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Assembly of a New Family of Mercury(II) Zwitterionic Thiolate Complexes from a Preformed Compound $[Hg(Tab)_2](PF_6)_2$ [Tab = 4-(Trimethylammonio)benzenethiolate]

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Reactions of $Hg(OAc)_2$ with 2 equiv of $TabHPF_6$ [TabH = 4-(trimethylammonio)benzenethiol] in MeCN/MeOH afforded a mononuclear linear complex $[Hg(Tab)_2](PF_6)_2$ (**1**). By using **1** as a precursor, a new family of mercury(II) zwitterionic thiolate complexes, $[Hg_2(Tab)_6](PF_6)_4$·2MeCN (**2**·2MeCN), $[Hg(Tab)_2(SCN)](PF_6)$ (**3**), $[Hg(Tab)_2(SCN)_2]$ (**4**), $[Hg(Tab)I_2]$ (**5**), $\{[Hg(Tab)_2]_4[HgI_2][Hg_2I_6]\}(PF_6)_2(NO_3)_4$ (**6**), $[Hg(Tab)_2][HgI_4]$ (**7**), $[Hg(Tab)_2][HgCl_2(SCN)_2]$ (**8**), $[Tab–Tab]_2[Hg_3Cl_{10}]$ (**9**), and $[Hg_2(Tab)_6]_3(PF_6)Cl_{11}$ (**10**), were prepared and characterized by elemental analysis, IR spectra, UV–vis spectra, ^1H NMR, and single-crystal X-ray crystallography. The $[Hg_2(Tab)_6]^{4+}$ tetracation of **2** or **10** contains an asymmetrical Hg_2S_2 rhomb with an inversion center lying on the midpoint of the Hg···Hg line. The Hg atom of the $[Hg(Tab)_2]^{2+}$ dication of **3** is coordinated to one SCN^-, forming a rare T-shaped coordination geometry, while in **4**, the Hg atom of $[Hg(Tab)_2]^{2+}$ is coordinated to two SCN^-, forming a seesaw-shaped coordination geometry. Through weak secondary Hg···S coordinations, each cation in **3** is further linked to afford a one-dimensional zigzag chain. The trigonal $[Hg(Tab)I_2]$ molecules in **5** are held together by weak secondary Hg···I and Hg···S interactions, forming a one-dimensional chain structure. In **6**, the four $[Hg(Tab)_2]^{2+}$ dications, one HgI_2 molecule, one $[Hg_2I_6]^{2-}$ dianion, one PF_6^-, and four NO_3^- anions are interconnected by complicated secondary Hg···I and Hg···O interactions, forming a scolopendra-like chain structure. The secondary Hg···I interactions, $[Hg(Tab)_2]^{2+}$ and $[HgI_4]^{2-}$ in **7**, are combined to generate a one-dimensional chain structure, while $[Hg(Tab)_2]^{2+}$ and $[HgCl_2(SCN)_2]^{2-}$ in **8** are interconnected by secondary Hg···N interactions to form a one-dimensional zigzag chain structure. Compound **9** consists of two $[Tab–Tab]^{2+}$ dications and one $[Hg_3Cl_{10}]^{4-}$ tetraanion. The facile approach to the construction of **2**–**8** and **10** from **1** may be applicable to the mimicking of a coordination sphere of the Hg sites of metallothioneins.

Introduction

As in past decades, mercury thiolate complexes have received much attention as a result of their rich chemistry,[1] their application in the resistance response in bacteria at the level of gene activation,[2] their relation to the detoxification of Hg by metallothioneins,[3] and their involvement in a DNA-binding protein[1a] and in mercury reductases and related proteins.[1b] The linear {Hg(S−Cys)$_2$}, trigonal {Hg(S−Cys)$_3$}, and tetrahedral {Hg(S−Cys)$_4$} coordination geometries have been proposed for Hg^{II} in the mercury metallothioneins.[1f,4] Studies in these respects have stimulated more interest in structural probes that might be used to determine the nature of the coordination of the Hg^{II} ion to the proteins. So far, a large number of mercury thiolate compounds have been prepared and structurally characterized: mononuclear $Hg(SR)_n$ ($n = 2-4$),[5] dinuclear $Hg_2(SR)_n$ ($n = 3$ and 6),[4a,6] trinuclear $Hg_3(SR)_4$,[6a] tetranuclear $Hg_4(SR)_6$,[7] pentanuclear $Hg_5(SR)_8$,[2] and polynuclear $[Hg(SR)_n]_\infty$.[5c] Most of these compounds have been prepared from a one-pot reaction of simple Hg^{II} salts with RSH or from redox reactions of organic

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disulfides with Hg in organic solvents.[8] However, reactions of the preformed mercury thiolates with other donor ligands or metal ions seem to be less explored for the preparation of new mercury(II) thiolate complexes.[7b,9]

On the other hand, we are interested in the preparation of metal thiolate complexes from an unique zwitterionic thiolate $TabHPF_6$ [TabH = 4-(trimethylammonio)benzenethiol].[10] Being that this is an an extension of this study and, especially, being aware that few examples of mercury(II) zwitterionic thiolate complexes have been reported,[11] we carried out the reactions of $Hg(OAc)_2$ with $TabHPF_6$ and isolated a mononuclear mercury thiolate complex $[Hg(Tab)_2](PF_6)_2$ (**1**). As discussed later in this paper, the coordination is unsaturated either for the Hg atom or for the two S atoms of the Tab ligands in **1**, implying that **1** may be used as a precursor for the preparation of new Hg^{II}/Tab complexes. Herein we report the reactions of **1** with additional donor ligands (e.g., Tab, SCN^-, I^-) or metal salts (e.g., Hg^{2+}, Au^{3+}) and the structural characterization of **1** along with the resulting nine new Hg^{II}/Tab complexes. These represent a new family of mercury(II) zwitterionic thiolate complexes with interesting structural motifs and may provide insight into the nature of the coordination of the Hg^{II} ion to the proteins.

Experimental Section

General Procedures. $TabHPF_6$ was prepared according to the literature method.[12] 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. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon. The IR spectra were recorded on a Nicolet Magna-IR 550 as the KBr disk (4000−400 cm^{-1}). The elemental analyses for C, H, and N were performed on an EA1110 CHNS elemental analyzer. ^1H NMR spectra were recorded at ambient temperature on a Varian UNITY-400 spectrometer. ^1H NMR chemical shifts were referenced to the deuterated dimethyl sulfoxide (DMSO-d_6) signal. UV−vis spectra were measured on a Hitachi U-2810 spectrophotometer.

Synthesis. $[Hg(Tab)_2](PF_6)_2$ (1). To a solution containing $TabHPF_6$ (0.626 g, 2 mmol) in MeCN (5 mL) was added a solution of $Hg(OAc)_2$ (0.318 g, 1 mmol) in MeOH (5 mL). The resulting mixture was heated to 70 °C and stirred for 1 h to form a colorless homogeneous solution. After it was cooled to ambient temperature, diethyl ether (20 mL) was layered onto the filtrate to form colorless plates of **1** in several days, which were collected by filtration, washed by Et_2O, and dried in vacuo. Yield: 0.82 g (99.4% based on Hg). Anal. Calcd for $C_{18}H_{26}F_{12}HgN_2P_2S_2$: C, 26.20; H, 3.18; N, 3.40. Found: C, 26.32; H, 3.02; N, 3.12. IR (KBr disk): 1581 (w), 1489 (m), 1126 (w), 1010 (w), 960 (m), 830 (s), 744 (w), 559 (m) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 230 (19 700). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.56−7.65 (m, 4H, Ph), 3.50 (s, 9H, NMe_3).

$[Hg_2(Tab)_6](PF_6)_4$ (2). To a solution containing **1** (0.825 g, 1 mmol) in MeCN (15 mL) was added a solution of Tab (0.167 g, 1 mmol) in MeOH (5 mL). The resulting mixture was stirred for 1 h to form a colorless homogeneous solution. A workup similar to that used in the isolation of **1** afforded colorless block crystals of **2**. Yield: 0.89 g (90.0% based on Hg). Anal. Calcd for $C_{54}H_{78}F_{24}Hg_2N_6P_4S_6$: C, 32.68; H, 3.96; N, 4.23. Found: C, 32.62; H, 4.23; N, 4.59. IR (KBr disk): 1581 (w), 1489 (m), 1126 (w), 1010 (w), 956 (m), 833 (s), 744 (w), 555 (m) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 240 (10 900). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.47−7.63 (m, 4H, Ph), 3.47 (s, 9H, NMe_3).

$[Hg(Tab)_2(SCN)](PF_6)$ (3). To a solution containing **1** (0.825 g, 1 mmol) in MeCN (15 mL) was added a solution of KSCN (0.097 g, 1 mmol) in MeOH (10 mL). The resulting mixture was stirred for 0.5 h and filtered. Slow evaporation of solvents from the colorless filtrate for 1 week produced colorless block crystals of **3**. Yield: 0.657 g (89.0% based on Hg). Anal. Calcd for $C_{19}H_{26}F_6HgN_3PS_3$: C, 30.91; H, 3.55; N, 5.69. Found: C, 30.62; H, 3.42;

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N, 5.46. IR (KBr disk): 2079 (s), 1581 (w), 1489 (m), 1126 (w), 1010 (w), 952 (m), 830 (s), 740 (w), 555 (m) cm^{-1}. UV−Vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 235 (22 200). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.53−7.62 (m, 4H, Ph), 3.42 (s, 9H, NMe_3).

[Hg(Tab)$_2$(SCN)$_2$] (4). The similar reaction of **1** (0.825 g, 1 mmol) with 2 equiv of KSCN (0.195 g, 2 mmol) in MeOH followed by a workup similar to that used in the isolation of **3** afforded colorless triangle crystals of **4**. Yield: 0.605 g (92.9% based on Hg). Anal. Calcd for $C_{20}H_{26}HgN_4S_4$: C, 36.88; H, 4.02; N, 8.60. Found: C, 36.45; H, 4.29; N, 8.72. IR (KBr disk): 2080 (s), 1581 (w), 1489 (m), 1126 (w), 1010 (w), 953 (m), 831 (s), 740 (w), 555 (m) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 230 (17 400). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.51−7.63 (m, 4H, Ph), 3.48 (s, 9H, NMe_3).

