Effect of the NH---S Hydrogen Bond on the Nature of Hg−S Bonding in Bis[2-(acylamino)benzenethiolato]mercury(II) and Bis[2,6-bis(acylamino)benzenethiolato]mercury(II) Complexes

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2-(Acylamino)benzenethiolate complexes of Hg(II) having an intramolecular NH---S hydrogen bond, Hg[2-(pivaloylamino)benzenethiolato]$_2$ and Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$, were synthesized and the crystal structures were determined. The crystal structure of Hg[2-(pivaloylamino)benzenethiolato]$_2\cdot{}^1/_2H_2O$ shows the presence of two distinct conformers with different C−S−(Hg)−S−C torsion angles (81.7 and 176.6°). The crystal structure of Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$ indicates the presence of ordinary Hg−S bonds (2.335(2) and 2.342(2) Å) and a straight linear coordination (S−Hg−S = 174.7(1)°) with a weak interaction of one of the amide CO groups toward Hg(II). A weak NH---S hydrogen bond in both complexes is detected from the IR spectra in the solid state. The ^{199}Hg NMR spectra show the high-field shift with a decrease in the S → Hg(II) ligand-to-metal charge transfer by the NH---S hydrogen bonding. The high-field shift by the double NH---S hydrogen bond is far greater than that by the *p*-substituent effect of the electron-withdrawing group (OMe, H, NHCOCH$_3$, Cl, NO$_2$) on the benzenethiolate ring.

Introduction

Thiolate ligands have a high affinity for Hg(II) to produce various complexes, such as Hg(SR)$_2$, [Hg(SR)$_3$]$^-$,[1−3] and [Hg(SR)$_2$Cl$_2$]$^{2-}$.[4] The common coordination form for the thiolate complexes is a linear dicoordination with a short Hg−S distance. The Hg(II) binding site in mercury reductase has been proposed to be dicoordinate on the basis of an EXAFS analysis.[5] On the other hand, MerR is believed to have a trigonal Hg(II) site on the basis of the characteristic ligand-to-metal charge transfer transition of S → Hg in the UV region as that of trigonal planar (NEt$_4$)[Hg(S-*t*-Bu)$_3$].[3] In view of these electrochemical properties, the reduction of Hg(II) sites in Hg proteins seems to be difficult using conventional biological reductants because di-, tri-, or tetracoordinate thiolate complexes have been reported to exhibit relatively negative reduction potentials.[6] Although the thermodynamically preferable reduction of the Cys-thiolate-ligated Hg(II) ion by flavin adenine dinucleotide or NADPH may be explained as an enzymatic reaction,[5,7−11] it still remains unclear. Actually, the X-ray crystallographic analysis of reduced mercuric reductase has indicated the binding of only two thiolate groups.[12] A recent study proposed the importance of adjacent Tyr phenoxy groups around Hg(II) in mercuric reductase.[13] It is important to study the effect of functional groups of neighboring amino acid residues on the properties of the Hg−S group.

Previously, we reported that the NH---S hydrogen bond contributes to the positive shift in the redox potential in Cys-containing oligopeptide Fe(II) complexes as models of the Fe center of iron−sulfur proteins.[14,15] The NH---S hydrogen bond has been found to clearly shift the redox potential in [Mo^{V}O-(2-(acetylamino)benzenethiolato)$_4$]$^-$.[16] Thus, NH---S hydrogen bonding can possibly produce a positive shift in the redox potential in any metal thiolate complex.

The presence of two NH---S hydrogen bonds on one thiolate S has been known in the crystal structures of the metal centers of rubredoxin and azurin.[17,18] 2,6-Bis(acylamino)benzenethiolate is one of the suitable ligands having two NH---S hydrogen

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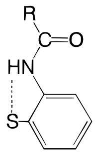
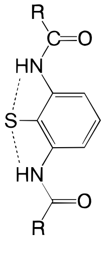
bonds as models of the Cys-containing peptide chain. The presence of such hydrogen bonds in Mo(V), Mo(IV), Fe(II), Co(II), and Cu(I) complexes has already been reported.[16,19,20]

