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Relation between Intramolecular NH···S Hydrogen Bonds and Coordination Number in Mercury(II) Complexes with Carbamoylbenzenethiol Derivatives

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A novel series of bis(carbamoylthiophenolato)mercury(II) complexes, $[Hg(S\text{-}RNHCOC_6H_4)_2]$ (**1**, R = 2-*t*-Bu; **2**, R = 2-CH_3; **3**, R = 2-$C_6H_5CH_2$; **4**, R = 4-*t*-Bu), and a tetrakis(carbamoylthiophenolato)mercury(II) complex, $(NEt_4)_2[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_4]$ (**5**), were synthesized and characterized by ^1H NMR, IR, ^{199}Hg NMR, and crystallographic analyses. The bis(carbamoylthiophenolato)mercury complexes **1**–**3** do not have intramolecular NH···S hydrogen bonds between the amide NH group and the sulfur atom coordinated to mercury, whereas the tetrakis(thiophenolato)mercury complex **5** does have an intramolecular NH···S hydrogen bond. A relatively weak NH···S hydrogen bond in **5** can be seen in the ^1H NMR spectra and the IR spectra in chloroform and in the solid state. The ^{199}Hg NMR spectra in bis(carbamoylthiophenolato)mercury complexes **1**–**4** show a downfield shift, with an increase in the flow of electrons to mercury(II) from the oxygen atom due to the intramolecular Hg···O bonding interaction. Conversely, the ^{199}Hg NMR spectra in **5** show a high-field shift with a decrease in the flow of electrons to mercury(II) from the sulfur atom due to the intramolecular NH···S hydrogen bond.

Introduction

The mercuric(II) ion has a high affinity for the sulfur atom of thiolate, which is a soft donor having large polarizability. Most mononuclear mercury thiolate complexes have a low coordination number and exist as neutral linear dicoordinated complexes ($Hg(SR)_2$); there are several other types of coordination environments in mononuclear anionic complexes, such as $[Hg(SR)_3]^-$ [1,2] and $[Hg(SR)_4]^{2-}$.[3,4] A previous study of mercury thiolate complexes suggests that dicoordinate complexes form easily in dilute solutions, whereas tetracoordinate complexes, with tetrahedral structure, form with difficulty except in concentrated solutions containing excess thiolate ligand.[5] It has been suggested that MerR has a trigonal tricoordinate structure in the chemistry of the Hg(II) ion in vivo.[6−8] Researchers have consequently begun investigating the stabilizing factor of the tri- and tetracoodinate state in vivo. Gruff et al. have synthesized and determined the crystal structure of the di- and tricoordinate complex with the $[S\text{-}2,4,6\text{-}((CH_3)_2CH)_3C_6H_2]^-$ ligand and reported that the Hg−S bond length increases with increasing coordination number.[1] Yamamura et al. showed that the change from dicoordination ($Hg(SR)_2$) to tricoordination ($[Hg(SR)_3]^-$) by the addition of the thiolate anion takes place with a change of the peptide conformation in the Hg(Cys-X-Y-Cys) complex (Scheme 1).[9]

We have previously reported that the NH···S hydrogen bond contributes to the positive shift in the redox potential

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10.1021/ic0481780 CCC: $30.25

Scheme 1

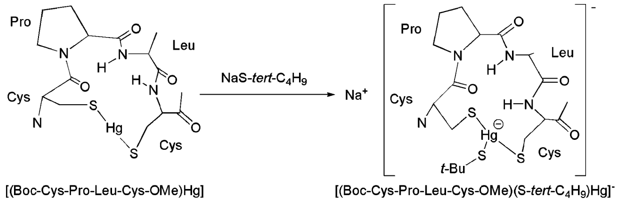
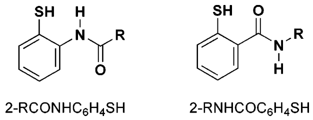
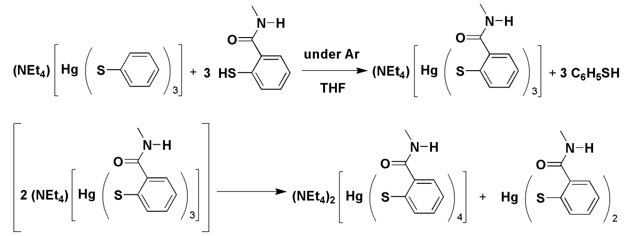


Chart 1



Scheme 2



and to the remarkable shortening or elongation of the metal−sulfur bond distance in some transition metal complexes.[10−17] The 2-(acylamino)benzenethiolate complex of mercury(II), [Hg(S-2-$RCONHC_6H_4)_2$], has a five-membered ring structure based on a weak intramolecular NH···S hydrogen bond, according to X-ray analysis.[18] However, 2,6-(acylamino)-benzenethiolate, with the amide group in both *o*-positions of the sulfur atom complex of mercury(II), [Hg(S-2,6-$RCONHC_6H_3)_2$], has a structure that forms not only three intramolecular NH···S hydrogen bonds but also one Hg···O═C interaction. This suggests that the carbonyl oxygen coordinates to the mercuric ion, in view of the weak NH···S hydrogen bond. In fact, it is not clear whether the mercury(II) complex prefers the NH···S hydrogen bond. The previous works suggest that the formation of the NH···S hydrogen bond decreases the electron density on the S atom which coordinates to the metal.[10−17] Consequently, it is expected that the NH···S hydrogen bond stabilizes the extra negative charge on metal center in the anionic Hg complex with a high coordination number.

This paper finds and studies a relation between the intramolecular NH···S hydrogen bond and the coordination number in the bis(carbamoylthiophenolato)mercury(II) complexes [Hg(S-$RNHCOC_6H_4)_2$] (**1**, R = 2-*t*-Bu; **2**, R = 2-CH_3; **3**, R = 2-$C_6H_5CH_2$; **4**, R = 4-*t*-Bu) and the tetrakis(carbamoylthiophenolato)mercury(II) complex $(NEt_4)_2$[Hg(S-2-$CH_3NHCOC_6H_4)_4$] (**5**) (Chart 1). The 2-substituted thiophenol ligand, 2-$RNHCOC_6H_4SH$, has been found to have distinct conformations in the thiol form and the thiolate anion form. The thiol form has a structure with an intramolecular SH···O═C hydrogen bond, but the thiolate anion form has an intramolecular NH···S hydrogen bond due to the rotation of the amide plane.[19] Also, the platinum complex with this ligand, [Pt(bpy)(S-2-$CH_3NHCOC_6H_4)_2$], has a structure with a weak intramolecular NH···S hydrogen bond.[20] We have investigated the intra- and intermolecular interaction and the orientation of the amide plane in the Hg−thiophenolate complexes with differing terminal substituents and differing coordination numbers using X-ray analysis and NMR and IR measurements.

