited the parent cation $[MeHg(Tab)]^+$ at m/z = 384.1 (Fig. 1b), the patterns of which match well with its theoretical isotopic distributions. For **4**, the positive ESI-MS showed not only a parent cation peak at m/z = 551.2 for $[MeHg(Tab)_2]^+$ (Fig. 1c), but also a $[Hg(Tab)_2]^{2+}$ fragment peak at m/z = 268.1 (Fig. 1d). The positive-ion ESI-MS of **6** exhibited a $[Hg(Tab)_2]^{2+}$ fragment peak at m/z = 268.1, implying that **6** was dissociated under the mass conditions.

As shown in Fig. 2, the electronic spectra of **1**–**4** and **6** in MeCN exhibited a strong and broad absorption with maxima values ranging from 234 to 286 nm and a long absorption tail to *ca*. 400 nm. Because the absorption spectrum of the free Tab in MeCN had a broad absorption band at 314 nm, the main peaks

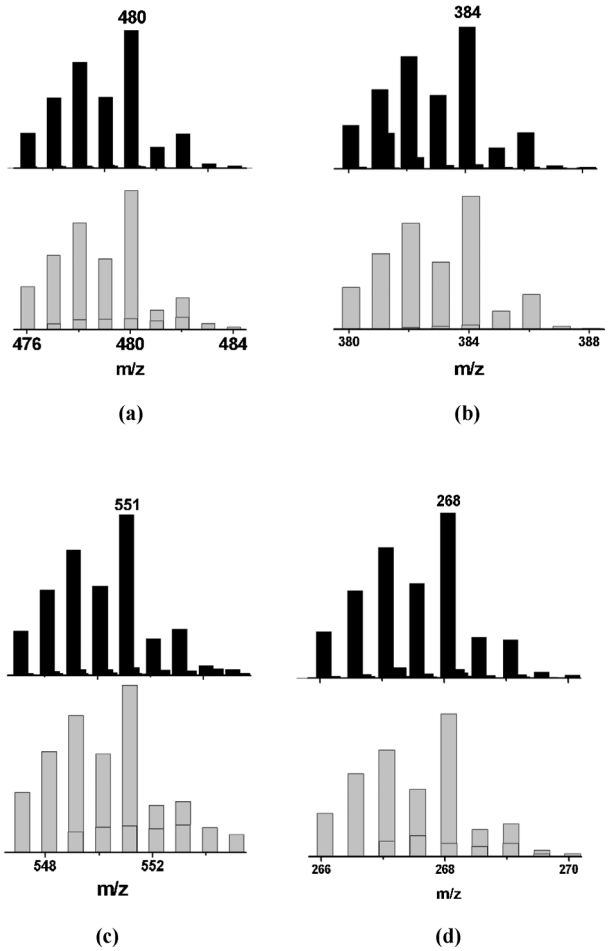


Fig. 1 (a) The observed (upper) and the calculated (lower) isotopic patterns for $[Hg(4,6\text{-}Me_2pymS)_2]$. (b) The observed (upper) and the calculated (lower) isotopic patterns for the $[MeHg(Tab)]^+$ cation in **1**–**3**. (c) The observed (upper) and the calculated (lower) isotopic patterns for the $[MeHg(Tab)_2]^+$ cation in **4**. (d) The observed (upper) and the calculated (lower) isotopic patterns for the $[Hg(Tab)_2]^{2+}$ cation in **4** and **6**.