This paper describes the influence of the intramolecular NH---S hydrogen bond on the Hg−S bond character and the chemical properties of dicoordinate $Hg(SAr)_2$ complexes having 2-(acylamino)benzenethiolate and 2,6-bis(acylamino)benzenethiolate ligands. The presence of the NH---S hydrogen bond has been discussed only in $Hg(HDz)_2$ (HDz = dithizonate).[21]





Experimental Section

All solvents were dried over calcium hydride and purified by distillation just before use. Thiols RSH (R = *p*-OMe-C_6H_4, *p*-Cl-C_6H_4, *p*-NO_2-C_6H_4) were commercially obtained. Bis[2-(acetylamino)phenyl] disulfide, $(o\text{-aabt})_2$, and bis[4-(acetylamino)phenyl] disulfide, $(p\text{-aabt})_2$, were prepared using the literature method.[16] Bis(2,6-diaminophenyl) disulfide was prepared using the reported method.[22] $[(n\text{-Bu})_4N][Hg(SPh)_3]$ was prepared using the literature method.[23] The synthesis of bis[2,6-bis(pivaloylamino)phenyl] disulfide was carried out using the same previously reported procedure.[24,25]

Bis(benzenethiolato)mercury(II). This complex was prepared using the same procedure as reported in the literature.[26] Anal. Calcd for $C_{12}H_{10}S_2Hg$: C, 34.30; H, 2.41. Found: C, 34.41; H, 2.45.

Bis[2-(acetylamino)benzenethiolato]mercury(II), Hg(*o*-aabt)$_2$. To a methanol solution (10 mL) of bis[2-(acetylamino)phenyl] disulfide (208 mg, 0.6 mmol) was added tetraethylammonium borohydride (113 mg, 0.8 mmol) at room temperature. After the solution was stirred for 5 min, acetic acid (1.5 mL) was added to hydrolyze excess tetraethylammonium borohydride. Mercury dichloride (166 mg, 0.6 mmol) was added to the solution to give a white precipitate, which was collected by filtration. The crude precipitate was recrystallized from methanol and gave fine colorless needles. Yield: 105 mg (32%). ^1H NMR (Me_2SO-d_6): δ 9.16 (s, 2H), 7.74 (d, 2H), 7.52 (d, 2H), 7.12 (t, 2H), 6.94 (t, 2H), 2.07 (s, 6H). ^{13}C NMR (Me_2SO-d_6): δ 168.20, 138.95, 135.22, 127.96, 126.28, 124.09, 123.15, 23.74. Anal. Calcd for $C_{16}H_{16}N_2O_2S_2Hg$: C, 36.05; H, 3.03; N, 5.26. Found: C, 36.08; H, 3.08; N, 5.29.

Bis[2-(pivaloylamino)benzenethiolato]mercury(II)·$^1/_2$H$_2$O, Hg(*o*-pabt)$_2$. This complex was synthesized by the above method. The crude complex was recrystallized from diethyl ether/*n*-hexane to give slightly yellowish plates. Yield: 7%. ^1H NMR (Me_2SO-d_6): δ 9.02 (s, 2H), 7.96 (d, 2H), 7.54 (d, 2H), 7.14 (t, 2H), 6.94 (t, 2H), 1.22 (s, 18H). ^{13}C NMR (Me_2SO-d_6): δ 175.65, 139.25, 135.55, 126.79, 126.60, 123.56, 121.08. Anal. Calcd for $C_{22}H_{29}N_2O_{2.5}S_2Hg$: C, 42.20; H, 4.67; N, 4.47. Found: C, 42.08; H, 4.61; N, 4.50.

Bis[4-(acetylamino)benzenethiolato]mercury(II), Hg(*p*-aabt)$_2$. The complex was synthesized by the same method described above for the synthesis of Hg(*o*-aabt)$_2$ and obtained as a colorless powder in 49% yield. ^1H NMR (Me_2SO-d_6): δ 9.83 (s, 2H), 7.38 (d, 4H), 7.28 (d, 4H), 2.00 (s, 6H). ^{13}C NMR (Me_2SO-d_6): δ 167.94, 136.68, 132.28, 129.90, 119.25, 23.87. Anal. Calcd for $C_{16}H_{16}N_2O_2S_2Hg$: C, 36.05; H, 3.03; N, 5.26. Found: C, 36.02; H, 3.13; N, 5.24.