Results and Discussion

Synthesis of $(NEt_4)_2$[Hg(S-2-$CH_3NHCOC_6H_4)_4$] (5). Synthesis of $(NEt_4)_2$[Hg(S-2-$CH_3NHCOC_6H_4)_4$] (**5**) was accomplished by the ligand exchange reaction from the tris(thiophenolate) complex (NEt_4)[Hg($SC_6H_5)_3$] in tetrahydrofuran, as shown in Scheme 2. The resulting tricoordinate complex forms the tetracoordinate complex in equilibrium. Complex **5** is the most insoluble under these conditions and was obtained as fine crystals.

Crystal Structures of the Bis(carbamoylthiophenolate) Complexes, [Hg(S-2-*t*-$BuNHCOC_6H_4)_2$] (1), [Hg(S-2-$CH_3NHCOC_6H_4)_2$] (2), and [Hg(S-2-$C_6H_5CH_2NHCOC_6H_4)_2$] (3). Figures 1 and 2 show the crystal structures and intermolecular interactions of complexes **1**−**3** as determined by X-ray analysis. Table 1 shows selected bond distances and bond angles for the three complexes. Complex **1** crystallized in the $P\bar{1}$ space group with $Z = 4$. The complex therefore contains two distinct conformers/unit cell. Both molecules have similar S−Hg−S angles (177.3 and 176.9°); one conformer has 66.8° for the C11−S1−Hg1−S2−C21 torsion angle, and the other shows −89.1° for the C31−S3−Hg2−S4−C41 torsion angle. The amide NH (H2, H4) for one of the two thiophenolate ligands is directed to form an intramolecular NH···O═C hydrogen bond with the carbonyl oxygen (O1, O3) of the other thiophenolate ligand (N···O = 2.98, 3.00 Å). The other amide NH (H1, H3) is directed to form an intermolecular NH···O═C hydrogen bond (N···O = 2.91, 2.92 Å). As a result, the crystal structure in **1** forms one-dimension chains with the alternating intra- and intermolecular hydrogen bonds. The carbonyl oxygen (O1, O3) with the intramolecular hydrogen bond lies very close to the mercury atom (2.65, 2.68 Å). In general, the distance of Hg···O van der Waals bonding is ca. 3.0 Å,[21] so

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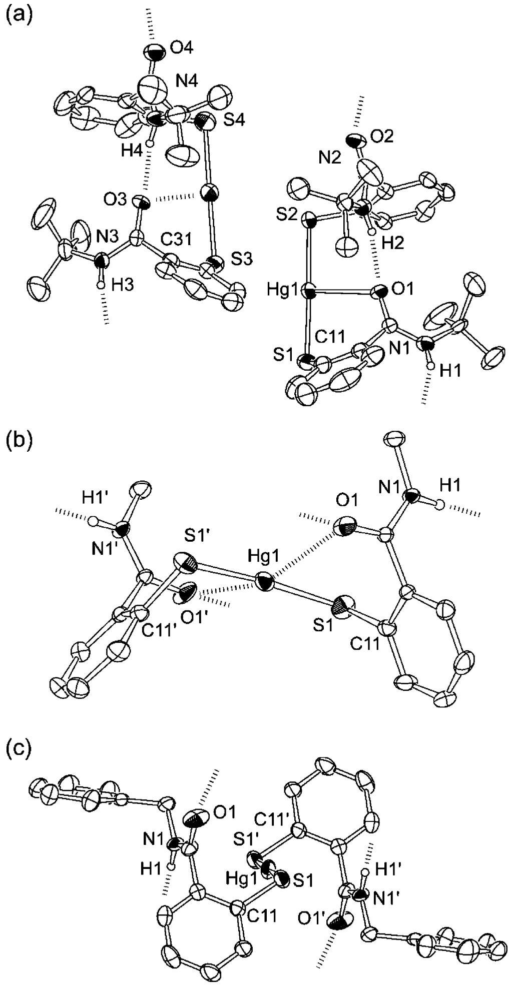

Figure 1. Crystal structures of (a) $[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$ (**1**), (b) $[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2]$ (**2**), and (c) $[Hg(S\text{-}2\text{-}C_6H_5CH_2NHCOC_6H_4)_2]$ (**3**). The hydrogen atoms except for amide proton have been omitted for clarity. Dotted lines refer to intra- and intermolecular interactions.

that the Hg···O1 and Hg···O3 bonding comprise the bonding interactions of Hg···O.

Complex **2** crystallized with the *C*2/*c* space group with $Z = 4$. The complex therefore contains half of the molecule/unit cell, and the two thiophenolate ligands have the same structure as the center of symmetry is mercury. The carbonyl oxygen (O1) of the thiophenolate ligand lies close to mercury (3.06 Å). This suggests the existence of the Hg···O binding interactions. The angles of S1−Hg1−O1, S1−Hg1−O1′, and O1−Hg1−O1′ are respectively 84.4, 96.5, and 158.3°, and complex **2** has a tetrahedral-like structure due to the sulfur and the carbonyl oxygen. The intermolecular distance of O1−N1 is 2.81 Å, and an intermolecular NH···O=C hydrogen bond forms. In addition, the mercury undergoes an intermolecular interaction with the sulfur of the neighboring molecule.

Complex **3** crystallized in the $P\bar{1}$ space group with $Z = 1$. The complex therefore also contains half of the molecule/unit cell, and the two thiophenolate ligands have the same structure as the center of symmetry of mercury. The structure in **3** does not permit an intramolecular NH···S hydrogen bond or Hg···O=C interaction but does give rise to an intermolecular NH···O=C hydrogen bond (N···O = 2.75 Å) and Hg···O=C interaction (Hg···O = 3.24 Å). In addition, the thiophenol rings undergo an intermolecular $\pi-\pi$ stacking interaction.