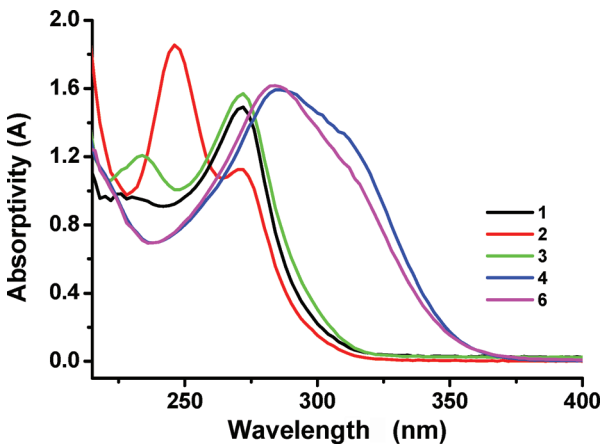


Fig. 2 Electronic spectra of **1** (2.0×10^{-5} M), **2** (2.5×10^{-5} M), **3** (1.8×10^{-5} M), **4** (3.3×10^{-5} M) and **6** (2.2×10^{-5} M) in MeCN in a 1 cm–thick glass cell.

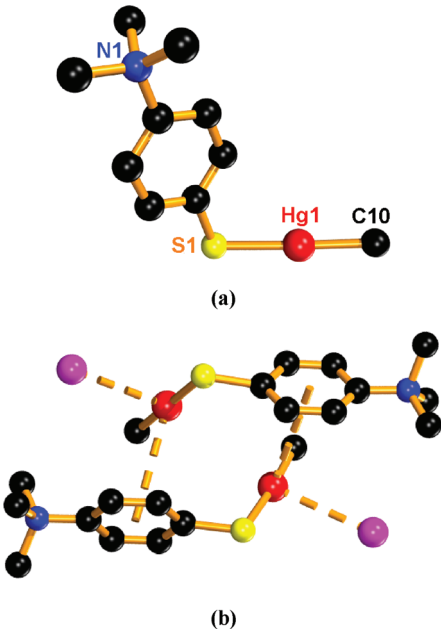


Fig. 3 (a) Perspective view of one of the two $[MeHgTab]^+$ cations of **2**. (b) Dimeric structure formed by the Hg···I secondary interactions and Hg···C interactions in **2**. All hydrogen atoms are omitted for clarity.

observed in the spectra of **1**–**4** and **6** were blue-shifted and may be due to the ligand(Tab)-to-metal charge transfer (LMCT).[17] The peaks observed in the spectra of **4** and **6** were red-shifted relative to the peak of **1**–**3**, which may be ascribed to the different coordination environments about the Hg atoms in these compounds. The identities of **2**, **3**, **4** and **6** were further confirmed by X-ray crystallography.

Crystal structure of [MeHg(Tab)]I·0.25H_2O (2·0.25H_2O) and [MeHg(Tab)]SCN (3). Compounds **2**·0.25H_2O and **3** crystallize in the monoclinic space group $P2_1/c$ and the asymmetric unit of **2** consists of two crystallographically independent $[MeHg(Tab)]^+$ cations, two iodides and half a water solvent molecule, while that of **3** contains one $[MeHg(Tab)]^+$ cation and one SCN^- anion. Because the two cations of **2** and the cation of **3** are structurally very similar, only a perspective view of one of the two cations of **2** is shown in Fig. 3a and the pertinent bond lengths and angles of the two cations are compared in Table 2. In the $[MeHg(Tab)]^+$ cations of **2** and **3**, each Hg(II) center is coordinated by one S atom from one Tab ligand and one C atom of the methyl group to afford an approximately linear coordination geometry. The Hg–C bond length of **3** (2.056(8) Å) is shorter than that of **2** (2.076(9) Å) and [LHgEt](BF_4) (2.092(5) Å; L = 2-mercapto-1-*t*-butylimidazole),[10b] but comparable to that of [PhSHgMe] (2.06(2) Å).[18] The mean Hg–S bond lengths of **2** (2.348(3) Å) and **3** (2.3500(15) Å) are slightly shorter than those of the corresponding ones found in other two-coordinated methylmercury thiolate compounds such as [LHgMe] (2.396(2) Å, L = tris(2-mercapto-1-*t*-butylimidazolyl)hydroborato),[10a] [PhSHgEt] (2.369(2) Å),[18a] [PhSHgMe] (2.383(2) Å), [MeHgL] (2.375(6) Å, HL = 2-mercaptobenzothiazole),[18b] and [MeHg($S_2CC_5H_6NH_2$-2)] (2.393(3) Å).[18c]