Bis[2,6-bis(acetylamino)phenyl] Disulfide, (*o,o*′-daabt)$_2$. Bis(2,6-diaminophenyl) disulfide (0.4 g, 1.4 mmol) was dissolved in acetic acid anhydride (5 mL), and the solution was refluxed for 1 h. Any unreacted acid anhydride was decomposed by the addition of water. The solid materials were collected by filtration and successively washed with 2% aqueous HCl solution, water, 2% aqueous $NaHCO_3$ solution, and water. The crude product was recrystallized from ethanol. Yield: 70%. The products include EtOH as crystal solvent. ^1H NMR (Me_2SO-d_6): δ 9.01 (s, 4H), 7.54 (d, 4H), 7.34 (t, 2H), 1.96 (s, 12H). ^{13}C NMR (Me_2SO-d_6): δ 168.75, 140.54, 130.73, 120.72, 119.97, 23.42. Anal. Calcd for $C_{20}H_{22}N_4O_4S_2(C_2H_6O)$: C, 53.64; H, 5.73; N, 11.32. Found: C, 53.51; H, 5.78; N, 11.38.

Bis[2,6-bis(acetylamino)benzenethiolato]mercury(II), Hg(*o,o*′-daabt)$_2$. The complex was synthesized by the same method described above for the synthesis of Hg(*o*-aabt)$_2$ and obtained as fine colorless needles in 49% yield. ^1H NMR (Me_2SO-d_6): δ 9.39 (s, 4H), 7.62 (d, 4H), 7.15 (t, 2H), 2.07 (s, 12H). ^{13}C NMR (Me_2SO-d_6): δ 168.06, 140.63, 126.46, 118.42, 23.85. Anal. Calcd for $C_{20}H_{22}N_4O_4S_2Hg$: C, 37.12; H, 3.43; N, 8.66. Found: C, 37.32; H, 3.47; N, 8.59.

Bis[2,6-bis(pivaloylamino)benzenethiolato]mercury(II), Hg(*o,o*′-dpabt)$_2$. The complex was synthesized by a method similar to that described above for the synthesis of Hg(*o*-aabt)$_2$. The crude material was recrystallized from methanol to give colorless columns (44 mg, 67% yield). ^1H NMR (Me_2SO-d_6): δ 8.71 (s, 4H), 7.70 (d, 4H), 7.41 (t, 2H). ^{13}C NMR (Me_2SO-d_6): δ 175.83, 140.52, 131.32, 119.59, 118.64. Anal. Calcd for $C_{32}H_{46}N_4O_4S_2Hg$: C, 47.13; H, 5.69; N, 6.87. Found: C, 46.81; H, 5.55; N, 6.74.

Bis(4-chlorobenzenethiolato)mercury(II), Hg(*p*-Cl-bt)$_2$. To a solution containing 4-chlorobenzenethiol (584 mg, 4 mmol) in MeOH (30mL) was added $HgCl_2$ (559 mg, 2 mmol). A white solid was immediately produced, and the solution was stirred at room temperature for 3 h. The solid was collected by filtration and washed with MeOH. The crude precipitate was recrystallized from DMF/diethyl ether/*n*-hexane and gave colorless fine crystals. Yield: 37%. ^1H NMR (Me_2SO-d_6): δ 7.38 (d, 4H), 7.22 (d, 4H). ^{13}C NMR (Me_2SO-d_6): δ 136.52, 133.34, 129.35, 128.23. Anal. Calcd for $C_{12}H_8S_2Cl_2Hg$: C, 29.55; H, 1.65. Found: C, 29.36; H, 1.73.

Bis(4-nitrobenzenethiolato)mercury(II), Hg(*p*-NO$_2$-bt)$_2$. This complex was prepared by the same method described above for the synthesis of Hg(*p*-Cl-bt)$_2$ and obtained as fine colorless crystals by the recrystallization from CH_3CN/diethyl ether. Yield: 178.7 mg (36%). ^1H NMR (Me_2SO-d_6): δ 8.04 (d, 4H), 7.63 (d, 4H). ^{13}C NMR (Me_2SO-d_6): δ 150.26, 133.34, 129.35, 128.23. Anal. Calcd for $C_{12}H_8N_2O_4S_2Hg$: C, 28.41; H, 1.56; N, 5.55. Found: C, 28.32; H, 1.58; N, 5.50.