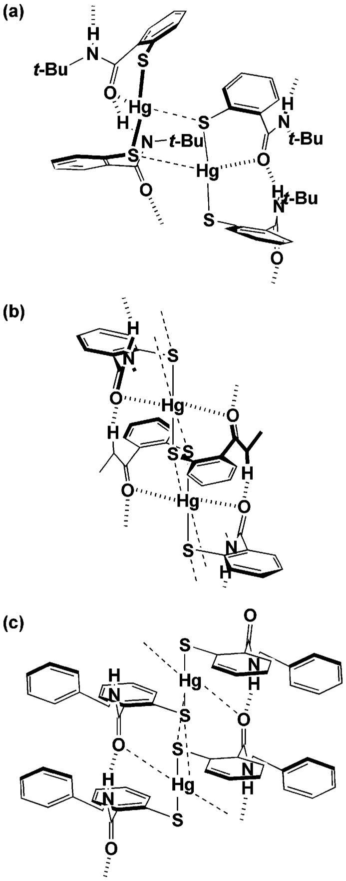

Figure 2. Intra- and intermolecular contacts in (a) $[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$ (**1**), (b) $[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2]$ (**2**), and (c) $[Hg(S\text{-}2\text{-}C_6H_5CH_2NHCOC_6H_4)_2]$ (**3**).

The reported mononuclear $Hg(S\text{-}2\text{-}RCONHC_6H_4)_2$ complexes have a structure that forms an intramolecular NH···S hydrogen bond, because the amide NH binding directs to the S atoms.[18] However, these three bis(carbamoylthiophenolate) complexes do not give rise to an intramolecular NH···S hydrogen bond. The thiolate anions $(NEt_4)(2\text{-}RCONHC_6H_4S)$ and $(NEt_4)(2\text{-}RNHCOC_6H_4S)$ form an intramolecular NH···S hydrogen bond.[19] Consequently, the ionicity of the sulfur coordinated to mercury appears to be low and formation of an intramolecular NH···S hydrogen bond is difficult.

Crystal Structure of the Tetrakis(carbamoylthiophenolate) Complex, $(NEt_4)_2[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_4]$ (5). Figure 3 shows an ORTEP view of **5**, and selected bond distances and bond angles are listed in Table 1. Complex **5** has a tetrahedral coordination, like the reported molecular structure of $[Hg(SAr)_4]^{2-}$.[3,4] The distance between the mercury atom and the sulfur atom is 2.55 Å, greater by about 0.2 Å than in the above-mentioned bis(carbamoylthiophenolate) complexes. These distances are the same as in the reported molecular structures of the bis(carbamoylthiophenolate) and tetrakis(carbamoylthiophenolate) complexes,[1,3] and any difference in the metal−sulfur bond lengths due to the intramolecular NH···S hydrogen bond is not detectable.

Table 1. Selected Bond Distances (Å), Intra- and Intermolecular Contacts (Å), and Bond Angles (deg) for [Hg(S-2-*t*-BuNHCOC$_6$H$_4$)$_2$] (**1**), [Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_2$] (**2**), [Hg(S-2-C$_6$H$_5$CH$_2$NHCOC$_6$H$_4$)$_2$] (**3**), and (NEt$_4$)$_2$[Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_4$] (**5**)

Complex **1**			
Hg(1)−S(1)	2.351(4)	Hg(2)−S(3)	2.325(4)
Hg(1)−S(2)	2.345(4)	Hg(2)−S(4)	2.321(5)
S(1)−Hg(1)−S(2)	177.3(2)	S(3)−Hg(2)−S(4)	176.9(2)
Hg(1)−S(1)−C(11)	103.4(6)	Hg(2)−S(3)−C(31)	102.5(5)
Hg(1)−S(2)−C(21)	101.1(4)	Hg(2)−S(4)−C(41)	99.2(6)
C(11)−S(1)−Hg(1)−S(2)−C(21)	66.8	C(31)−S(3)−Hg(2)−S(4)−C(41)	−89.1
Hg(1)···O(1)(intra)	2.65(1)	Hg(2)···O(3)(intra)	2.68(1)
Hg(1)···S(3)(inter)	3.358(5)	Hg(2)···S(2)(inter)	3.625(4)
N(2)···O(1)(intra)	2.98(2)	N(4)···O(3)(intra)	3.00(2)
N(1)···O(4)(inter)	2.91(1)	N(3)···O(2)(inter)	2.92(2)
Complex **2**			
Hg(1)−S(1)	2.333(3)		
S(1)−Hg(1)−S(1′)	175.18(9)	Hg(1)−S(1)−C(11)	102.2(2)
C(11)−S(1)−Hg(1)−S(1′)−C(11′)	109.9		
Hg(1)···O(1)(intra)	3.06	N(1)···O(1)(inter)	2.810(7)
S(1)−Hg(1)−O(1)	84.4	S(1)−Hg(2)−C(2)	95.7(3)
O(1)−Hg(1)−O(1′)	158.3		
Complex **3**			
Hg(1)−S(1)	2.338(1)		
S(1)−Hg(1)−S(1′)	180.0	Hg(1)−S(1)−C(11)	100.9(1)
C(11)−S(1)−Hg(1)−S(1′)−C(11′)	180.0		
Hg(1)···O(1)(inter)	3.243(5)	N(1)···O(1)(inter)	2.754(6)
Complex **5**			
Hg(1)−S(1)	2.551(3)		
S(1)−Hg(1)−S(1′)	115.13(8)	S(1)−Hg(1)−S(1″)	115.13(8)
S(1)−Hg(1)−S(1‴)	98.67(14)	Hg(1)−S(1)−C(11)	107.0(4)
N(1)−C(17)−C(16)−C(11)	−15(2)		
N(1)···S(1)	3.02(1)		

The intramolecular distances between the nitrogen atom and the sulfur atom in the four thiophenolate ligands are about 3.00 Å. This suggests the formation of the intramolecular NH···S hydrogen bond. The X-ray analyses suggest that the anionic ionicity of the sulfur atom coordinated to mercury in tetrakis(carbamoylthiophenolate) complex **5** is greater than in bis(carbamoylthiophenolate) anion **2**, leading to rotation of the amide plane and formation of the intramolecular NH···S hydrogen bond in complex **5**.