[Hg(Tab)I$_2$] (5). To a solution containing **1** (0.825 g, 1 mmol) in MeCN (5 mL) was added a solution of Bu_4NI (0.739 g, 2 mmol) in MeCN (5 mL). The mixture was stirred for 1 h, and a large amount of yellow precipitate was developed and then filtered. The resulting solid was redissolved in DMF (5 mL) and filtered again. A workup similar to that used in the isolation of **1** led to the formation of yellow block crystals of **5**. Yield: 0.590 g (95.0% based on Hg). Anal. Calcd for $C_9H_{13}HgI_2NS$: C, 17.39; H, 2.11; N, 2.25. Found: C, 17.12; H, 2.53; N, 2.64. IR (KBr disk): 1581 (w), 1481 (m), 1122 (s), 1010 (s), 952 (w), 844 (s), 744 (s), 547 (s) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 235 (24 800). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.51−7.62 (m, 4H, Ph), 3.41 (s, 9H, NMe_3).

{[Hg(Tab)$_2$]$_4$[HgI$_2$][Hg$_2$I$_6$]}(PF$_6$)$_2$(NO$_3$)$_4$ (6). To a solution containing **1** (0.825 g, 1 mmol) in DMF (5 mL) was added a solution of HgI_2 (0.454 g, 1 mmol) in DMF (5 mL). The mixture was stirred for 1 h, and a large amount of yellow precipitate was developed. After filtration, the resulting solid was dissolved in 5 mL of hot DMF/H_2O (3:2, v/v) containing KNO_3 (0.101 g, 1 mmol) to give rise to a clear solution. A workup similar to that used in the isolation of **1** afforded yellowish block crystals of **6**. Yield: 0.838 g (78.0% based on **1**). Anal. Calcd for $C_{72}H_{104}F_{12}Hg_7I_8N_{12}O_{12}P_2S_8$: C, 20.13; H, 2.44; N, 3.91. Found: C, 20.54; H, 2.13; N, 3.79. IR (KBr disk): 1581 (w), 1485 (m), 1350 (s), 1126 (w), 1010 (w), 956 (m), 830 (s), 744 (m), 559 (w) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 235 (96 100). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.43−7.58 (m, 4H, Ph), 3.42 (s, 9H, NMe_3).

[Hg(Tab)$_2$][HgI$_4$] (7). To a solution containing HgI_2 (0.454 g, 1 mmol) in DMF (5 mL) was added a solution of Bu_4NI (0.739 g, 2 mmol) in DMF (5 mL). The resulting yellow solution was stirred for 0.5 h and then treated with a solution of **1** (0.825 g, 1 mmol) in DMF (5 mL). The mixture was stirred for another 2 h and filtered. A workup similar to that used in the isolation of **1** generated yellow block crystals of **7**. Yield: 1.032 g (83.0% based on Hg). Anal. Calcd for $C_{18}H_{26}Hg_2I_4N_2S_2$: C, 17.39; H, 2.11; N, 2.25. Found: C, 17.52; H, 2.13; N, 2.49. IR (KBr disk): 1577 (s), 1481 (m), 1122 (w), 1006 (w), 949 (m), 844 (s), 744 (w), 544 (m) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 235 (17 200). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.49−7.67 (m, 4H, Ph), 3.45 (s, 9H, NMe_3).

[Hg(Tab)$_2$][HgCl$_2$(SCN)$_2$] (8). To a solution containing $HgCl_2$ (0.271 g, 1 mmol) in MeOH (5 mL) was added KSCN (0.194 g, 2 mmol). The resulting colorless solution was stirred for 0.5 h and then treated with a solution of **1** (0.825 g, 1 mmol) in MeCN (15 mL). The mixture was stirred for another 0.5 h and filtered to give a colorless solution. A workup analogous to that used in the isolation of **1** resulted in colorless block crystals of **8**. Yield: 0.867 g (94.0% based on Hg). Anal. Calcd for $C_{20}H_{26}Cl_2Hg_2N_4S_4$: C, 26.03; H, 2.84; N, 6.07. Found: C, 26.12; H, 2.69; N, 5.98. IR (KBr disk): 2114 (s), 1581 (w), 1485 (m), 1126 (w), 1010 (w), 952 (m), 844 (w), 848 (s), 744 (w), 547 (m) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 230 (46 000). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.42−7.59 (m, 4H, Ph), 3.49 (s, 9H, NMe_3).

[Tab−Tab]$_2$[Hg$_3$Cl$_{10}$] (9). To a solution containing **1** (0.825 g, 1 mmol) in MeCN (15 mL) was added a solution of $HAuCl_4{\cdot}4H_2O$ (0.412 g, 1 mmol) in MeOH (5 mL). The resulting mixture was stirred for 0.5 h and filtered to give a colorless solution. Slow evaporation of solvents from the filtrate overnight produced colorless flakes of **9**, which were collected by filtration, washed by Et_2O, and dried in vacuo. Yield: 0.341 g (62.9% based on Hg). Anal. Calcd for $C_{36}H_{52}Cl_{10}Hg_3N_4S_4$: C, 26.60; H, 3.22; N, 3.45. Found: C, 26.35; H, 3.38; N, 3.67. IR (KBr disk): 1581 (w), 1481 (m), 1122 (w), 1006 (w), 956 (m), 829 (s), 744 (w), 547 (m), 481 (m) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 230 (25 996). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.73−7.81(m, 4H, Ph), 3.65 (s, 9H, NMe_3).

[Hg$_2$(Tab)$_6$]$_3$(PF$_6$)Cl$_{11}$ (10). To a solution of Tab (0.668 g, 4 mmol) in MeOH (10 mL) was added a solution of $HAuCl_4{\cdot}4H_2O$ (0.412 g, 1 mmol) in MeOH (5 mL). The resulting colorless solution was treated with a solution of **1** (0.825 g, 1 mmol) in MeCN (15 mL) and stirred for 0.5 h. After filtration, diethyl ether (40 mL) was allowed to diffuse into the filtrate at ambient temperature for 2 weeks, forming colorless long block crystals of **10** coupled with two byproducts, $Au(Tab)_2(PF_6)$ (colorless blocks) and [Tab−Tab](PF_6)$_2$ (light yellow needles), which were separated mechanically under a microscope. Yield for **10**: 0.673 g (85.0% based on Hg). Anal. Calcd for $C_{162}H_{234}Cl_{11}F_6Hg_6N_{18}PS_{18}$: C, 40.97; H, 4.97; N, 5.31. Found: C, 40.83; H, 4.59; N, 4.87. IR (KBr disk): 1581 (w), 1489 (m), 1415 (w), 1126 (w), 1010 (w), 956 (m), 832 (s), 744 (w), 555 (m) cm^{-1}. UV−vis [DMF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 240 (62 000). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.50−7.65 (m, 4H, Ph), 3.43 (s, 9H, NMe_3). Yield for $Au(Tab)_2(PF_6)$: 0.523 g. Anal. Calcd for $C_{18}H_{26}AuF_6N_2PS_2$: C, 31.96; H, 3.87; N, 4.14. Found: C, 32.15; H, 3.39; N, 3.81. IR (KBr disk): 1579 (w), 1484 (m), 1409 (w), 1121 (w), 1007 (w), 960 (m), 839 (s), 742 (w), 555 (m) cm^{-1}. Yield for [Tab−Tab](PF_6)$_2$: 0.045 g. Anal. Calcd for $C_{18}H_{26}F_{12}N_2P_2S_2$: C, 34.62; H, 4.20; N, 4.49. Found: C, 34.23; H, 4.18; N, 4.72. IR (KBr disk): 1583 (w), 1482 (m), 1126 (w), 1009 (w), 958 (m), 835 (s), 745 (w), 555 (m), 483 (m) cm^{-1}.

X-ray Structure Determination. X-ray-quality crystals of **1**−**10** were obtained directly from the above preparation. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite-monochromated Mo Kα (λ = 0.710 70 Å). Crystals of **1**−**10** were mounted with grease at the top of a glass fiber and cooled at 193 K in a liquid-nitrogen stream. Cell parameters were refined by using the program *CrystalClear* (Rigaku and MSC, version 1.3, 2001). The collected data were reduced by using the program *CrystalClear* (Rigaku and MSC, version 3.60, 2004), while an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1**−**10** were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXTL-97* program.[13] All non-H atoms except the Cl atoms in **10** were refined anisotropically. All H 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 $U_{iso}(H) = 1.2U_{eq}(C)$ for phenyl groups and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups. In the final Fourier

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Table 1. Crystallographic Data for **1**−**10**