Bis(4-methoxybenzenethiolato)mercury(II), Hg(*p*-OMe-bt)$_2$. This complex was prepared by the same method described for Hg(*p*-Cl-bt)$_2$. The white crude product was recrystallized from CH_3CN in 34% yield. ^1H NMR: δ 7.28 (d, 4H), 6.76 (d, 4H). ^{13}C NMR: δ 157.29, 133.39, 126.36, 114.23, 55.06. Anal. Calcd for $C_{14}H_{14}O_2S_2Hg$: C, 35.11; H, 2.95. Found: C, 34.97; H, 2.88.

Physical Measurements. ^1H NMR and ^{13}C NMR spectra were recorded at 30 °C using a JEOL EX 270 spectrometer operating at 270.05 MHz (^1H) and 67.80 MHz (^{13}C). ^{199}Hg NMR spectra were obtained on a 71.35 MHz JEOL GSX 400 spectrometer using dimethylmercury in DMF as a standard for the chemical shift. All ^{199}Hg NMR spectra were run on 0.02 M solutions in DMF at 30 °C. IR spectra in the solid state were taken using a Jasco FT/IR-8300 spectrometer.

X-ray Structure Determinations. Single crystals of Hg[2-(pivaloylamino)benzenethiolato]$_2$, Hg(*o*-pabt)$_2$·$^1/_2$H$_2$O, and Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$, Hg(*o,o*′-dpabt)$_2$, were sealed in a glass capillary for the X-ray measurements. These were performed at 23 °C using a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a 12 kW rotating-anode generator. The basic crystallographic parameters for Hg(*o*-pabt)$_2$ and Hg(*o,o*′-dpabt)$_2$ are listed in Table 1. Unit cell dimensions were refined with 25 reflections. Three standard reflections were chosen and monitored with every 100 reflections and did not show any significant change. The

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Table 1. Crystallographic Data for Hg[2-(pivaloylamino)benzenethiolato]$_2$ and Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$

empirical formula	$C_{22}H_{29}N_2O_{2.5}S_2Hg$	$C_{32}H_{46}N_4O_4S_2Hg$
fw	626.19	815.45
crystal system	monoclinic	monoclinic
a (Å)	15.899(2)	16.440(3)
b (Å)	19.623(3)	13.950(3)
c (Å)	16.360(3)	17.496(4)
β (deg)	99.81(1)	113.63(1)
V (Å$^{3)}$	5030(1)	3676(1)
Z	8	4
space group	$P2_1/n$	$P2_1/a$
μ (cm^{-1})	62.97	43.30
d_{calc} (g cm^{-3})	1.654	1.473
radiation	Mo Kα	Mo Kα
$2\theta_{max}$ (deg)	45	50
scan type	$\omega-2\theta$	$\omega-2\theta$
no. of reflns measd		
total	7154	7027
unique	6866	6821
no. of observns with $I > 3\sigma(I)$	3226	3916
R^a	0.040	0.033
$R_w{}^b$	0.043	0.034
no. of parameters	533	388
GOF	1.33	1.12

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

data were corrected for Lorentz and polarization effects. An empirical absorption correction based on the ψ scans was applied. The structures were solved by direct methods for Hg(o,o'-dapt)$_2$ and by the Patterson method for Hg(o-pabt)$_2$ using the TEXSAN crystallographic software package. The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed on calculated positions except for those of the water molecule. The final refinement was carried out using full-matrix least-squares techniques with non-hydrogen atoms. The refinement converged at $R = 0.040$ for Hg(o-dabt)$_2$ and at $R = 0.033$ for Hg(o,o'-dpabt)$_2$. Atom scattering factors and dispersion corrections were taken from ref 27.[27]

EHMO Calculations. In order to elucidate the energetic difference of two conformers in one unit cell of Hg(o-pabt)$_2$, EHMO calculations of the two conformers for a simple model complex, Hg(SH)$_2$, using a Kodansha Co. EHMO program were done. The parameters for Hg(II) were obtained from the literature.[28] The bond lengths 2.33 and 1.34 Å for Hg−S and S−H were adopted for the calculations, respectively. The angles 180 and 105° were used for S−Hg−S and Hg−S−H, respectively.