Table 2 Selected bond distances (Å) and angles (°) for **2**, **3**, **4** and **6**

Compound **2**			
Hg(1)–C(10)	2.089(9)	Hg(1)–S(1)	2.347(3)
Hg(1)···I(1)	3.3819(13)	Hg(2)–C(20)	2.062(9)
Hg(2)–S(2)	2.349(3)	Hg(2)···I(2)	3.4014(9)
C(10)–Hg(1)–S(1)	175.6(3)	C(10)–Hg(1)···I(1)	100.8(3)
S(1)–Hg(1)···I(1)	83.50(7)	C(20)–Hg(2)–S(2)	177.7(3)
C(20)–Hg(2)···I(2)	99.8(3)	S(2)–Hg(2)···I(2)	82.38(7)
Compound **3**			
Hg(1)–C(10)	2.056(8)	Hg(1)–S(1)	2.3500(15)
C(10)–Hg(1)–S(1)	175.3(3)		
Compound **4**			
Hg(1)–C(19)	2.051(12)	Hg(1)–S(1)	2.422(2)
Hg(1)–S(2)	2.737(2)	C(19)–Hg(1)–S(1)	160.0(5)
C(19)–Hg(1)–S(2)	121.4(5)	S(1)–Hg(1)–S(2)	78.54(6)
Compound **6**			
Hg(1)–S(2)	2.4903(11)	Hg(1)–S(4)	2.5014(10)
Hg(1)–S(1)	2.5074(10)	Hg(1)–S(3)	2.5921(11)
Hg(2)–S(8)	2.4801(10)	Hg(2)–S(7)	2.4821(10)
Hg(2)–S(6)	2.5668(9)	Hg(2)–S(5)	2.5788(10)
Hg(3)–S(11)	2.4693(11)	Hg(3)–S(10)	2.4840(12)
Hg(3)–S(9)	2.5627(10)	Hg(3)–S(12)	2.5757(10)
S(2)–Hg(1)–S(4)	113.35(4)	S(2)–Hg(1)–S(1)	118.02(3)
S(4)–Hg(1)–S(1)	109.88(3)	S(2)–Hg(1)–S(3)	107.00(4)
S(4)–Hg(1)–S(3)	91.72(3)	S(1)–Hg(1)–S(3)	113.88(3)
S(8)–Hg(2)–S(7)	123.00(3)	S(8)–Hg(2)–S(6)	108.32(3)
S(7)–Hg(2)–S(6)	101.50(3)	S(8)–Hg(2)–S(5)	101.09(3)
S(7)–Hg(2)–S(5)	111.32(3)	S(6)–Hg(2)–S(5)	111.77(3)
S(11)–Hg(3)–S(10)	120.82(3)	S(11)–Hg(3)–S(9)	112.97(3)
S(10)–Hg(3)–S(9)	99.63(4)	S(11)–Hg(3)–S(12)	102.63(3)
S(10)–Hg(3)–S(12)	110.60(4)	S(9)–Hg(3)–S(12)	110.27(3)