	1	**2**	**3**	**4**	**5**
mol formula	$C_{18}H_{26}F_{12}HgN_2P_2S_2$	$C_{58}H_{84}F_{24}Hg_2N_8P_4S_6$	$C_{19}H_{26}F_6HgN_3PS_3$	$C_{20}H_{26}HgN_4S_4$	$C_9H_{13}HgI_2NS$
fw	825.08	2066.75	738.17	651.32	621.66
cryst syst	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$	*Pccn*	*Cc*
size (mm^3)	0.40 × 0.25 × 0.05	0.22 × 0.19 × 0.12	0.40 × 0.22 × 0.10	0.40 × 0.28 × 0.10	0.15 × 0.15 × 0.10
a (Å)	6.165(3)	9.6164(13)	10.431(2)	8.2168(8)	11.995(2)
b (Å)	8.403(4)	10.8605(14)	28.455(6)	16.2964(14)	15.022(3)
c (Å)	13.120(5)	19.202(3)	25.414(5)	17.6858(19)	7.9580(11)
α (deg)	74.77(2)	91.996(3)			
β (deg)	82.74(3)	100.047(4)	92.84(3)		98.383(4)
γ (deg)	88.03(3)	96.313(4)			
V ($Å^3$)	650.6(5)	1959.7(5)	7534(3)	2368.2(4)	1418.6(4)
Z	1	1	12	4	4
T (K)	193	193	193	193	193
D_{calc} (g cm^{-3})	2.10	1.751	1.952	1.829	2.911
λ(Mo Kα) (Å)	0.71070	0.71070	0.71070	0.71070	0.71070
μ (cm^{-1})	62.97	42.53	65.00	68.66	153.17
$2\theta_{max}$ (deg)	55.0	50.6	50.7	55.0	55.0
total reflns	6751	19710	71820	24638	7843
unique reflns	2960 ($R_{int} = 0.049$)	7142 ($R_{int} = 0.039$)	27159 ($R_{int} = 0.105$)	2715 ($R_{int} = 0.036$)	1634 ($R_{int} = 0.032$)
no. of obsvns	2756 [$I > 2.00\sigma(I)$]	6339 [$I > 2.00\sigma(I)$]	18233 [$I > 2.00\sigma(I)$]	2484 [$I > 2.00\sigma(I)$]	2517 [$I > 2.00\sigma(I)$]
no. of param	173	266	1381	133	131
R^a	0.0632	0.0398	0.0949	0.0324	0.0238
wR^b	0.1694	0.0748	0.2229	0.0787	0.0434
GOF^c	1.422	1.108	1.088	1.135	0.759
$\Delta\rho_{max}$ (e $Å^{-3}$)	1.451	0.942	2.903	0.782	0.963
$\Delta\rho_{min}$ (e $Å^{-3}$)	−1.476	−0.965	−2.635	−0.942	−0.992

	6	**7**	**8**	**9**	**10**
mol formula	$C_{72}H_{104}F_{12}Hg_7I_8N_8P_2S_8$	$C_{18}H_{26}Hg_2I_4N_2S_2$	$C_{20}H_{26}Cl_2Hg_2N_4S_4$	$C_{36}H_{52}Cl_{10}Hg_3N_4S_4$	$C_{162}H_{234}Cl_{11}F_6Hg_6N_{18}PS_{18}$
fw	4295.50	1243.31	922.81	1625.3	4749.39
cryst syst	orthorhombic	orthornombic	monoclinic	monoclinic	trigonal
space group	*Pmmn*	$Pmn2_1$	$P2_1/m$	$P2_1/c$	$R\bar{3}$
size (mm^3)	0.26 × 0.20 × 0.13	0.25 × 0.20 × 0.17	0.27 × 0.24 × 0.15	0.24 × 0.20 × 0.08	0.47 × 0.30 × 0.20
a (Å)	16.504(3)	16.791(3)	6.3897(9)	13.9906(19)	20.8335(11)
b (Å)	28.009(5)	10.850(2)	27.699(4)	16.2749(18)	
c (Å)	11.859(2)	9.0570(18)	7.5773(11)	11.5464(12)	42.762(3)
α (deg)					
β (deg)			93.234(4)	103.053(3)	
γ (deg)					120
V ($Å^3$)	5482.1(17)	1650.0(6)	1339.0(3)	2561.1(5)	16073.5(16)
Z	2	2	2	2	3
T (K)	193	193	193	193	193
D_{calc} (g cm^{-3})	2.602	2.503	2.289	2.108	1.472
λ(Mo Kα) (Å)	0.71070	0.71070	0.71070	0.71070	0.71070
μ (cm^{-1})	122.75	131.69	119.81	96.86	46.53
$2\theta_{max}$ (deg)	50.6	50.6	50.6	50.0	55.0
total reflns	44808	15360	13109	24920	60779
unique reflns	5180 ($R_{int} = 0.082$)	1659 ($R_{int} = 0.068$)	2513 ($R_{int} = 0.040$)	4666 ($R_{int} = 0.063$)	8187 ($R_{int} = 0.040$)
no. of obsvns	4422 [$I > 2.00\sigma(I)$]	2737 [$I > 2.00\sigma(I)$]	2338 [$I > 2.00\sigma(I)$]	4047 [$I > 2.00\sigma(I)$]	7519 [$I > 2.00\sigma(I)$]
no.of param	302	135	155	561	343
R^a	0.1236	0.0734	0.0256	0.0352	0.0654
wR^b	0.3133	0.1771	0.0508	0.0911	0.1961
GOF^c	1.237	1.115	1.124	1.016	1.219
$\Delta\rho_{max}$ (e $Å^{-3}$)	1.942	1.554	0.812	1.066	1.291
$\Delta\rho_{min}$ (e $Å^{-3}$)	−1.953	−1.972	−1.196	−1.098	−1.350

[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 number of parameters refined.

maps, the largest electron-density peaks in **1** (1.451 e/$Å^3$), in **3** (2.903 e/$Å^3$), in **6** (1.942 e/$Å^3$), in **7** (1.554 e/$Å^3$), in **9** (1.066 e/$Å^3$), and in **10** (1.291 e/$Å^3$) were located 1.064(2) Å from atom Hg1 in **1**, 0.764(1) Å from atom Hg5 in **3**, 1.051(2) Å from atom Hg2 in **6**, 1.084(2) Å from atom Hg1 in **7**, 1.016(3) Å from atom Hg1 in **9**, and 0.313(3) Å from atom Cl3 in **10**, respectively. A summary of the key crystallographic information for **1**−**10** is given in Table 1.

Results and Discussion

Synthesis. Treatment of a methanol solution of $Hg(OAc)_2$ with an acetonitrile solution of 2 equiv of $TabHPF_6$ resulted in a colorless solution, which was heated to 70 °C and stirred for 0.5 h. A standard workup afforded colorless plates of **1** in an almost quantitative yield (Scheme 1). During the reaction, a strong smell of acetic acid was evolved out of the solution because $TabHPF_6$ has stronger acidity than acetic acid, and thus the liberation of acetic acid may be the driving force for this reaction.[10]

Given the linear geometry of the dication of **1** discussed later in this paper, we anticipated that compound **1** might serve as a useful precursor for the preparation of new Hg/Tab complexes with two options. One option is that the Hg

Scheme 1

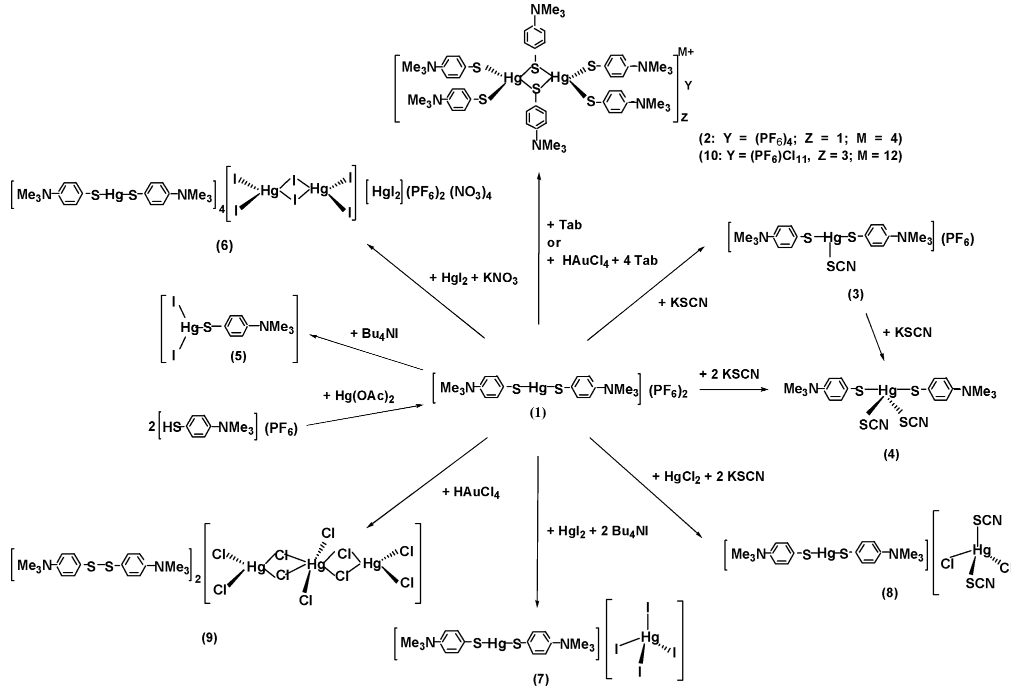
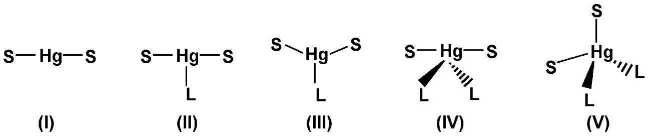


Chart 1



atom may further complete its coordination sphere by the addition of one or two Tab ligands or other donor ligands such as halides and pseudohalides. Therefore, the linear HgS_2 geometry (type I) in **1** may be converted to a T-shaped (type II), trigonal-planar (type III), seesaw-shaped (type IV), or tetrahedral (type V) coordination geometry (Chart 1).

In this context, we carried out the reactions of **1** with Tab in a 1:1 molar ratio (Scheme 1). Intriguingly, it did not form the expected three-coordinated monomer species $[Hg(Tab)_3]^{2+}$ but produced a four-coordinated dimeric compound **2**·2MeCN in a relatively high yield of 90.0%. This compound was the only product isolated in a crystalline form regardless of the **1**/Tab molar ratios. However, a 1:1 or 1:2 reaction mixture of **1** and KSCN gave rise to the corresponding 1:1 and 1:2 products **3** and **4** in high yields, respectively. If the molar ratio of **1**/KSCN was over 1:2, only **4** was isolated in a high yield. In addition, compound **4** could be formed in a quantitative yield when compound **3** was treated with one or more equiv of KSCN. In the case of **1** and Bu_4NI in a 1:2 molar ratio, we did not isolate the expected 1:2 compound $[Hg(Tab)_2I_2]$ but an unexpected neutral compound **5** in 95.0% yield. Intriguingly, one Tab of **1** was lost during the reaction. The formation of **5** may be attributed to its low solubility in MeCN. A mixture of **1**/Bu_4NI in molar ratios between 2:1 and 1:4 only produced **5**.