IR Spectra in the Solid State and Solution. Figure 4 shows the IR spectra of the bis(carbamoylthiophenolate) complexes, [Hg(S-2-*t*-BuNHCOC$_6$H$_4$)$_2$] (**1**), [Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_2$] (**2**), and [Hg(S-2-C$_6$H$_5$CH$_2$NHCOC$_6$H$_4$)$_2$] (**3**), and of the tetrakis(carbamoylthiophenolate) complex, (NEt$_4$)$_2$[Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_4$] (**5**), in the solid state. Table 2 lists the IR data in the amide region ν(NH) and ν(C═O) bands for the mercury complexes, the free ν(NH) and ν(C═O) bands of the corresponding thiol and disulfide compounds, and the shift values. Complex **1** exhibits two NH bands at 3302 and 3250 cm^{-1} and two CO bands at 1650

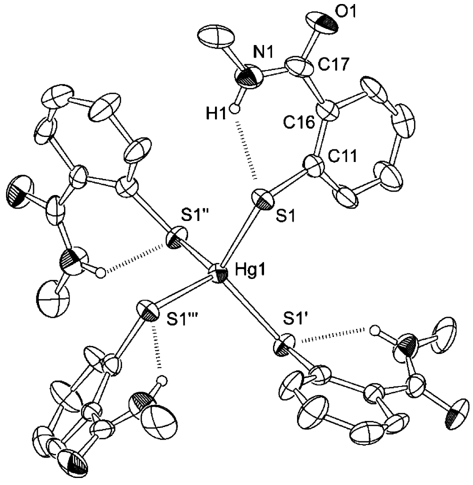

Figure 3. Crystal structure of (NEt$_4$)$_2$[Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_2$] (**5**). Dotted lines refer to the intramolecular NH···S hydrogen bond.

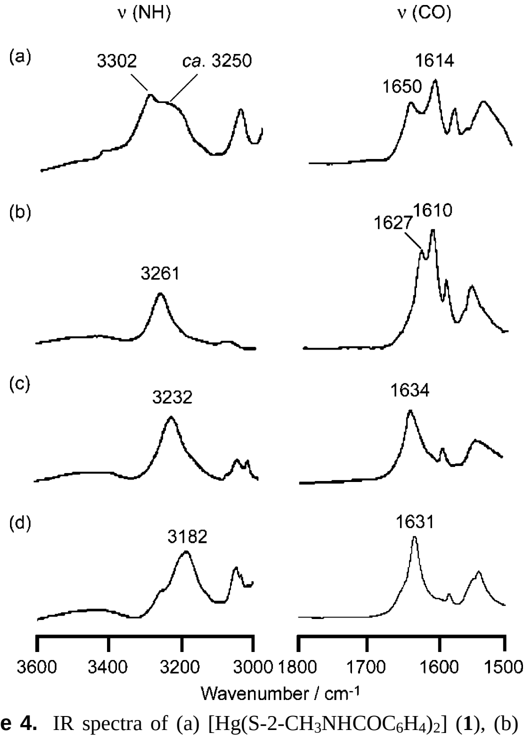

Figure 4. IR spectra of (a) [Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_2$] (**1**), (b) [Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_2$] (**2**), (c) [Hg(S-2-C$_6$H$_5$CH$_2$NHCOC$_6$H$_4$)$_2$] (**3**), and (d) (NEt$_4$)$_2$[Hg(S-2-*t*-BuNHCOC$_6$H$_4$)$_2$] (**5**) in the solid state.

Table 2. IR Spectral Data ($\mathrm{cm^{-1}}$) for Mercury(II) Complexes and Related Compounds in the Solid State and in Chloroform (10 mM)

	in solid state		in chloroform	
compd	ν(NH)	ν(CO)	ν(NH)	ν(CO)
$[\mathrm{Hg(S\text{-}2\text{-}\mathit{t}\text{-}BuNHCOC_6H_4)_2}]$ (**1**)	3261	1627, 1610	3450	1638
$[\mathrm{Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2}]$ (**2**)	3232	1634	3432	1637
$[\mathrm{Hg(S\text{-}2\text{-}C_6H_5CH_2NHCOC_6H_4)_2}]$ (**3**)	3302	1650, 1614	3424, 3348	1650, 1631
$\mathrm{(NEt_4)_2[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_4]}$ (**5**)	3182	1631	ca. 3200, 3451	1627
$\mathrm{(S\text{-}2\text{-}\mathit{t}\text{-}BuNHCOC_6H_4)_2}$	3294	1634	3429	1659
$\mathrm{2\text{-}\mathit{t}\text{-}BuNHCOC_6H_4SH}$	3303	1632	3431	1658
$\mathrm{(NEt_4)(2\text{-}\mathit{t}\text{-}BuNHCOC_6H_4S)}$	3154	1618	3153	1618
$[\mathrm{Hg(S\text{-}2\text{-}\mathit{t}\text{-}BuCONHC_6H_4)_2}]$	3345	1685, 1665, 1649		
$[\mathrm{Hg(S\text{-}2\text{-}CH_3CONHC_6H_4)_2}]$	3228	1658		

and 1614 $\mathrm{cm^{-1}}$, as shown in Figure 4a. From the X-ray analyses, one of the two carbonyl oxygens forms an intramolecular NH···O═C hydrogen bond with the amide proton and the bonding interaction with mercury, while the other carbonyl oxygen forms the intermolecular NH···OC hydrogen bond. It follows that the amide NH groups of the two thiophenolate ligands in **1** are not equivalent, and the CO band with the Hg···O═C interaction is detected as a low-wavenumber band (3250 $\mathrm{cm^{-1}}$).

Complex **2** exhibits an NH band at 3261 $\mathrm{cm^{-1}}$ and two CO bands at 1627 and 1610 $\mathrm{cm^{-1}}$, as shown in Figure 4b. From the X-ray analyses, the two carbonyl oxygens participate in the intramolecular Hg···O═C interaction, but two CO bands are detected because the two Hg···O distances are different (2.98(3) and 3.15(2) Å). Complex **3** exhibits an NH band at 3232 $\mathrm{cm^{-1}}$ and a CO band 1634 $\mathrm{cm^{-1}}$, as shown in Figure 4c. From the X-ray analyses, the two thiophenolate ligands have the same structure as the center of symmetry is mercury and are equivalent. As a result, the NH and CO bands are each detected as a single band. The CO band with the intermolecular Hg···O═C interaction in the crystal structure appears at high-wavenumber compared with **2** with the intramolecular Hg···O═C interaction.