Results and Discussion

Crystal Structures of Hg[2-(pivaloylamino)benzenethiolato]$_2$·$^1/_2$H$_2$O and Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$. Hg(SPh)$_2$, Hg(p-aabt)$_2$, Hg(o-aabt)$_2$, and Hg(o,o'-daabt)$_2$ were obtained as fine needles. Unfortunately they could not be analyzed by X-ray diffraction. The elemental analyses of these complexes indicate a dicoordinate structure as already crystallographically established for Hg(S-2-SiMe$_3$C$_6$H$_4$)$_2$.[29]

Figures 1 and 2 show the crystal structures of Hg(o-pabt)$_2$·$^1/_2$H$_2$O and Hg(o,o'-dpabt)$_2$, respectively, determined by X-ray analysis. Tables 2 and 3 show selected bond distances and bond angles for the two complexes. Hg(o-pabt)$_2$·$^1/_2$H$_2$O, having a single amide group, crystallizes in the space group $P2_1/n$ (monoclinic) with $Z = 8$. Therefore, the complex contains two distinct conformers in a unit cell as shown in Figure 1. Both conformers exhibit similar S−Hg−S angles (177.9(2) and 179.2(2)°); one conformer has 81.7° for the C11−S1−(Hg1)−S2−C21 torsion angle, and the other shows 176.6° for the C31−S3−(Hg2)−S4−C41 torsion angle.

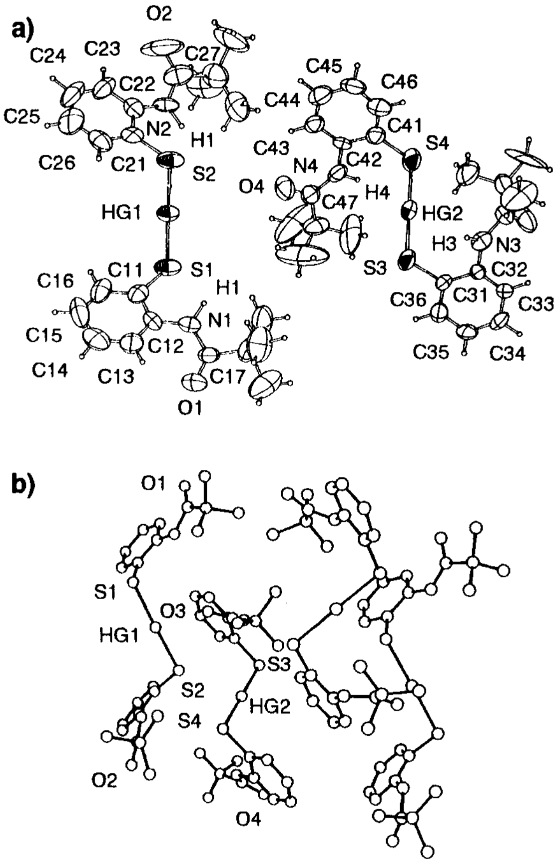

Figure 1. (a) Crystal structure of Hg[2-(pivaloylamino)benzenethiolato]$_2$ and (b) intra- and intermolecular contacts.

Table 2. Selected Intra- and Intermolecular Distance (Å) and Bond Angle (deg) Data for the Two Conformers (**A** and **B**) in Hg[2-(pivaloylamino)benzenethiolato]$_2$·$^1/_2$H$_2$O

A		B	
Bond Lengths			
Hg−S1	2.333(4)	Hg−S3	2.326(5)
Hg−S2	2.323(4)	Hg−S4	2.336(6)
mean	2.328	mean	2331
Hg1−O3	2.78(1)	Hg2−S2	3.157(4)
Hg1−O4	2.90(1)	Hg2−S1	3.162(4)
Bond Angles			
S1−Hg1−S2	177.9(2)	S3−Hg2−S4	179.2(2)
S1−Hg1−O3	92.6(3)	S3−Hg−S2	99.1(1)
S1−Hg1−O4	85.3(3)	S3−Hg−S1	77.2(1)
S2−Hg1−O3	85.3(3)	S2−Hg−S1	163.0(1)
S2−Hg1−O4	94.9(3)		
O3−Hg1−O4	105.2(4)		
Hg1−S1−C11	103.6(6)	Hg2−S3−C31	104.1(6)
Hg1−S2−C21	107.3(5)	Hg2−S4−C41	105.9(6)
mean	105.45	mean	105
C11−S1−(Hg)−S2−C21	82	C31−S3−(Hg)−S4−C41	177
Hg1−S1−C11−C12	−108(1)	Hg2−S3−C31−C32	68(2)
Hg1−S2−C21−C22	−101(1)	Hg2−S4−C41−C42	−74(2)