The other option is that compound **1** may further combine other Hg atoms or other metal atoms to form polynuclear complexes via the bridging ability of the S atoms of its two Tab ligands. In this respect, we first ran the reactions of **1** with equimolar HgI_2 (Scheme 1). It produced a yellow solid, which was dissolved in a hot DMF/H_2O (3:2, v/v) solution containing KNO_3. A standard workup afforded yellowish block crystals of **6** in 78.0% yield. On the other hand, when a solution of **1** was combined with a solution consisting of HgI_2 and Bu_4NI in a 1:1:2 molar ratio, an ionic compound **7** was isolated in 83.0% yield. In the case of **1**/$HgCl_2$/KSCN (1:1:2), another ionic compound **8** was obtained in 94.0% yield.

Intriguingly, when compound **1** reacted with $HAuCl_4$, it only produced an unexpected disulfide compound **9** (Scheme 1). The result may be due to the fact that the thiol-to-disulfide conversion could also be completed via oxygen in the presence of certain metal ions.[14,15] In our case, the formation of the Tab−Tab dication in **9** may be due to the protonation and dissociation of Tab from **1** in the presence of $HAuCl_4$ and the subsequent oxidation of $TabH^+$ via Au^{3+} and/or oxygen in open air. We also carried out the reaction of **1** with a mixture of $HAuCl_4$ and excessive Tab (1:1:4) in MeOH/MeCN. This reaction produced no mercury disulfide compound but a binuclear complex **10** in high yield along with two products, $[Au(Tab)_2](PF_6)$ and $[Tab-Tab](PF_6)_2$. Both $[Au(Tab)_2](PF_6)$ and $[Tab-Tab](PF_6)_2$ were confirmed by elemental analysis, IR spectra, and X-ray fluorescence analysis. The formation of these two compounds may be attributed to the fact that Tab may reduce Au^{3+} in $HAuCl_4$ into Au^+, forming the $[Tab-Tab]^{2+}$ species. The resulting Au^+ may further react with excess Tab to afford this Au/Tab complex $[Au(Tab)_2](PF_6)$.

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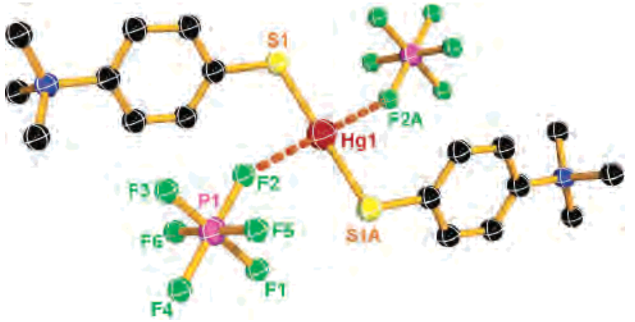

Figure 1. Perspective view of the structure of **1** with 50% thermal ellipsoids. All H atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Hg1−S1 2.331(3), S1−Hg1−S1A 180.00(14).

Crystal Structure of 1. Compound **1** crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit of **1** contains half of the $[Hg(Tab)_2]^{2+}$ dication and one PF_6^- anion. A perspective view of **1** is shown in Figure 1. In the $[Hg(Tab)_2]^{2+}$ dication, the Hg atom, lying at the crystallographic center of symmetry, is strongly coordinated by two S atoms of the two Tab moieties, forming a linear HgS_2 coordination geometry (type I) with two $C_6H_4NMe_3$ groups oriented at opposite directions. Such a structure closely resembles those of mercury complexes containing zwitterionic thiolate ligands such as $[Hg\{SCH(CH_2CH_2)_2NHMe_2\}_2](ClO_4)_2$,[11a] $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$,[11b] $[Hg\{S(CH_2)_2NH_3\}_2]Cl_2$,[11e] and its silver analogue $[Ag(Tab)_2](PF_6)$.[10b] The mean Hg1−S bond length and the S1−Hg1−S1A angle in **1** are 2.331(3) Å and 180.00(14)°, respectively, while the corresponding ones found in other two-coordinated mercury thiolate compounds are 2.330(1) Å and 176.96(2)° for $[Hg\{SCH(CH_2CH_2)_2NHMe_2\}_2](ClO_4)_2$, 2.340(1) Å and 178.9(3)° for $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$, 2.336(9) Å and 168.53(3)° for $[Hg\{S(CH_2)_2NH_3\}_2]Cl_2$, 2.339(2) Å and 180.0(5)° for $[Hg(SCH_2COOH)_2]$,[5f] and 2.34(3) Å and 174.7(1)° for $[Hg(SBz)_2]_n$ (Bz = benzyl), respectively.[5e]

The $[Hg(Tab)_2]^{2+}$ dications are parallel to each other, and the Hg···Hg separation between two neighboring cations is 6.165 Å. Interestingly, the PF_6^- anions are located between the two dications, and thus the two F atoms from two neighboring PF_6^- anions have weak interactions with the Hg1 atom [Hg1···F2) (or F2A) separation = 2.992(1) Å]. Furthermore, two H-bonding interactions between F2 and the methyl group with C8 ($x + 1$, $y - 1$, z) and between F4 and the methyl group with C8 ($-x + 1$, $-y + 1$, $-z + 1$) led to the formation of a two-dimensional network extended along the *ac* plane (see the Supporting Information).

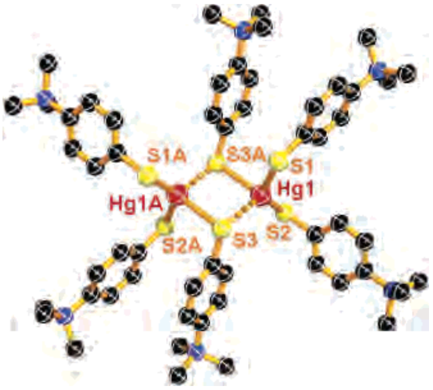

Figure 2. Perspective view of the $[Hg_2(Tab)_6]^{4+}$ tetracation of **2** with 50% thermal ellipsoids. All H atoms were omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2** and **10**

Complex 2			
Hg1−S1	2.4138(14)	Hg1−S2	2.4346(14)
Hg1−S3	2.7323(13)	Hg1−S3A	2.6467(13)
S1−Hg1−S2	133.93(5)	S1−Hg1−S3	96.69(4)
S2−Hg1−S3	104.26(5)	S1−Hg1−S3A	125.45(5)
S2−Hg1−S3A	93.37(4)	S3−Hg1−S3A	94.94(4)
Complex 10			
Hg1−S1	2.441(12)	Hg1−S2	2.421(13)
Hg1−S3	2.787(12)	Hg1−S3A	2.602(12)
S1−Hg1−S2	132.0(5)	S1−Hg1−S3	97.8(4)
S2−Hg1−S3	104.8(4)	S1−Hg1−S3A	104.7(4)
S2−Hg1−S3A	113.9(4)	S3−Hg1−S3A	96.5(3)

Crystal Structures of 2·2MeCN and 10. Compound **2** crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit of **2** consists of half of the $[Hg_2(Tab)_6]^{4+}$ tetracation, two PF_6^- anions, and one solvent MeCN molecule. Compound **10** crystallizes in the trigonal space group $R\bar{3}$, and the asymmetric unit contains half of the $[Hg_2(Tab)_6]^{4+}$ tetracation, one-sixth of the PF_6^- anion, one-third of Cl^-, two halves of Cl^-, and three one-sixths of Cl^-. Because the tetracations in **2** and **10** are structurally similar, only a perspective view of the tetracation of **2** is depicted in Figure 2 and their important bond lengths and angles are compared in Table 2. The structure of the $[Hg_2(Tab)_6]^{4+}$ tetracation of **2** or **10** is similar to those reported in $[Et_4N]_2[Hg_2(SMe)_6]$,[6b] $[Me_4N]_2[Hg_2(SPh)_6]$,[4a] and $[(DME)_3Ln(SC_6F_5)_2]_2[Hg_2(SC_6F_5)_6]$ (Ln = La, Ce, Pr, Nd, Sm, Gd).[16a] The tetracation of **2** or **10** consists of an asymmetrical Hg_2S_2 rhomb, with Hg1−μ-S3/Hg1−μ-S3A bond lengths being 2.7323(13)/2.6467(13) Å (**2**) and 2.787(12)/2.602(12) Å (**10**). An inversion center lies on the midpoint of the Hg1···Hg1A line in **2** or **10**. The Hg1···Hg1A contact is 3.637(2) Å (**2**) or 3.592(2) Å (**10**), which excludes any metal−metal interaction. Each Hg atom is coordinated by four S atoms from two terminal and two bridging Tab ligands, forming a strongly distorted tetrahedral coordination geometry (type V) with the S−Hg−S angles in the ranges of 93.37(4)−133.93(5)° (**2**) and 96.5(3)−132.0(5)° (**10**). The mean terminal and bridging Hg1−S bond lengths [2.4242(14) Å vs 2.6895(13) Å (**2**); 2.4310(13) Å vs 2.6945(12) Å (**10**)] are comparable to those containing tetrahedrally coordinated Hg^{II} such as $[Et_4N]_2[Hg_2(SMe)_6]$ [2.456(2) vs 2.668(2) Å] and $[Me_4N]_2[Hg_2(SPh)_6]$ [2.437(2) vs 2.686(2) Å].

The tetracations in the crystals of **2** or **10** are parallel to each other. The Hg···Hg separations between two cations are ca. 8.252 Å in **2** and ca. 8.826 Å in **10**. The associated $[PF_6]^-$ anions in **2** are surrounded by the paralleled tetracations. In **2**, three H-bonding interactions between S1 and the phenyl group with C6 ($-x + 2$, $-y + 1$, $-z$), between S1 and the phenyl group with C23 ($x - 1$, y, z), and between

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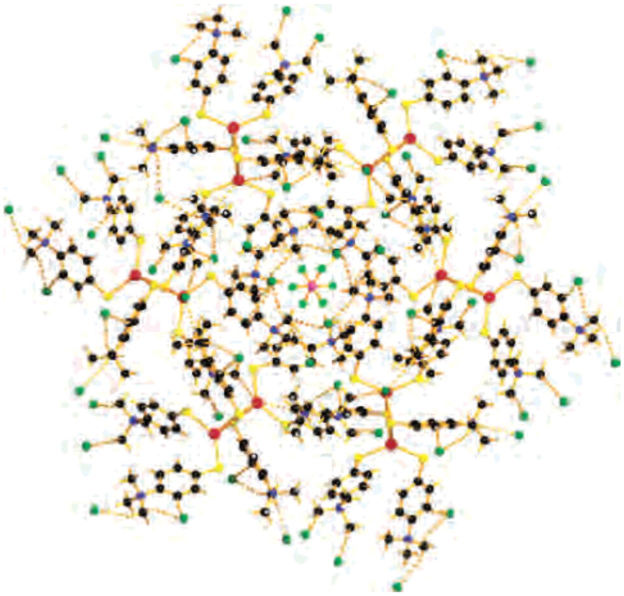

Figure 3. Stacking of **10** along the *c* axis, which highlights a $[PF_6]^-$ anion acting as an anionic template.