The tetrakis(carbamoylthiophenolate) complex **5** exhibits an NH band at 3182 $\mathrm{cm^{-1}}$ and a CO band at 1631 $\mathrm{cm^{-1}}$. This large $\Delta\nu$(NH) value for **5**, compared with that of the thiol compound and bis(carbamoylthiophenolate) complexes, is ascribed to the intramolecular NH···S hydrogen bond and is additional to the values detected as a result of the NH···S hydrogen bond in the corresponding thiophenolate anion compounds.[17] The intramolecular NH···S hydrogen bond does not form, because of a reduction in the ionicity for the sulfur atom coordinated to mercury in the bis(carbamoylthiophenolate) complex. However, an increase of the ionicity for the sulfur atom with increasing coordination number gives rise to an intramolecular NH···S hydrogen bond in the tetrakis(carbamoylthiophenolate) complex. The crystal structure in **5** does not form an intermolecular interaction, suggesting that the intramolecular NH···S hydrogen bond is strong.

Table 2 summarizes the IR data in the amide region ν(NH) and ν(C═O) bands in chloroform-d_1 for the mercury complexes, free ν(NH) and ν(C═O) bands of the corresponding thiol and disulfide compounds, and the shift values. Complex **1** exhibits two NH bands at 3424 and 3348 $\mathrm{cm^{-1}}$ and two CO bands at 1650 and 1631 $\mathrm{cm^{-1}}$. This suggests that, in solution as well as the crystal structure, complex **1** has two distinct amide groups, and the NH and CO bands with the intramolecular NH···O═C hydrogen bond are observed at 3348 and 1631 $\mathrm{cm^{-1}}$, respectively, and those without the hydrogen bond are observed at 3424 and 1650 $\mathrm{cm^{-1}}$. Complex **2** exhibits an NH band at 3450 $\mathrm{cm^{-1}}$ and a CO band at 1638 $\mathrm{cm^{-1}}$. Complex **3** exhibits an NH band at 3432 $\mathrm{cm^{-1}}$ and a CO band at 1637 $\mathrm{cm^{-1}}$. The NH bands in both complexes have values rather similar to that in the corresponding thiol compound.[19] Consequently, complexes **2** and **3** do not form an NH···O═C and NH···S hydrogen bond in solution.

The tetrakis(carbamoylthiophenolate) complex **5** exhibits a broad NH band at ca. 3200 $\mathrm{cm^{-1}}$, a free NH band at 3451 $\mathrm{cm^{-1}}$, and a CO band at 1631 $\mathrm{cm^{-1}}$. This large shift of the NH band suggests that complex **5** has an intramolecular NH···S hydrogen bond in solution as well as in the solid state. In view of the NH band in bis(carbamoylthiophenolate) complex **2** (3450 $\mathrm{cm^{-1}}$), these results suggest that the NH band with the intramolecular NH···S hydrogen bond and the NH band without the hydrogen bond due to rotation of the amide plane are detected separately. The $\Delta\nu$(NH) value for **5** is ca. 100 $\mathrm{cm^{-1}}$ below that of the thiol compound. This value is much smaller than that for the corresponding thiolate anion (-278 $\mathrm{cm^{-1}}$) but is similar to that of the reported platinum complex $[\mathrm{Pt(bpy)(S\text{-}2\text{-}\mathit{t}\text{-}BuNHCOC_6H_4)_2}]$ (-126 $\mathrm{cm^{-1}}$).[20] The intramolecular NH···S hydrogen bond in the tetrakis(carbamoylthiophenolate) complex **5** is not as strong as that in the thiophenolate anion but is similar in strength to that in the platinum complex in solution. The weaker NH···S hydrogen bond in the mercury complex is ascribed to a lowering of the ionicity of the sulfur atom by the strongly covalent Hg−S bond.

^{1}H NMR Spectra. Table 3 summarizes the ^{1}H chemical shifts of the amide NH for the bis(carbamoylthiophenolate) complexes, $[\mathrm{Hg(S\text{-}2\text{-}\mathit{t}\text{-}BuNHCOC_6H_4)_2}]$ (**1**), $[\mathrm{Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2}]$ (**2**), $[\mathrm{Hg(S\text{-}2\text{-}C_6H_5CH_2NHCOC_6H_4)_2}]$ (**3**), and $[\mathrm{Hg(S\text{-}4\text{-}\mathit{t}\text{-}BuNHCOC_6H_4)_2}]$ (**4**), and the tetrakis(carbamoylthiophenolate) complex, $\mathrm{(NEt_4)_2[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_4]}$ (**5**), and the corresponding disulfide, thiol, and thiolate anion compounds. The amide NH signals appear at 6.19 ppm in **1**, 6.52 ppm in **2**, 6.77 ppm in **3**, and 6.52 ppm in **4**. These values are similar to that of the corresponding thiol compound, and the large downfield shift by the intramolecular NH···S hydrogen bond such as the corresponding thiophenolate anion compound[19] is not detectable. However, the amide NH signal in **5** is detected at 9.20 ppm and is largely shifted downfield compared with the bis(carbamoylthiophe-

Table 3. ^{1}H Chemical Shifts (ppm) of Amide NHs in Chloroform-d_1 and ^{199}Hg Chemical Shifts (ppm) in Dimethylformamide-d_7 of Mercury(II) Complexes and Related Compounds

compd	^{1}H/ppm	^{199}Hg/ppm[a]
$[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$ (**1**)	6.19	−1032
$[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2]$ (**2**)	6.52	−934
$[Hg(S\text{-}2\text{-}C_6H_5CH_2NHCOC_6H_4)_2]$ (**3**)	6.77	−1059
$[Hg(S\text{-}4\text{-}t\text{-}BuNHCOC_6H_4)_2]$ (**4**)	5.85	−1059
$(NEt_4)_2[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_4]$ (**5**)	9.20	−466[b]
$(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2$	5.83	
$2\text{-}t\text{-}BuNHCOC_6H_4SH$	5.72	
$(NEt_4)(2\text{-}t\text{-}BuNHCOC_6H_4S)$	12.16	
$[Hg(S\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2]$	8.51	−1142
$Hg(SC_6H_5)_2$		−1058