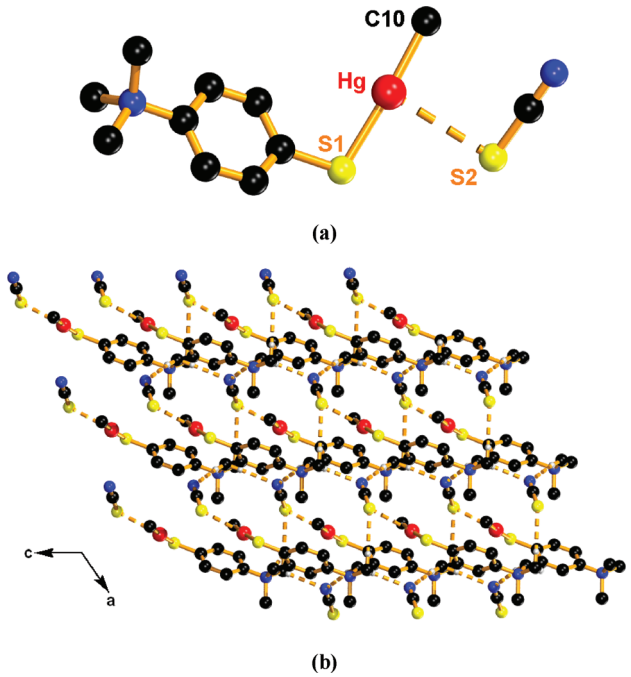


Fig. 4 (a) View of the [MeHgTab]SCN structure of **3**. (b) 2D structure formed by hydrogen-bonding interactions in **3** (looking along the *b* axis). All H atoms except those involved in hydrogen-bonding interactions were omitted.

Although the two independent cations of **2** are not parallel to each other, the MeHgS species of one cation is almost parallel to one Tab unit of the neighboring cation (Fig. 3b). The Hg atom interacts with the phenyl ring of Tab ligand with Hg···C contact of 3.7149(12) and 3.8645(7) Å, thereby forming a dimeric structure. Due to the existence of Hg···I secondary interactions (3.3819(13) and 3.4014(9) Å) in **2** and Hg···S secondary interactions (3.2308(7) Å) in **3**, the Hg centers in **2** and **3** may be considered as having a pseudo-three-coordinated T-shaped geometry. For **3**, there exist several intermolecular hydrogen-bonding interactions among the H atoms of the methyl groups of Tab ligands and the S atom of SCN^- anions [C7···S2 (x, y, 1 + z)], the N atoms of SCN^- anions [C9···N2 ($-1 + x$, $1/2 - y$, $1/2 + z$); C9···N2 ($-1 + x$, y, $1 + z$)], which lead to the formation of a 2D hydrogen-bonded network (Fig. 4b).

Crystal structure of $[MeHg(Tab)_2]PF_6$ (4). Compound **4** crystallizes in the monoclinic space group $P2_1/c$ and its asymmetric unit consists of a $[MeHg(Tab)_2]^+$ cation and one PF_6^- anion. In the cation of **4**, the central Hg1 atom is coordinated by two S atoms of the two Tab ligands and one C atom of the methyl group, forming a unique distorted trigonal-planar coordination geometry (Fig. 5a). The two Tab ligands take a *trans* configuration with a dihedral angle of 65.6°. The Hg–C length (2.051 (12) Å) is similar to that of the three-coordinated methylmercury complex [MeHg(2,2′-bpy)]NO_3 (2.066(58) Å).[19] It is noted that the Hg1–S1 bond distance (2.422(2) Å) is significantly longer than the Hg–S2 bond length (2.737(2) Å). The two C–Hg–S bond angles are 160.0(5)° and 121.4(5)°, which are much smaller than the linear coordinated compounds. The smaller

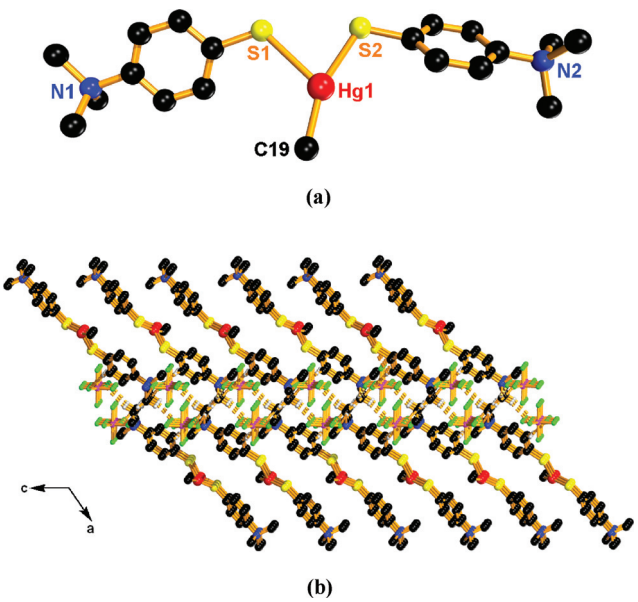


Fig. 5 (a) View of the $[MeHg(Tab)_2]^+$ cation of **4**. (b) 2D network formed by hydrogen-bonding interactions in **4** (looking along the *b* axis). All H atoms except those involved in hydrogen-bonding interactions were omitted.