Figure 4. Perspective view of one of the six $[Hg(Tab)_2(SCN)]^+$ cations of **3** with 50% thermal ellipsoids. All H atoms were omitted for clarity.

the N4 from the MeCN molecule and the methyl group with C9 ($-x + 2$, $-y + 1$, $-z$) led to the formation of a one-dimensional chain extended along the *b* axis (see the Supporting Information). The S···H−C contacts are 2.66 and 2.82 Å, which are comparable to those reported in $[Fe(PM{-}BiA)_2(NCS)_2]$ [2.77−2.81 Å; PM = *N*-2′-pyridylmethylene and BiA = 4-(aminobiphenyl)].[16b] Looking down the *c* axis, it appears that $[PF_6]^-$ in **10** is acting as an anionic template, with six symmetry-related quaternary ammonium ions arranged around the ion forming a ball-like structure (Figure 3). Looking down the 3-fold axis, a stunning two-dimensional sheet is apparent. Chloride ions appear to be sandwiched between these sheets with complicated H-bonding interactions (see the Supporting Information).

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3**

Hg1−S1	2.340(7)	Hg4−S10	2.341(7)
Hg1−S2	2.336(7)	Hg4−S11	2.367(7)
Hg1−S3	2.801(8)	Hg4−S12	2.811(8)
Hg2−S4	2.318(8)	Hg5−S13	2.330(7)
Hg2−S5	2.352(7)	Hg5−S14	2.321(9)
Hg2−S6	2.797(8)	Hg5−S15	2.809(8)
Hg3−S7	2.368(6)	Hg6−S16	2.398(9)
Hg3−S8	2.352(7)	Hg6−S17	2.291(10)
Hg3−S9	2.823(8)	Hg6−S18	2.837(7)
S2−Hg1−S1	172.7(3)	S10−Hg4−S11	173.0(2)
S2−Hg1−S3	95.5(3)	S10−Hg4−S12	97.1(2)
S1−Hg1−S3	91.8(2)	S11−Hg4−S12	89.6(2)
S4−Hg2−S5	171.7(3)	S14−Hg5−S13	173.9(3)
S4−Hg2−S6	97.0(3)	S14−Hg5−S15	83.9(3)
S5−Hg2−S6	90.5(2)	S13−Hg5−S15	101.1(2)
S8−Hg3−S7	173.8(2)	S17−Hg6−S16	173.8(3)
S8−Hg3−S9	98.6(2)	S17−Hg6−S18	104.5(3)
S7−Hg3−S9	87.5(2)	S16−Hg6−S18	81.4(2)

Crystal Structures of 3−5. Compound **3** crystallizes in the monoclinic space group $P2_1$, and the asymmetric unit comprises six crystallographically independent $[Hg(Tab)_2(SCN)]^+$ cations and six PF_6^- anions. Because the six cations are structurally very similar, a perspective view of only one of them is shown in Figure 4 and the pertinent bond lengths and angles of the six cations are compared in Table 3. Each Hg atom in these $[Hg(Tab)_2(SCN)]^+$ cations is coordinated weakly by one S atom from SCN^- and strongly by two S atoms from two Tab ligands, forming an uncommon T-shaped coordination geometry (type II) with the (Tab)S−Hg−S(Tab) angle in the range of 171.7(3)−173.9(3)°. Such a T-shaped structure was observed in $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}HgPh][BPh_4]$.[17] Apparently, the Hg−S(Tab) bond lengths are significantly shorter than those of the Hg−S(SCN) bonds. The mean Hg−S(Tab) bond length [2.342(1) Å] is close to that of **1** [2.331(3) Å]. The average Hg−S(SCN) bond length [2.813(3) Å] is 0.242 Å longer than the average terminal Hg−S(SCN) bond length in $\{[La(SCN)[(NMe_2)_3PO]_5](\mu\text{-}SCN)[Hg(SCN)_2Cl]\}$ [2.571(2) Å].[18] Interestingly, each cation in **3** is further interconnected in an up-and-down way via long Hg···S secondary coordination (3.6148−3.9237 Å), forming a one-dimensional zigzag chain extended along the *c* axis (Figure 5). There are no evident H-bonding interactions between the cations and associated PF_6^- anions.

Compound **4** crystallizes in the orthorhombic space group *Pccn*, and the asymmetric unit contains half of the $[Hg(Tab)_2(SCN)_2]$ molecule. A perspective view of **4** is shown in Figure 6, while its important bond lengths and angles are given in Table 4. The central Hg1 atom, lying at a crystallographic inversion center, is strongly coordinated by two S atoms of the two Tab ligands and loosely coordinated by two S atoms of the two SCN^- anions, forming a unique seesaw-shaped coordination geometry (type IV).[19] The mean Hg−S(Tab) bond length is 2.3715(11) Å, which is somewhat longer than those observed in **1** and **3** but shorter than those containing four-coordinated Hg complexes such as two polymorphic compounds $[Hg(SPy)_2(SCN)_2]$ [2.4790(1) and 2.480(1) Å; SPy = pyridinium-2-thiolato].[20] The mean Hg−S(SCN) bond length is 2.9281(12) Å, which is longer than those of **3** [2.813(3) Å] and $Hg(SPy)_2(SCN)_2$ [2.635(1) and

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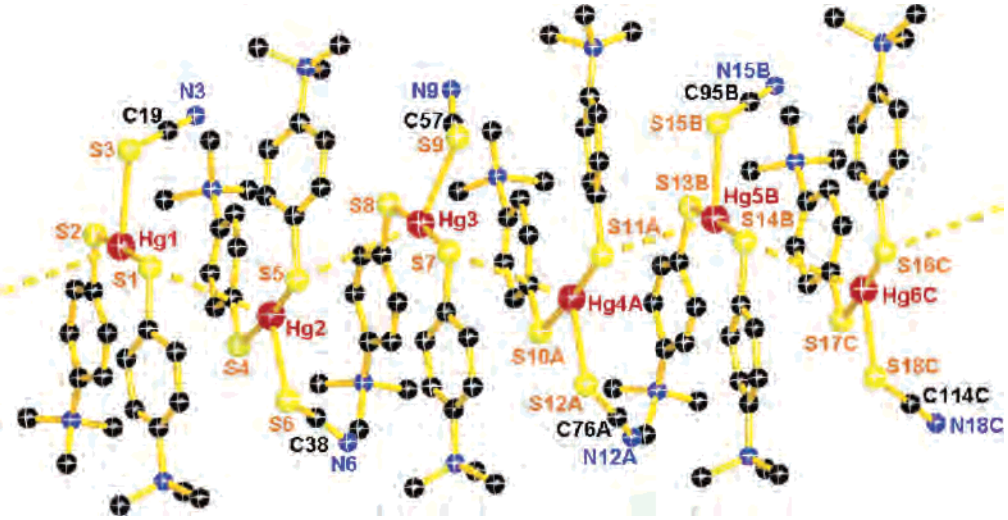

Figure 5. One-dimensional zigzag chain (extended along the *c* axis) formed via weak Hg···S secondary interactions in **3**.

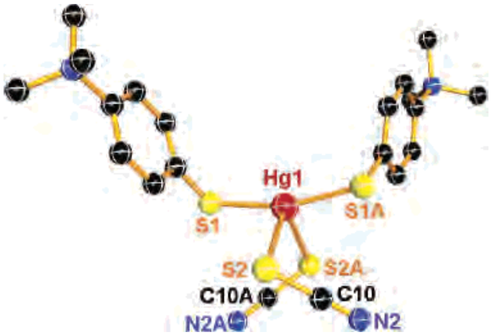

Figure 6. Molecular structure of **4** with 50% thermal ellipsoids. All H atoms were omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **4** and **5**

	Complex **4**		
Hg1−S1	2.3715(11)	Hg1−S2	2.9281(12)
S1−Hg1−S2	90.31(4)	S1−Hg1−S1A	163.64(6)
S1−Hg1−S2A	99.32(4)	S2−Hg1−S2A	107.94(5)
	Complex **5**		
Hg1−S1	2.432(2)	Hg1−I1	2.7718(7)
Hg1−I2	2.7316(7)		
S1−Hg1−I1	115.46(5)	S1−Hg1−I2	130.67(5)
I2−Hg1−I1	113.23(2)		

2.596(1) Å]. The S(Tab)−Hg−S(Tab) angle of 163.64(6)° is smaller than those of **1** (180.00°) and **3** [173.15(2)°] but significantly larger than the S(SPy)−Hg−S(SPy) angle in the two polymorphic compounds Hg(SPy)$_2$(SCN)$_2$ [116.74(5) and 122.03(4)°]. The S(SCN)−Hg−S(SCN) angle is 107.94(5)°, which is close to that observed in [Hg(SPy)$_2$(SCN)$_2$] [100.27(2)°] and much smaller than that in [Hg(tu)$_2$(SCN)$_2$] [171.61(2)°; tu = thiourea].[19b]

In the crystal of **4**, the S2 atom from the SCN$^-$ ion interacts with the methyl group with C8 [$x - 1, -y + {}^3/_2, z - {}^1/_2$] to afford intermolecular H bonds, thereby forming a two-dimensional H-bonded network structure along the *ac* plane (Figure 7).