The EHMO calculations of a simple model, Hg(SH)$_2$, indicate that the structure in the most stable total energy level has a 90° H−S−(Hg)−S−H torsion angle. Two similar energy level HOMOs, an antibonding Hg(dπ)−S(pπ) MO (−13.288 eV) and a bonding Hg(pπ)−S(pπ) MO (−13.284 eV), are found at the 90° H−S−(Hg)−S−H torsion angle as shown in Figure 3. The former antibonding energy level has a minimum at 90° and

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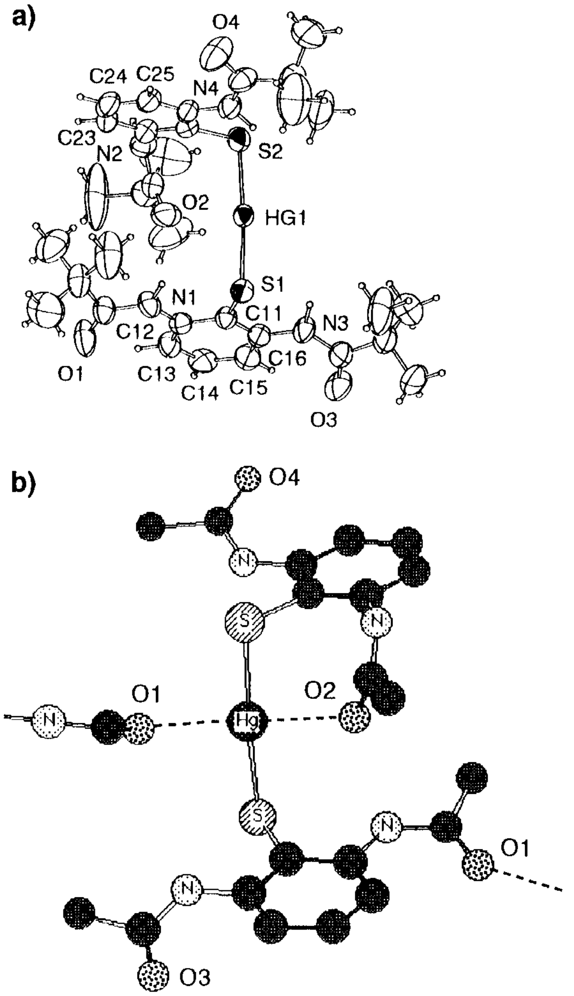

Figure 2. (a) Crystal structure of Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$ and (b) intermolecular Hg- - -O contacts in the complex.

Table 3. Selected Intramolecular Distance (Å) and Bond Angle (deg) Data for Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$

	Bond Lengths (Å)		
Hg−S1	2.335(2)	Hg−O1	2.826(6)
Hg−S2	2.342(2)	Hg−O2	2.722(6)
mean	2.339	Hg−O3	3.189(6)
	Bond Angles (deg)		
S1−Hg−S2	174.7(1)	Hg−S1−C11	102.2(2)
S1−Hg−O1	103.2(2)	Hg−S2−C21	98.3(2)
S1−Hg−O2	97.7(1)	mean	100.3
S1−Hg−O3	71.6(1)	Hg−S1−C11−C12	−86.6(6)
S2−Hg−O1	82.0(2)	Hg−S2−C21−C22	−89.6(6)
S2−Hg−O2	80.2(1)	C11−S1−(Hg)−S2−C21	104
S2−Hg−O3	106.6(1)	C11−C12−N1−C17	−167.1(7)
O1−Hg−O2	121.2(2)	C21−C22−N2−C27	69(1)
O2−Hg−O3	137.2(2)	C11−C16−N3−C37	157.0(8)
O3−Hg−O1	101.6(2)	C21−C26−N4−C47	152.6(9)

gradually increases to the 180° H−S−(Hg)−S−H torsion angle, while the latter bonding energy level has a maximum at 90° and gradually decreases until 180°. The total energies of these complexes indicate that one conformer is a slightly more energetically preferable form than the other. Actually, most of the reported mononuclear Hg(SR)$_2$ complexes possess narrow C−S−(Hg)−S−C angles near 120°, e.g. [Hg(SC$_5$H$_9$NH(CH$_3$)$_2$]-(ClO$_4$)$_2$ and [Hg(S-*o*-SiMe$_3$C$_6$H$_4$)$_2$],[29,30] although a large C−S−(Hg)−S−C torsion angle near 180° was reported for Hg(SEt)$_2$, having an intermolecular Hg---S contact.[31]