S–Hg–C angle corresponds to the longer Hg–S distance. Because the PF_6^- anions are located between the $[MeHg(Tab)_2]^+$ cations, several F atoms interact with the H atoms of the methyl groups [C18···F1 ($-x$, $1 - y$, $2 - z$); C18···F3 ($-x$, $-1/2 + y$, $5/2 - z$); C18···F4 (x, $1/2 - y$, $-1/2 + z$)] and the H atoms of the

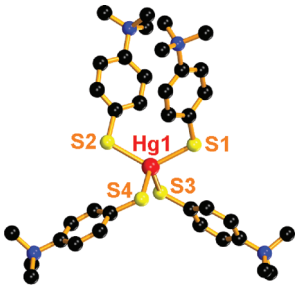


Fig. 6 View of one of the three independent $[Hg(Tab)_4]^{2+}$ cations of **6**. All hydrogen atoms have been omitted for clarity.

phenyl groups [C11···F1] of the Tab ligands, forming a 2D hydrogen-bonded network (Fig. 5b).

Crystal structure of $[Hg(Tab)_4]_3(PF_6)_6$·MeOH·2MeCN (6·MeOH·2MeCN). Compound **6**·MeOH·2MeCN crystallizes in the monoclinic space group *Pc* and its asymmetric contains three crystallographically independent $[Hg(Tab)_4]^{2+}$ dications, six PF_6^- anions, two halves of methanol solvent molecules, one and two halves of MeCN solvent molecules. The structure of the $[Hg(Tab)_4]^{2+}$ dication (Fig. 6) resembles those observed in $(Me_4N)_2[Hg(SPhCl\text{-}p)_4]$,[20a] $[Hg(SpyH)_4(ClO_4)_2]$ (Spy^- = pyridine-4-thiolate),[20b] $(NEt_4)_2[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_4]$.[20c] Each Hg atom is coordinated by four S atoms from four Tab ligands, forming a strongly distorted tetrahedral coordination geometry with the S–Hg–S angles in the range of 91.72(3)–123.00(3)°. The average Hg–S distance (2.5242(12) Å) is close to that of $(Me_4N)_2[Hg(SPhCl\text{-}p)_4]$ (2.540(5) Å), but substantially longer than those of the corresponding ones in $[Hg(Tab)_2](PF_6)_2$ (2.331 (3) Å) and $[Hg_2(Tab)_6](PF_6)_4$ (2.4242(14) Å).[13a] In the crystal of **6**·MeOH·2MeCN, there exist very complicated hydrogen-bonding interactions among the methyl groups of Tab ligands, the F atoms of the PF_6^- anions, and MeOH solvent molecules, which may not be described in this paper.

Conclusions

In the work reported here, we demonstrate the isolation of the two-coordinated methylmercury complex **1** from reactions of MeHgI with Ag_2O and $TabHPF_6$. The Hg–C bond of **1** was inert when **1** was treated with KI and KSCN to form two anion-exchange products **2** and **3**. In the case of Tab, the linear coordination geometry of the Hg(II) center of **1** was converted into the trigonal-planar coordination geometry of the Hg(II) center of **4**. However, the Hg–C bond of **1** was readily cleaved by a weak acid NH_4SCN to give a tetrahedrally-coordinated Hg(II) complex **5**. When complex **4** was treated with other weak acids such as 4,6-Me_2pymSH or EtSH, the cleavage of the Hg–C bond of **4** was also observed to form another tetrahedrally-coordinated Hg(II) complex **6**. These results revealed that in our system, increasing the coordination number of the Hg(II) center by donor ligands like Tab may not promote the cleaving Hg–C bond in the methylmercury complexes. The cleavage of the Hg–C bond in MeHg complexes **1** and **4** could be completed by enhancement of Hg(II) coordination number through S-donor ligands (SCN^- and RS^-) and protonation of the methyl group *via* weak acids like NH_4^+, 4,6-Me_2pymSH or EtSH in a cooperative way, which may provide a simple approach to detoxification of organomercury compounds.