[a] ppm from $Hg(CH_3)_2$. [b] In chloroform-d_1.

nolate) complex and the corresponding thiol compound. This shift is ascribed to the formation of the intramolecular NH···S hydrogen bond in solution expected from the IR data. However, the ^{1}H signals are all broad, suggesting that complex **5** is the equilibrium state described by eq 1 in solution.

$$(NEt_4)_2[Hg(SAr)_4] \rightleftharpoons Hg(SAr)_2 + 2(NEt_4)(SAr) \qquad (1)$$

The amide NH signal in **5** at −30 °C is not split into two signals by the equilibrium but is detected at 9.7 ppm and largely shifts downfield by 0.5 ppm. It follows that the equilibrium shifts to the tetracoordinate state forming the intramolecular NH···S hydrogen bond at low temperature in solution. These findings suggest that the amide proton detected separately in the IR measurement is observed on the average by the rotation of the amide plane in the ^{1}H NMR measurement.

^{199}Hg NMR Spectra. The ^{199}Hg NMR spectra in complexes **1**−**5** were measured to investigate the electronic states around the mercury. Table 3 summarizes the results and the ^{199}Hg chemical shifts of the reported mercury complexes. $Hg(CH_3)_2$ was used as the external reference for the mercury resonance. The signals appear at −1032 ppm in **1**, −934 ppm in **2**, and −1059 ppm in **3**. The signal in *p*-substituted thiophenolate complex **4**, which is synthesized to take into account the electronic effect of the substituent, is detected at −1059 ppm and is similar or shifted downfield relative to the *o*-substituted thiophenolate complexes **1**−**3**. The signal in the reported mercury complex $Hg(S\text{-}2\text{-}RCONHC_6H_4)_2$ forming the intramolecular NH···S hydrogen bond shifts to high field compared with $Hg(S\text{-}4\text{-}RCONHC_6H_4)_2$.[18] Figure 5 plots the chemical shifts of the ^{199}Hg signals in dimethylformamide-d_7 of $Hg(SC_6H_4R)_2$ with Hammett σ_p constants. The plots of the *p*-substituents, OMe, $NHCOCH_3$, Cl, and NO_2, follow a straight line apart from those for the *p*-substituent, H. Deviation of $Hg(SC_6H_5)_2$ from the line with a high-field chemical shift is probably due to contamination by polymeric structures with tri- and tetracoordinate geometry.[22]

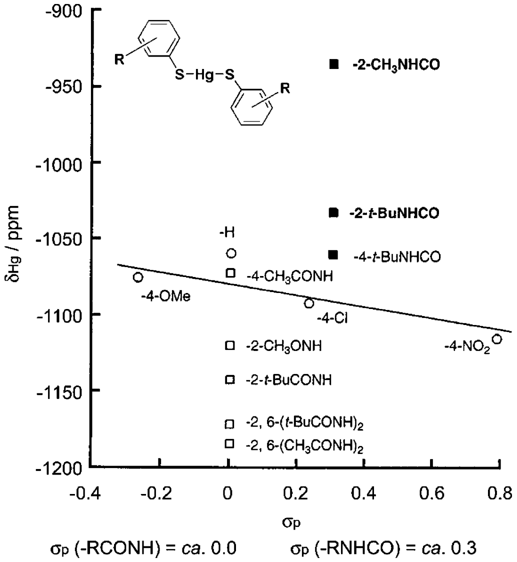

Figure 5. Correlation of ^{199}Hg NMR chemical shifts in dimethylformamide with Hammett σ_p constants in $Hg(SC_6H_4R)_2$.

The electron contribution of the carbamoyl group at the *o*-position shows an electron-withdrawing effect ($\sigma_p = 0.3$). Introduction of carbamoyl groups at the *o*-position of the thiophenol ring results in a largely downfield shift of the ^{199}Hg signals, especially for complex **2**. From NMR theoretical studies of the elements in group 12 (Zn, Cd), the chemical shift is the sum of diamagnetic terms and paramagnetic terms, and the chemical shift is strongly influenced by the paramagnetic terms.[23] In the case of an element in group 12, this paramagnetic term is affected by flow of the electron in the ligand to the unoccupied p-orbital of the metal. In the reported mercury complexes forming the intramolecular NH···S hydrogen bond, the flow of an electron to the p-orbital of Hg(II) is less, because of the overlap between the s-orbital of the amide proton and the p-orbital of the sulfur atom.[18] However, in the complexes **1** and **2** the paramagnetic term is large because of both the flow of the electron from the sulfur atom and also the flow of the electron from the oxygen atom involved in the intramolecular Hg···O bonding interactions; the result suggests that the ^{199}Hg signal shifts downfield. The ^{199}Hg signal is detected at −1059 cm^{-1} in **3** without the intramolecular interaction and at 1032 cm^{-1} in **1** with a single intramolecular Hg···O═C interaction and shifts downfield. In addition, the ^{199}Hg signal is detected at −934 cm^{-1} in **2** with two intramolecular Hg···O═C interactions and shifts further downfield.

The ^{199}Hg signal in tetrakis(carbamoylthiophenolate) complex **5** appears at −466 ppm in chloroform-d_1. The value is largely shifted downfield relative to the bis(carbamoylthiophenolate) complex. As well as the results of Gruff et al.,[1] this suggests that the flow of the electron in the ligand to the unoccupied p-orbital of the mercury atom increases due to the increase in the coordination number, and the paramagnetic term increases.