Compound **5** crystallizes in the monoclinic space group *Cc*, and the asymmetric unit of **5** contains one discrete [Hg(Tab)I$_2$] molecule. A perspective view of **5** is shown in Figure 8, and the selected bond lengths and angles are listed in Table 4. The Hg1 atom in **5** is coordinated by one S from a Tab ligand and two I atoms, forming a typical trigonal-planar geometry (type III). The Hg1−S1 bond length of 2.432(2) Å is comparable to the theoretically calculated value

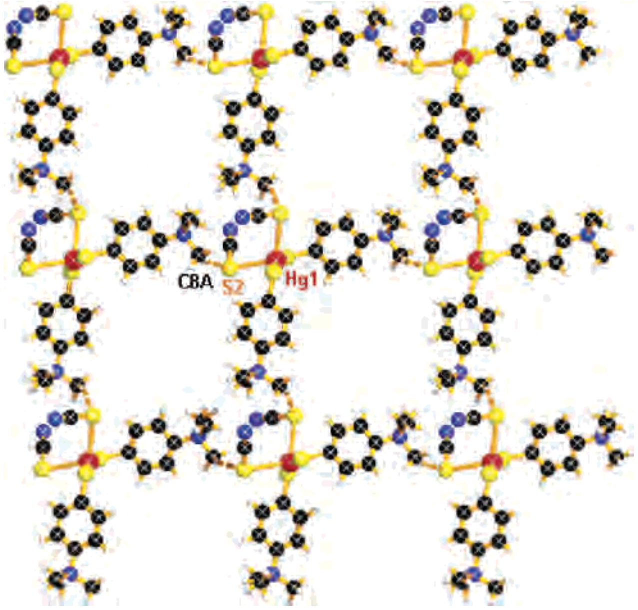

Figure 7. Two-dimensional network along the *ac* plane formed via H-bonding interactions in **4**.

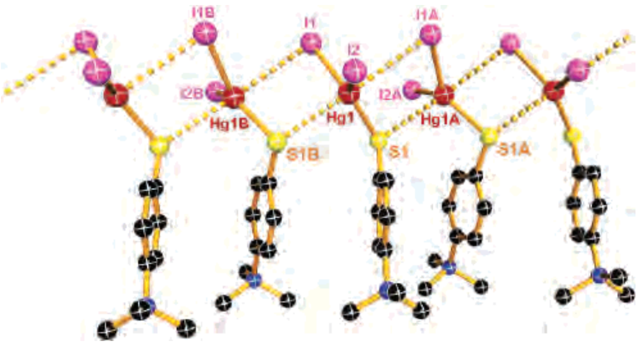

Figure 8. One-dimensional chain (extended along the *c* axis) formed via Hg···S and Hg···I secondary interactions in **5**.

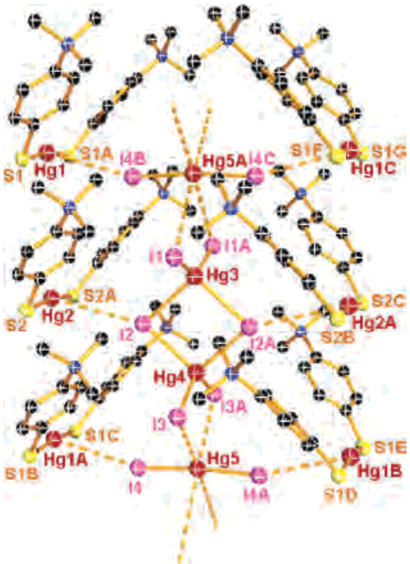

Figure 9. One-dimensional scolopendra-like structure (extended along the *c* axis) formed by Hg$\cdots$I secondary interactions among $[Hg(Tab)_2]^{2+}$, $[Hg_2I_6]^{2-}$, and HgI_2 in **6**.

for the sum of the covalent radii of trigonal Hg and S atoms [2.43(1) Å][21] but longer than those in **1**, **3**, and **4**. The mean Hg−I bond length is 2.7517(7) Å, which is longer than the average Hg−I bond length in $[Hg(C_4H_8N_2S)I_2]$ [2.6958(2) Å; $C_4H_8N_2S$ = 3,4,5,6-tetrahydropyrimidinium-2-thiolato-*S′*].[21] It should be noted that the $[Hg(Tab)I_2]$ molecules in the crystal of **5** are held together by long secondary Hg1$\cdots$S1B [3.126(2) Å] and Hg1$\cdots$I1A [3.617(3) Å] interactions to give a one-dimensional chain structure extended along the *c* axis. Furthermore, two H-bonding interactions between I2 and the methyl group with C8 ($x - 1, y, z$) and C8 ($x - {}^1/_2, -y + {}^3/_2, z + {}^1/_2$) between chains lead to the formation of a two-dimensional H-bonded network extended along the *ac* plane (see the Supporting Information).

Crystal Structures of 6−8. An X-ray analysis revealed that **6** crystallizes in the orthorhombic space group *Pmmn*, and the asymmetric unit is composed of two halves of the $[Hg(Tab)_2]^{2+}$ dications, one-quarter of the HgI_2 molecule, one-quarter of the $[Hg_2I_6]^{2-}$ dianion, two one-quarters of the PF_6^- anions, and two halves of the NO_3^- anions. A perspective views of the $[Hg(Tab)_2]^{2+}$ dications and the $[Hg_2I_6]^{2-}$ dianions coupled with the neutral HgI_2 molecule in **6** is depicted in Figure 9. Selected bond lengths and angles for **6** are listed in Table 5. As shown in Figure 9, all Hg atoms in **6** are lying on the same crystallographic *bc* plane. In the structure of each of the dications of **6**, Hg1 or Hg2 is coordinated by the terminal Tab ligands, forming a slightly bent linear HgS_2 coordination geometry (type I) with S1−Hg1−S1A angles of 171.2(3)° or S2−Hg2−S2A angles of 170.3(3)°. The deviation of the S−Hg−S angles to 180° may be due to the weak secondary interactions between Hg1 and I4B from the HgI_2 molecule and between Hg2 and I2 from the $[Hg_2I_6]^{2-}$ dianion. The two Hg−S bond lengths for Hg1 or Hg2 are comparable to those of **1**. These dications are parallel to each other, and the Hg$\cdots$Hg separation between two cations is ca. 5.893 Å. Interestingly, compound **6** contains a slightly bent HgI_2 [I4−Hg5−I4A = 174.62(17)°] molecule. Such a deviation of the I−Hg−I angle to 180° may also be ascribed to the weak interactions between its I atoms and the neighboring Hg atoms of the dications. The terminal Hg−I bond length in the HgI_2 molecule is 2.557(2) Å, which is comparable to that observed in HgI_2 vapor [2.554 (3) Å][22] but shorter than those found in $[N(C_2H_5)_4]_2[Hg_2I_6]\cdot HgI_2$ [2.574(1) Å][23] and in the 1:1 complex between 18-crown-6 and HgI_2 [2.622(1) Å].[24] The structure of the dimeric $[Hg_2I_6]^{2-}$ anion in **6** is an edge-shared bitetrahedron and very similar to those found previously.[23,25] The bridging I atoms are not equidistant from the bonded Hg atoms [2.923(3) Å and 2.970(3) Å], which is different from that observed in $[N(C_2H_5)_4]_2[Hg_2I_6]\cdot HgI_2$ [2.934(3) Å]. The four Hg−I terminal distances [average 2.700(3) Å] are comparable to those in $[N(C_2H_5)_4]_2[Hg_2I_6]\cdot HgI_2$ [2.6895(2) Å]. The Hg−

Table 5. Selected Bond Distances (Å) and Angles (deg) for **6−8**

Complex **6**			
Hg1−S1	2.334(6)	Hg2−S2	2.322(6)
Hg3−I1	2.733(3)	Hg3−I2	2.923(3)
Hg4−I3	2.667(3)	Hg4−I2	2.970(3)
Hg5−I4	2.557(2)		
S1A−Hg1−S1	171.2(3)	S2A−Hg2−S2	170.3(3)
I1A−Hg3−I1	122.09(14)	I1A−Hg3−I2A	108.28(4)
I1−Hg3−I2A	108.28(4)	I1A−Hg3−I2	108.28(4)
I1−Hg3−I2	108.28(4)	I2A−Hg3−I2	99.22(12)
I3A−Hg4−I3	136.20(17)	I3A−Hg4−I2	104.29(5)
I3−Hg4−I2	104.29(5)	I3A−Hg4−I2A	104.29(5)
I3−Hg4−I2A	104.29(5)	I2−Hg4−I2A	97.14(12)
I4−Hg5−I4A	174.62(17)	Hg3−I2−Hg4	81.82(8)
Complex **7**			
Hg1−S1	2.383(7)	Hg1−I2	3.223(3)
Hg2−I1	2.762(3)	Hg2−I3	2.7622(19)
Hg2−I2	2.894(3)		
S1−Hg1−S1A	167.4(5)	S1−Hg1−I2	94.27(18)
S1A−Hg1−I2	94.27(17)	I1−Hg2−I3	111.34(6)
I1−Hg2−I3A	111.34(6)	I3−Hg2−I3A	116.65(9)
I1−Hg2−I2	110.46(9)	I3−Hg2−I2	103.15(6)
I3A−Hg2−I2	103.15(6)	Hg2−I2−Hg1	138.54(10)
Complex **8**			
Hg1−S1	2.3219(14)	Hg1−N2	2.970(5)
Hg2−Cl1	2.5312(17)	Hg2−Cl2	2.4603(17)
Hg2−S2	2.5144(13)		
S1−Hg1−S1A	180.000(1)	S1−Hg1−N2	106.80(10)
S1A−Hg1−N2	73.20(10)	Cl2−Hg2−S2	113.56(4)
S2−Hg2−S2A	108.95(6)	Cl2−Hg2−Cl1	104.43(6)
S2−Hg2−Cl1	107.99(5)		

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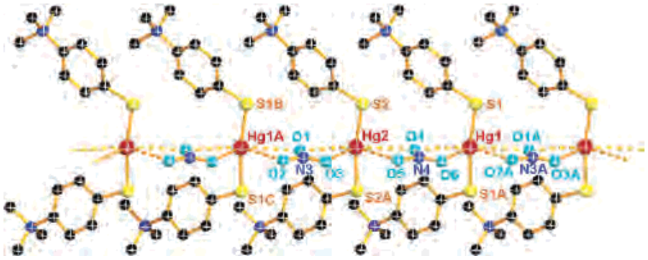

Figure 10. One-dimensional wavelike chain (extended along the *c* axis) formed by Hg···O secondary interactions between $[Hg(Tab)_2]^{2+}$ and NO_3^- in **6**.