Acknowledgements

The authors thanked the National Natural Science Foundation of China (90922018 and 21171124), the Nature Science Key Basic Research of Jiangsu Province for Higher Education (09KJA150002), the Specialized Research Fund for the Doctoral Program of higher Education of Ministry of Education (20093201110017), the State Key Laboratory of Coordination Chemistry of Nanjing University for financial support. J. P. Lang also highly appreciated the support for the Qin-Lan and the "333" Projects of Jiangsu Province, the Priority Academic Program Development of Jiangsu Higher Education Institutions, and the "*SooChow* Scholar" Program and Program for Innovative Research Team of Suzhou University. The authors also greatly appreciate the helpful comments from the editor and the reviewers.

References

1 (*a*) H. R. Sunshine and S. J. Lippard, *Nucleic Acids Res.*, 1974, **1**, 673; (*b*) J. W. Sekowski, L. H. Malkas, Y. T. Wei and R. J. Hickey, *Toxicol. Appl. Pharmacol.*, 1997, **145**, 268; (*c*) I. Onyido, A. R. Norris and E. Buncel, *Chem. Rev.*, 2004, **104**, 5911; (*d*) B. N. Ahamed, M. Arunachalam and P. Ghosh, *Inorg. Chem.*, 2010, **49**, 4447.
2 (*a*) H. Strasdeit, A. Döllen, W. Saak and M. Wilhelm, *Angew. Chem.*, 2000, **112**, 803; (*b*) L. Magos, *Metal Ions in Biological Systems*, (ed., (A. Sigel and H. Sigel), Dekker, New York, 1997, **34**, 327.
3 (*a*) R. E. Hecky, D. J. Ramsey, R. A. Bodaly and N. E. Strange, *Advances in Mercury Toxicology*, 1991, 33; (*b*) C. A. Kelly, J. W. M. Rudd, R. A. Bodaly, N. P. Roulet, V. L. Louis, A. Heyes, T. R. Moore, S. Schiff, R. Aravena, K. J. Scott, B. Dyck, R. Harris, B. Warner and G. Edwards, *Environ. Sci. Technol.*, 1997, **31**, 1334; (*c*) J. G. Wiener, D. P. Krabbenhoft, G. H. Heinz and A. M. Scheuhammer, *Handbook of Ecotoxicology*, 2003, 409; (*d*) J. G. Wiener, D. P. Krabbenhoft, G. H. Heinz and A. M. Scheuhammer, *Handbook of Ecotoxicology*, 2003, 409; (*e*) F. M. M. Morel, A. M. L. Krepiel and M. Amyot, *Annu. Rev. Ecol. Syst.*, 1998, **29**, 543.
4 W. F. Fitzgerald and T. W. Clarkson, *Environ. Health Perspect.*, 1991, **96**, 159.
5 (*a*) T. W. Clarkson, L. Magos and G. J. Myers, *N. Engl. J. Med.*, 2003, **349**, 1731; (*b*) P. A. D'Itri and F. M. D'Itri, *Environ. Manage.*, 1978, **2**, 3.
6 (*a*) M. Uchino, Y. Tanaka, Y. Ando, T. Yonehara, A. Hara, I. Mishima, T. Okajima and M. Ando, *J. Environ. Sci. Health, Part B*, 1995, **30**, 699; (*b*) T. W. Clarkson and L. Magos, *Crit. Rev. Toxicol.*, 2006, **36**, 609; (*c*) D. L. Rabenstein, *Acc. Chem. Res.*, 1978, **11**, 100.
7 (*a*) T. W. Clarkson and L. Magos, *Crit. Rev. Toxicol.*, 2006, **36**, 609; (*b*) J. Mutter, J. Naumann and C. Guethlin, *Crit. Rev. Toxicol.*, 2007, **37**, 537; (*c*) T. W. Clarkson, *Environ. Health Perspect.*, 2002, **110**, 11; (*d*) T. W. Clarkson, *Crit. Rev. Clin. Lab. Sci.*, 1997, **34**, 369; (*e*) N. J. Langford and R. E. Ferner, *J. Hum. Hypertens.*, 1999, **13**, 651; (*f*) D. W. Boening, *Chemosphere*, 2000, **40**, 1335; (*g*) L. Magos, *Met. Ions Biol. Sys.*, 1997, **34**, 321; (*h*) A. R. Hutchison and D. A. Atwood, *J. Chem. Crystallogr.*, 2003, **33**, 631; (*i*) L. Alessio, M. Campagna and R. Lucchini, *Am. J. Ind. Med.*, 2007, **50**, 779; (*j*) T. W. Clarkson, J. B. Vyas and N. Ballatorl, *Am. J. Ind. Med.*, 2007, **50**, 757; (*k*) J. F. Risher and C. T. De Rosa, *J. Environ. Health*, 2007, **70**, 9; (*l*) I. Onyido, A. R. Norris and E. Buncel, *Chem. Rev.*, 2004, **104**, 5911; (*m*) P. O. Ozuah, *Current Probl. Pediatr.*, 2000, **30**, 91.
8 (*a*) M. J. Moore, M. D. Distefano, L. D. Zydowsky, R. T. Cummings and C. T. Walsh, *Acc. Chem. Res.*, 1990, **23**, 301; (*b*) C. T. Walsh, M. D. Distefano, M. J. Moore, L. M. Shewchuk and G. L. Verdine, *FASEB J.*, 1988, **2**, 124.