Biological Relevance. The high coordination number state in the Hg^{2+} complex is important in reducing Hg^{2+} to Hg(0) in mercuric reductase. It has been proposed that MerR has a tricoordinate structure in the detoxification system of

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Hg^{2+} ion.[6-8] We have synthesized tetrakis(carbamoylthiophenolate) mercuric complex **5** and determined its crystal structure. Complex **5** has a tetrahedral structure with four intramolecular NH···S hydrogen bonds which are undetectable in the bis(carbamoylthiophenolate) complex. The tetrahedral Hg(II) structure with a NH···S hydrogen bond is similar to that of rubredoxin. The four Fe−S distances of the reduced rubredoxin are slightly longer than those of the oxidized form, whereas the six NH···S hydrogen bonds between the sulfur atoms of cysteines coordinated to the Fe atom and the neighboring amide NHs of the main chain are shorter than in the oxidized form.[24,25] As a result, the overall positions of the backbone atoms around the [Fe−S] redox center remain uncharged with the change in oxidation state. The model complexes $[Fe(S\text{-}2\text{-}CH_3CONHC_6H_4)_4]^{2-}$ [15] and $[Fe(cys\text{-}X\text{-}Y\text{-}cys)_2]^{2-}$ [26] show a positive shift of redox potential due to the NH···S hydrogen bond. Our investigation suggests that the NH···S hydrogen bonds in tetrakis(carbamoylthiophenolato)mercuric complex stabilize the extra negative charge due to the increase in the coordination number.

We have also reported previously that the NH···S hydrogen bond reduces the pK_a of thiol.[19] Lowering of the pK_a stabilizes the thiolate anion state and increases the complexation constant. This effect also indicates that NH···S hydrogen bonds are the stabilizing factor in the tri- and tetracoordinate mercury complexes. The present results therefore suggest that the combined effects of NH···S hydrogen bonds stabilize the high coordination number of the Hg^{2+} complex proposed as the intermediate in the reduction of Hg^{2+} in vivo.

Conclusions

The bis(carbamoylthiophenolate) mercury complexes $[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$ (**1**), $[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2]$ (**2**), and $[Hg(S\text{-}2\text{-}C_6H_5CH_2NHCOC_6H_4)_2]$ (**3**) and tetrakis(carbamoylthiophenolate) mercury complex $(NEt_4)_2[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2]$ (**5**) were synthesized and their crystal structures determined. The bis(carbamoylthiophenolate) mercury complexes **1**−**3** do not form an intramolecular NH···S hydrogen bond because of lowering of the ionicity for the sulfur atom by the strongly covalent Hg−S bond. The orientation of the amide plane to the mercury atom differs with differing terminal substituents, and the intra- and intermolecular interactions are qualitatively different. The ^{199}Hg signal appears at −1059 ppm in **3** without the intramolecular interaction, at 1032 ppm in **1** with a single Hg···O═C interaction, and at −934 ppm in **2** with two Hg···O═C interactions, largely shifting downfield due to the Hg···O═C interaction. Differences in the orientation of the amide group and the terminal substituent control the structure of the mercury complex and the electronic state around the mercury ion.

The tetrakis(carbamoylthiophenolate) mercury complex **5** has a tetragonal structure and forms an intramolecular NH···S hydrogen bond. In addition, the distance between the mercury atom and the sulfur atom is longer by 0.2 Å than that in bis(carbamoylthiophenolate) complexes. In the tetrakis(carbamoylthiophenolato)mercury complex, the thiophenolate ligand becomes anionic because of the increase of ionic bonding between the mercury and the sulfur, and an intramolecular NH···S hydrogen bond is formed. The previous works show that the intramolecular NH···S hydrogen bond between the amide NH and the sulfur coordinated to metal reduces the π-donor capacity of the thiolate ligands. Consequently, formation of the intramolecular NH···S hydrogen bond in the tetrakis(carbamoylthiophenolate) complex stabilizes the extra negative charge by increasing of the coordination number and perhaps stabilizes the tri- and tetracoordinate mercury complexes existing in vivo.

Experimental Section

Materials. All operations were performed under an argon atmosphere. All solvents were dried and distilled under argon before use. The syntheses of 2-mercapto-*N*-alkylbenzamide and 4-mercapto-*N*-alkylbenzamide were carried out using the same previously reported procedure.[19]

Synthesis of $[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$ (1). To a methanol solution (10 mL) of 2-mercapto-*N*-(1,1-dimethylethyl)benzamide (490 mg, 2.4 mmol) was added mercury dichloride (350 mg, 1.3 mmol) at room temperature. After being stirred for 2 h, the solution was concentrated, and saturated NaCl(aq) was added (30 mL) to give a white precipitate which was collected with filtration. The resulting white solid was washed with saturated NaCl(aq) and water. Yield: 664 mg (92%). Anal. Calcd for $C_{22}H_{28}N_2O_2S_2Hg\cdot 2C_4H_8O$: C, 47.32; H, 5.82; N, 3.68. Found: C, 47.36; H, 5.20; N, 3.54. ESI-MS: *m*/*z* 641.2, $[M + Na]^+$. ^1H NMR (chloroform-d_1): δ 7.62 (d, 2H), 7.29 (d, 2H), 7.15 (t, 2H), 6.19 (s, 2H), 1.34 (s, 18H). $^{13}C\{H\}$ NMR (chloroform-d_1): δ 170.5, 141.0, 136.3, 131.2, 129.6, 127.3, 126.5, 52.2, 28.8.

Synthesis of $[Hg(S\text{-}2\text{-}CH_3NHCOC_6H_4)_2]$ (2). The complex was synthesized by the same method described above for the synthesis of $[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$. Yield: 98%. The crude product was recrystalized from methanol. Anal. Calcd for $C_{16}H_{16}N_2O_2S_2Hg\cdot 1/4C_6H_{14}$: C, 37.90; H, 3.54; N, 5.05. Found: C, 38.17; H, 3.32; N, 5.09. ESI-MS: *m*/*z* 556, $[M + Na]^+$. ^1H NMR (chloroform-d_1): δ 7.65 (d, 2H), 7.37 (d, 2H), 7.24 (t, 2H), 7.18 (t, 2H), 6.52 (s, 2H), 2.88 (s, 6H). $^{13}C\{H\}$ NMR (chloroform-d_1): δ 171.2, 139.8, 136.5, 131.8, 129.9, 127.8, 126.5, 26.7.

Synthesis of $[Hg(S\text{-}2\text{-}C_6H_5CH_2NHCOC_6H_4)_2]$ (3). The complex was synthesized by the same method described above for the synthesis of $[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$. Yield: 90%. Anal. Calcd for $C_{28}H_{24}N_2O_2S_2Hg$: C, 49.08; H, 3.53; N, 4.09. Found: C, 48.74; H, 3.33; N, 4.14. ^1H NMR (chloroform-d_1): δ 7.62 (d, 2H), 7.31 (d, 2H), 7.25 (m, 12H), 7.20 (t, 2H), 7.13 (t, 2H), 6.77 (s, 2H), 4.41 (d, 2H). $^{13}C\{H\}$ NMR (chloroform-d_1): δ 170.5, 139.7, 137.7, 136.6, 131.9, 129.9, 128.7, 128.0, 127.6, 126.5, 44.0.