μ-I−Hg angle is 81.82(8)°, which is comparable to that in $[N(C_2H_5)_4]_2[Hg_2I_6]\cdot HgI_2$ [83.81(4)°].

The secondary and H-bonding interactions in **6** are rather complicated. The $[Hg_2I_6]^{2-}$ dianions and the bent HgI_2 molecules are interconnected via weak I1···Hg5A [3.5284(5) Å] and Hg5···I3 [3.9567(5) Å] interactions, forming a one-dimensional $\{[Hg_2I_6\cdot HgI_2]^{2-}\}_n$ chain structure extended along the *c* axis. Along the $\{[Hg_2I_6\cdot HgI_2]^{2-}\}_n$ chain backbone, the HgI_2 molecules and the $[Hg_2I_6]^{2-}$ anions alternatively coordinate to the Hg atoms of the $[Hg(Tab)_2]^{2+}$ dications via Hg1···I4B [3.8210(6) Å] and Hg2···I2 [4.0858(7) Å] interactions. These weak interactions make it a one-dimensional scolopendra-like structure extended along the *c* axis (Figure 9). Furthermore, each NO_3^- anion is arranged between the two dications and acts as a rare tridentate ligand to Hg1 and Hg2 atoms with relatively long Hg···O contacts, forming a one-dimensional wavelike chain structure extended along the *c* axis (Figure 10).[26] The mean Hg···O separation is 2.987(5) Å, which are somewhat shorter than the sum of the van der Waals radii of Hg (1.73 Å) and O (1.4 Å).[27]

In the crystal of **6**, the S atoms of the Tab ligands interact with the H atoms of the phenyl groups of Tab to afford intermolecular H bonds [C15···S1 ($-x$, $-y + 1$, $-z$); C6···S2 ($-x$, $-y + 1$, $-z$)]. In addition, the two F atoms of PF_6^- interact with the H atoms of the methyl groups of Tab [C9···F6 ($x - 1$, y, z)] to give a one-dimensional double-chain structure extended along the *a* axis (Figure 11). The I atoms in the above $\{[Hg_2I_6\cdot HgI_2]^{2-}\}_n$ chain further bind to the Hg atoms of the $[Hg(Tab)_2]^{2+}$ dication in the double chain via Hg1···I4B and Hg2···I2 interactions, thereby forming a three-dimensional network (see the Supporting Information).

Compound **7** crystallizes in the orthorhombic space group $Pmn2_1$, and the asymmetric unit contains half of the $[Hg(Tab)_2]^{2+}$ dication and half of the $[HgI_4]^{2-}$ dianion. The structures of both dications and dianions of **7** are depicted in Figure 12, and the selected bond lengths and angles are listed in Table 5. The Hg1, Hg2, I1, and I2 atoms lie on the same crystallographic plane. Being similar to that in the dications of **6**, the Hg1 atom in the dication of **7** also adopts a bent linear HgS_2 coordination geometry with the S1−Hg1−S1A angle of 167.4(5)°. The Hg1−S bond lengths are normal relative to those in **1** and **6**. In the anion of $[HgI_4]^{2-}$, the Hg2−I bond lengths vary from 2.762(3) to 2.894(3) Å and the I−Hg2−I angles range from 103.15(6) to 116.65(6)°. Thus, the Hg2 atom adopts a distorted tetrahedral coordination geometry. The $[Hg(Tab)_2]^{2+}$ dications and $[HgI_4]^{2-}$ dianions are linked together by the secondary interactions between Hg1 and I2 [3.223(2) Å] and between Hg1 and I1A [3.7294(6) Å], forming a one-dimensional chain structure extended along the *c* axis.

Compound **8** crystallizes in the monoclinic space group $P2_1/m$, and the asymmetric unit consists of half of the $[Hg(Tab)_2]^{2+}$ dication and half of the $[Hg(SCN)_2Cl_2]^{2-}$ dianion. The structures of both dications and dianions of **8** are shown in Figure 13, and the selected bond lengths and angles are listed in Table 5. The Hg1 atom lies at an inversion center, while the Hg2, Cl1, and Cl2 atoms are located on the same crystallographic plane. The structure of the dication of **8** retains almost the same structure of **1**, judging from their Hg−S bond lengths and S−Hg−S angles. In the structure of the $[Hg(SCN)_2Cl_2]^{2-}$ dianion, the Hg2 atom also adopts a slightly distorted HgS_2Cl_2 tetrahedral geometry. The Hg−S(SCN) bond length [2.5144(13) Å] is significantly shorter than the corresponding ones in **3** [2.813(3) Å] and **4** [2.9281(12) Å] but comparable to that in $\{[C_{10}H_8S_8][C_{10}H_8S_8][HgCl_2(SCN)]\}_n$[28] {2.515(2) Å; $C_{10}H_8S_8$ = bis[bis(ethylenedithio)tetrathiafulvalene]}. The mean Hg−Cl bond length of 2.496(17) Å is slightly longer than that in $\{[C_{10}H_8S_8][C_{10}H_8S_8][HgCl_2(SCN)]\}_n$ [2.414(17) Å]. In addition, the secondary interactions between Hg1 in the dication and N2 (or N2B) of the SCN^- group in the dianions result in a one-dimensional zigzag chain extended along the *b* axis. The Hg···N bond length is 2.970(1) Å, is shorter than the sum of the van der Waals radii of N (1.55 Å)[29] and Hg (1.73 Å),[30] but is longer than that in $\{[C_{10}H_8S_8][C_{10}H_8S_8][HgCl_2(SCN)]\}_n$ [2.773(2) Å] and comparable to that in $\{[C_{10}D_8S_8]_2[C_{10}H_8D_8]_2[Hg_2Cl_2(SCN)_4]\}_n$ {3.035(2) Å; $C_{10}H_8D_8$ = tetrakis[octadeuteriobis(ethylenedithio)tetrathiafulvalene]}.[31]

Crystal Structure of 9. Compound **9** crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit contains a discrete Tab−Tab dication and half of the $[Hg_3Cl_{10}]^{4-}$ tetraanion. A perspective view of **9** is shown in Figure 14, and the selected bond lengths and angles are listed in Table 6. In this tetraanion, there is a crystallographic inversion center lying at Hg2. The linear structure of the $[Hg_3Cl_{10}]^{4-}$ tetraanion contains two Hg_2Cl_2 rhombs that are almost located on the same plane. The two terminal Hg1 and Hg3 atoms are coordinated by two terminal and two bridging Cl atoms, forming a tetrahedral geometry, while the central Hg2 atom is octahedrally coordinated by two terminal and four bridging Cl atoms. The terminal Hg−Cl bond lengths vary from 2.3046(16) to 2.5393(15) Å, while

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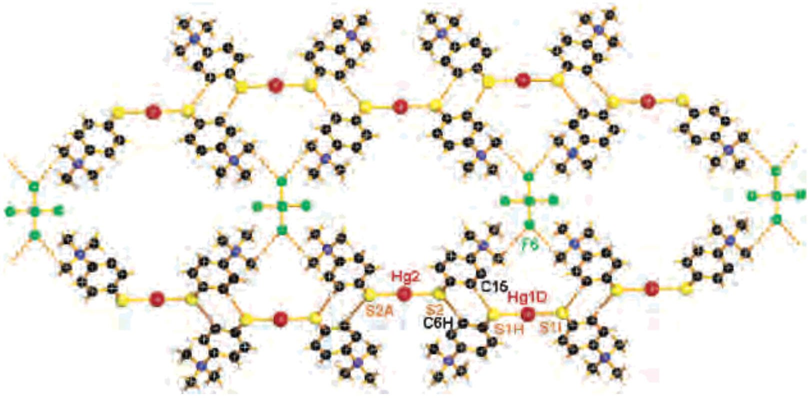

Figure 11. One-dimensional double-chain (extended along the *a* axis) formed via H-bonding interactions in **6**.

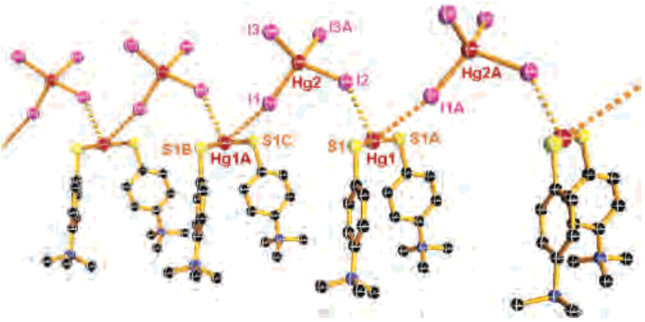

Figure 12. One-dimensional zigzag chain (extended along the *c* axis) formed by Hg···I secondary interactions in **7**.

the bridging Hg−Cl bond lengths range from 3.163(2) to 3.169(1) Å. These values are smaller than the sum of the van der Waals radii of Hg^{2+} and Cl^- (3.300 Å).[32] The mean Hg···Hg contact [3.750(1) Å] is comparable to those of $[Hg_6Cl_8(SCH_2CH_2NH_3)_8]Cl_4{\cdot}4H_2O$ [3.776(1) and 3.797(1) Å] and $[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}Br_{0.2})_3$ [3.605(2) and 3.750(1) Å].[1m]

On the other hand, the Tab−Tab dication has positive charges located on the NMe_3 groups. The S1−S2 bond length and the C1−S1−S2−C10 torsion angle of **9** are 2.034(3) Å and 81.5(3)°, respectively, which are similar to those in $[C_8H_{22}N_2S_2]Cl_2$ {2.075(5) Å and 82.39(2)°; $C_8H_{22}N_2S_2$ = bis[2-(*N*,*N*-dimethylamino)ethyl]disulfide dihydrochloride}[33] and $\{[C_{10}H_{10}N_2S_2][Cu_2Cl_6][BF_4]_2\}_n$ [2.034(3) Å and 81.5(3)°; $C_{10}H_{10}N_2S_2$ = bis(4-pyridinium)disulfide].[34] In the crystal of **9**, the H-bonding interactions are also abundant. The Cl atoms of the cluster anions interact with the H atoms of the methyl group or phenyl groups of the Tab−Tab to afford complicated intermolecular H bonds, forming a three-dimensional H-bonded structure (see the Supporting Information).