9 (*a*) J. M. Parks, H. Guo, C. Momany, L. Liang, S. M. Miller, A. O. Summers and J. C. Smith, *J. Am. Chem. Soc.*, 2009, **131**, 13278; (*b*) J. G. Omichinski, *Science*, 2007, **317**, 205; (*c*) H. Strasdeit, *Angew. Chem., Int. Ed.*, 2008, **47**, 828; (*d*) X. C. Li, R. Z. Liao, W. C. Zhou and G. J. Chen, *Phys. Chem. Chem. Phys.*, 2010, **12**, 3961; (*e*) Y. W. Chen, C. F. Huang, K. S. Tsai, R. S. Yang, C. C. Yen, C. Y. Yang, S. Y. Lin-Shiau and S. H. Liu, *Chem. Res. Toxicol.*, 2006, **19**, 1080; (*f*) A. J. Canty, N. Chaichit, B. M. Gatehouse and E. E. George, *Inorg. Chem.*, 1981, **20**, 4293.

10 (*a*) J. G. Melnick and G. Parkin, *Science*, 2007, **317**, 225; (*b*) J. G. Melnick, K. Yurkerwich and G. Parkin, *Inorg. Chem.*, 2009, **48**, 6763; (*c*) F. R. Jensen and B. Rickborn, *Electrophilic Substitution of Organomercurials*, McGraw-Hill, New York, 1968.

11 (*a*) P. Barbaro, F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini and A. Vacca, *Inorg. Chem.*, 1994, **33**, 6163; (*b*) J. S. Casas, M. S. García-Tasende and J. Sordo, *Coord. Chem. Rev.*, 1999, **193**, 283; (*c*) C. E. Holloway and M. Melník, *J. Organomet. Chem.*, 1995, **495**, 1.