Synthesis of $[Hg(S\text{-}4\text{-}t\text{-}BuNHCOC_6H_4)_2]$ (4). The complex was synthesized by the same method described above for the synthesis of $[Hg(S\text{-}2\text{-}t\text{-}BuNHCOC_6H_4)_2]$. Yield: 87%. Anal. Calcd for $C_{22}H_{28}N_2O_2S_2Hg$: C, 42.81; H, 4.57; N, 4.54. Found: C, 42.15; H, 4.34; N, 4.43. ESI-MS: *m*/*z* 641.2, $[M + Na]^+$. ^1H NMR (chloroform-d_1): δ 7.55 (d, 4H), 7.42 (d, 4H), 5.85 (s, 2H), 1.52 (s, 18H). $^{13}C\{H\}$ NMR (chloroform-d_1): δ 166.0, 134.2, 133.1, 129.1, 127.4, 51.8, 28.9.

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Table 4. Crystallographic Data for [Hg(S-2-*t*-BuNHCOC$_6$H$_4$)$_2$] (**1**), [Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_2$] (**2**), [Hg(S-2-C$_6$H$_5$CH$_2$NHCOC$_6$H$_4$)$_2$] (**3**), and (NEt$_4$)$_2$[Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_4$] (**5**)

	1	2	3	5
chem formula	$C_{22}H_{28}N_2O_2S_2Hg$	$C_{16}H_{16}N_2O_2S_2Hg$	$C_{28}H_{24}N_2O_2S_2Hg$	$C_{48}H_{72}N_6O_4S_4Hg$
fw	617.19	533.02	685.22	1125.96
T/K	296(1)	296(1)	296 (1)	296(1)
cryst system	triclinic	monoclinic	triclinic	tetragonal
lattice params				
a/Å	10.943(4)	21.993(5)	4.696(1)	12.679(3)
b/Å	15.062(5)	9.173(5)	11.835(2)	12.679(3)
c/Å	17.238(7)	8.950(5)	12.327(2)	33.381(6)
α/deg	82.15(3)	90	103.39(1)	90
β/deg	86.89(3)	104.09(3)	100.94(2)	90
γ/deg	85.89(3)	90	92.30(2)	90
V/Å^3	2804(1)	1751(1)	651.8(2)	5366(2)
Z	4	4	1	4
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$I4_1/a$ (No. 88)
D_{calc}/g·cm^{-3}	1.462	2.022	1.746	1.394
μ/cm^{-1}	56.59	90.36	60.91	30.77
reflcns collcd	10 439	2706	4195	2586
indep reflcns	9852	2551	3778	2358
R for $I > 2\sigma(I)$	0.073	0.053	0.033	0.053
wR$_2$ for all data	0.224	0.143	0.074	0.181

Synthesis of (NEt$_4$)$_2$[Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_4$] (5). To a tetrahydrofuran solution (7 mL) of (NEt$_4$)[Hg(SC$_6$H$_5$)$_3$] (130 mg, 0.19 mmol) was added a tetrahydrofuran solution (3 mL) of 2-mercapto-*N*-methylbenzamide (97 mg, 0.58 mmol), and the resulting solution was stirred overnight at room temperature. The reaction mixture was concentrated and added diethyl ether to precipitate a white powder. Yield: 98%. Anal. Calcd for $C_{48}H_{72}N_6O_4S_4Hg \cdot 3H_2O$: C, 48.86; H, 6.66; N, 7.12. Found: C, 48.46; H, 6.47; N, 6.78. ^{1}H NMR (chloroform-d_1): δ 9.20 (s, 4H), 7.73 (d, 4H), 7.43 (d, 4H), 6.86 (t, 8H), 2.85 (m, 28H), 1.01 (t, 24H).

Physical Measurements. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL GSX-400 spectrometer in chloroform-d_1 solution at 303 K. Tetramethylsilane (TMS) was used as the internal reference for proton resonance. ^{199}Hg NMR spectra were obtained on a Varian Unityplus 600 MHz spectrometer in dimethylformamide-d_7 or chloroform-d_1 solution at 303 K. IR spectra were taken on a Jasco FT/IR-8300 spectrometer. Samples were prepared as chloroform-d_1 solutions or KBr pellets. ESI-mass spectrometric analyses were performed on a Finniganmat LCQ-MS instrument in methanol or acetonitrile.

Structure Determinations. Suitable single crystals of [Hg(S-2-*t*-BuNHCOC$_6$H$_4$)$_2$] (**1**), [Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_2$] (**2**), [Hg(S-2-C$_6$H$_5$CH$_2$NHCOC$_6$H$_4$)$_2$] (**3**), and (NEt$_4$)$_2$[Hg(S-2-CH$_3$NHCOC$_6$H$_4$)$_4$] (**5**) were shielded in a glass capillary under an argon atmosphere. X-ray measurements were made at 300 K on a Rigaku AFC7R for **1** and AFC5R for **2**, **3**, and **5** diffractometer with graphite-monochromated Mo Kα radiation (0.710 69 Å). Unit cell dimensions were refined with 23 reflections for **1** and 25 reflections for **2**, **3**, and **5**. The basic crystallographic parameters for **1**−**3** and **5** are listed in Table 4. Three standard reflections were chosen and monitored with every 150 reflections and did not show any significant change. The data were collected up to $2\theta_{max} = 55°$ for **1** and **5** and 60° for **2** and **3**. An empirical absorption correction based on azimuthally scans three reflections was applied. The structures were solved by the direct method using the teXsan crystallographic software package.[27] Refinements were carried out on F for **1** and **2** and on F^2 for **3** and **5**, respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed on the calculated positions. The final refinement was carried out using full-matrix least-squares techniques with non-hydrogen atoms. The final difference Fourier map showed no significant features. Atom-scattering factors and dispersion corrections were taken from ref 28 In complex **5**, tetraethylammonium cation is disordered into two positions with site occupancy factors of each 0.500.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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