Spectral Aspects of 1−10. Solids **1−10** are relatively stable toward oxygen and moisture. Compounds **1−10** are soluble in DMSO and DMF. The elemental analyses of **1−10** were consistent with their chemical formulas. The characteristic P−F stretching vibrations of PF_6^- at ca. 830 and ca. 555 cm^{-1} were observed in the IR spectra of **1−3**, **6**, and **10**.[10] The peak at 1350 cm^{-1} in **6** indicated the presence of the NO_3^- anion.[35] The peaks at 2079 and 2080 cm^{-1} in **3** and **4** indicated the vibrations of the terminal SCN^-, while the peak at 2114 cm^{-1} in **8** was assigned to be the stretching vibration of the bridging SCN^-.[36] The peak at 481 cm^{-1} in **9** was assigned to be the S−S stretching vibration.[34] The ^1H NMR spectra of **1−10** in DMSO-d_6 at room temperature showed a multiplet for protons of Ph groups at 7.42−7.81 ppm and a singlet related to protons of NMe_3 at ca. 3.34 ppm.

As shown in Figure 15, the UV−vis spectra of **1** and **3−8** in DMF exhibited a strong and broad absorption ranging from 272 to 277 nm and a long absorption tail to ca. 400 nm. On the other hand, the spectra of **2** and **10** showed a broad peak at 287 nm for **2** or 284 nm for **10** and a shoulder peak at 312 nm for **2** or 314 nm for **10**. Because the absorption spectrum of the free Tab in DMF had a broad absorption band at 320 nm, the peaks observed in the spectra of **1−8** and **10** were blue-shifted and may be due to the ligand(Tab)-to-metal charge transfer (LMCT).[1m,37a] As discussed earlier in this paper, the structures of **2−4**, **6−8**, and **10** roughly keep the $[Hg(Tab)_2]^{2+}$ species of **1**, although the related Hg atoms possess somewhat different coordination geometries when they bind to other donor atoms. Therefore, those peaks

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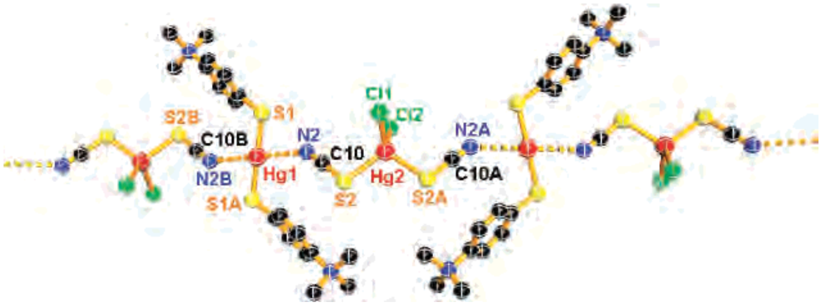

Figure 13. One-dimensional zigzag chain (extended along the *b* axis) formed by Hg···N secondary interactions in **8**.

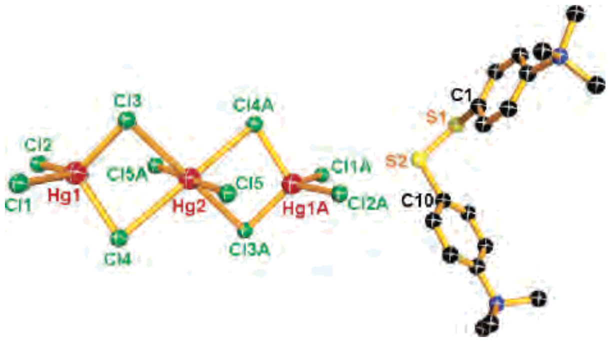

Figure 14. Perspective view of **9** with 50% thermal ellipsoids. All H atoms were omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for **9**

Hg1−Cl1	2.372(2)	Hg1−Cl3	2.4891(15)
Hg1−Cl2	2.5335(15)	Hg1−Cl4	2.5393(15)
Hg2−Cl5	2.3046(16)	S1−S2	2.034(3)
Cl1−Hg1−Cl3	123.23(9)	Cl1−Hg1−Cl2	109.01(8)
Cl3−Hg1−Cl2	101.95(5)	Cl1−Hg1−Cl4	115.70(7)
Cl3−Hg1−Cl4	102.81(5)	Cl2−Hg1−Cl4	101.29(5)
Cl5−Hg2−Cl5A	180.0		

Table 7. Principal Electronic Transitions in **1**−**10**, Tab and [Tab−Tab](PF_6)$_2$ and Other Mercury(II) Thiolate Compounds

Hg compounds	λ_{max}, nm	ref
$[Hg_6Cl_8(SCH_2CH_2NH_3)_8]]Cl_4 \cdot 4H_2O$	273	1m
$[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}Br_{0.2})_3$	268, 339 (sh)[b]	1m
[Hg(l-Cys)$_4$ peptide][a]	280	37a
$[Hg(SEt)_2]$	228, 282 (sh)	37b
$[Hg(Pr^i)_2]$	228, 262 (sh)	37b
$[Et_4N][Hg(SBu^t)_3]$	235, 260 (sh)	37b
Hg-MerR[c]	240, 260 (sh), 290 (sh)	37b
Hg-plastocynanin	247, 280 (sh)	37c
neurospora Hg$_3$-MT[d]	283	38a
Hg$_7$-MT	304	38b, 38c
1	272[e]	this work
2	287,[f] 312 (sh)	this work
3	275[g]	this work
4	271[h]	this work
5	273[i]	this work
6	273[j]	this work
7	274[k]	this work
8	277[l]	this work
9	273[m]	this work
10	284,[n] 314(sh)	this work
Tab	320,[o] 267 (sh)	this work
[Tab−Tab][PF_6]$_2$	271[p]	this work

[a] l-Cys = L-cysteine. [b] sh = shoulder. [c] MerR = metalloregulatory protein. [d] MT = metallothionein. [e] 1.25 × 10^{-4} M in DMF. [f] 2.58 × 10^{-4} M in DMF. [g] 1.22 × 10^{-4} M in DMF. [h] 1.22 × 10^{-4} M in DMF. [i] 7.72 × 10^{-5} M in DMF. [j] 2.68 × 10^{-5} M in DMF. [k] 1.44 × 10^{-4} M in DMF. [l] 5.86 × 10^{-5} M in DMF. [m] 9.68 × 10^{-5} M in DMF. [n] 2.54 × 10^{-5} M in DMF. [o] 1.25 × 10^{-4} M in DMF. [p] 1.52 × 10^{-4} M in DMF.

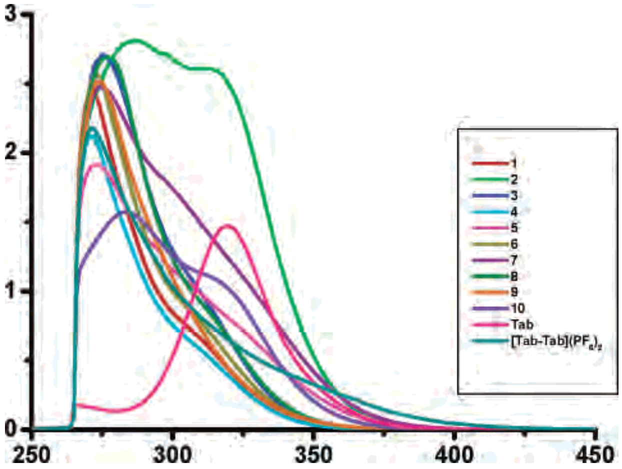

Figure 15. Absorption spectra of **1**−**10**, Tab, and [Tab−Tab](PF_6)$_2$ in DMF with a 1-mm optical length.

observed in the spectra of **2**−**4**, **6**−**8**, and **10** were red-shifted relative to the peak of **1**, which may be ascribed to the different coordination environments about the Hg atoms in these compounds. In addition, because the absorption spectrum of [Tab−Tab](PF_6)$_2$[12] in DMF had a broad absorption band at 271 nm, the peak at 273 nm observed in the spectrum of **9** in DMF probably originated from intraligand transitions (Table 7).

Conclusion

In the work reported here, we have demonstrated a facile route to a series of new mercury(II) zwitterionic thiolate complexes (**2**−**10**) from a performed complex **1**. Through coordination of Tab ligands or other donor ligands such as halides and pseudohalides, the Hg atom in the $[Hg(Tab)_2]^{2+}$ dication of **1** may turn its linear coordination sphere (type I) into T-shaped (type II), trigonal-planar (type III), seesaw-shaped (type IV), and tetrahedral (type V) coordination geometry. Meanwhile, compound **1** may further combine other Hg atoms to form polynuclear complexes (e.g., **6**−**8**) via the bridging ability of the S atoms of the two Tab ligands or through the Hg−X (X = I^-, SCN^-) contacts. The Hg^{II} electron deficiency in mercury dithiolate complexes may be readily remediated by binding to another donor ligand, which may be attributed to the formation of mercury dithiolate complexes **1**−**10**. These results in this paper may provide insight into the varieties of coordination spheres of the Hg sites in metallothioneins. Furthermore, it is expected that **1** may also be a good precursor for the generation of electronic, magnetic, and optical materials of heterobimetallic compounds such as lanthanide/mercury compounds.[16] Research is continuing in these areas.

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Supporting Information Available: Crystallographic data of compounds **1**−**10** (CIF) and cell packing diagrams highlighting Hg−X (X = F, I, O, S, etc.) secondary and H-bonding interactions (in PDF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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