12 (*a*) V. Barone, A. Bencini, F. Totti and M. G. Uytterhoeven, *Organometallics*, 1996, **15**, 1465; (*b*) M. Wilhelm, S. Deeken, E. Berssen, W. Saak, A. Lützen, R. Koch and H. Strasdeit, *Eur. J. Inorg. Chem.*, 2004, 2301.

13 (*a*) J. X. Chen, W. H. Zhang, X. Y. Tang, Z. G. Ren, Y. Zhang and J. P. Lang, *Inorg. Chem.*, 2006, **45**, 2568; (*b*) J. X. Chen, Q. F. Xu, Y. Xu, Y. Zhang, Z. N. Chen and J. P. Lang, *Eur. J. Inorg. Chem.*, 2004, 4247; (*c*) J. X. Chen, Q. F. Xu, Y. Zhang, Z. N. Chen and J. P. Lang, *J. Organomet. Chem.*, 2004, **689**, 1071; (*d*) J. X. Chen, W. H. Zhang, X. Y. Tang, Z. G. Ren, H. X. Li, Y. Zhang and J. P. Lang, *Inorg. Chem.*, 2006, **45**, 7671; (*e*) X. Y. Tang, J. X. Chen, G. F. Liu, Z. G. Ren, Y. Zhang and J. P. Lang, *Eur. J. Inorg. Chem.*, 2008, 2593; (*f*) X. Y. Tang, R. X. Yuan, Z. G. Ren, H. X. Li, Y. Zhang and J. P. Lang, *Inorg. Chem.*, 2009, **48**, 2639; (*g*) X. Y. Tang, A. X. Zheng, H. Shang, R. X. Yuan, H. X. Li, Z. G. Ren and J. P. Lang, *Inorg. Chem.*, 2011, **50**, 503; (*h*) A. X. Zheng, Z. G. Ren, L. L. Li, H. Shang, H. X. Li and J. P. Lang, *Dalton Trans.*, 2011, **40**, 589.

14 (*a*) B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr. and R. H. Holm, *J. Am. Chem. Soc.*, 1974, **96**, 4159; (*b*) A. Rodríguez, A. Sousa-Pedrares, J. A. García-Vázquez, J. Romero and A. Sousa, *J. Organomet. Chem.*, 2010, **695**, 1271.

15 (*a*) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany, 1997; (*c*) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

16 (*a*) A. K. Das and S. Seth, *J. Inorg. Biochem.*, 1997, **65**, 207; (*b*) A. Rodríguez, A. Sousa-Pedrares, J. A. García-Vázquez, J. Romero and A. Sousa, *Eur. J. Inorg. Chem.*, 2005, 2242.

17 (*a*) W. Y. Guo, Z. H. Peng, D. C. Li and Y. H. Zhou, *Polyhedron*, 2004, **23**, 1701; (*b*) A. Armas, V. Sonois, E. Mothes, H. Mazarguil and P. Faller, *J. Inorg. Biochem.*, 2006, **100**, 1672.

18 (*a*) J. G. Melnick, K. Yurkerwich, D. Buccella, W. Sattler and G. Parkin, *Inorg. Chem.*, 2008, **47**, 6421; (*b*) J. Bravo, J. S. Casas, M. V. Castaro, M. Gayoso, Y. P. Mascarenhas, A. Sanchez, C. O. P. Santos and J. Sordoi, *Inorg. Chem.*, 1985, **24**, 3435; (*c*) C. S. Lai and E. R. T. Tiekink, *CrystEngComm*, 2003, **5**, 253.

19 A. J. Canty and A. Marker, *Inorg. Chem.*, 1976, **15**, 425.

20 (*a*) S. Choudhury, I. G. Dance, P. J. Guerney and A. D. Rae, *Inorg. Chim. Acta*, 1983, **70**, 227; (*b*) K. S. Anjali, J. J. Vittal and P. A. W. Dean, *Inorg. Chim. Acta*, 2003, **351**, 79; (*c*) M. Kato, K. Kojima, T. Okamura, H. Yamamoto, T. Yamamura and N. Ueyama, *Inorg. Chem.*, 2005, **44**, 4437.