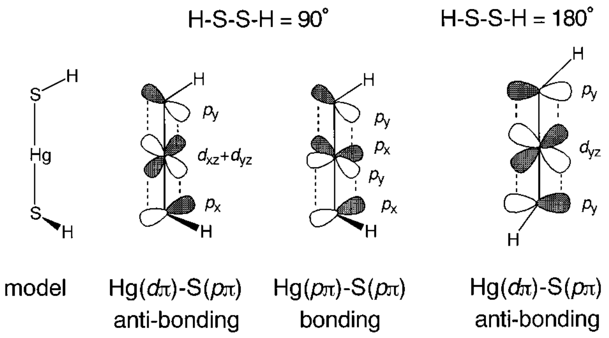

Figure 3. H−S−(Hg)−S−H torsion angle dependence of the HOMO in Hg(SH)$_2$ obtained using EHMO calculations.

For Hg(*o*-pabt)$_2$, no significant difference between the Hg1−S and Hg2−S distances or between the Hg1−S−C and Hg2−S−C angles was observed. However, the 68−108° range for the Hg−S−C−C torsion angle, namely the perpendicular orientation of the Hg−S bond to the benzene ring, indicates the lack of S pπ−phenyl pπ interaction and facilitates the preferable NH---S hydrogen bond formation between the S pπ orbital and the amide NH group. The benzene ring has been reported to be almost perpendicular to the Hg−S−C plane for Hg(S-2-SiMe$_3$C$_6$H$_4$)$_2$.[29]

Hg(*o,o′*-dpabt)$_2$ has a linear coordination (S−Hg−S = 174.69(7)°) like that (mean 178.6°) mentioned above for Hg(*o*-pabt)$_2$•$^1/_2$H$_2$O. The torsion angle Hg−S−C−C is about 90°, and the benzene ring is perpendicular to the Hg−S−C plane, similar to the case of Hg(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$.[2] The two bulky amide groups at the *o,o′*-positions in Hg(*o,o′*-dpabt)$_2$ also restrict the location of the S−C bond as shown in Figure 2. Three of the four amide NH groups face the sulfur atoms holding each planar amide plane. One remaining amide NH group is directed to the outside, and the carbonyl group gains access to Hg(II) with a short Hg---O distance (2.722(6) Å). The amide plane is displaced from the benzene ring with a C21−C22−N2−C27 torsion angle (69°). The distortion is ascribed to the preferred carbonyl coordination of the amide group to Hg(II). The linear S−Hg−S bond angle (174.69(7)°) is close to that (174.2(2)°) for Hg(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$ reported in the literature.[29] Furthermore, the Hg−S bonds of 2.335(2) and 2.342(2) Å and the Hg−S−C bond angles of 102.2(2) and 98.3(2)° for Hg(*o,o′*-dpabt)$_2$ are similar to those (2.322(6) and 2.322(5) Å) for the above Hg(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$. The carbonyl coordination overcomes the double NH---S hydrogen bonding, since the strength of the hydrogen bond is relatively weak, as described later. Thus, although the presence of the NH---S hydrogen bond in Hg(*o,o′*-dpabt)$_2$ is clear, the double NH groups at the *o,o′*-position are not cooperative for the formation of strong NH---S hydrogen bonding.

Figure 2b shows the intra- and intermolecular Hg---O contact in the crystal of Hg(*o,o′*-dpabt)$_2$. Besides the intramolecular Hg---O interaction by one of the four amide CO groups, other weak intermolecular interactions exist with a long Hg---O distance (2.826(6) Å). These shorter contacts arise from a Hg---O bonding interaction because the estimated van der Waals contact for Hg---O is about 3.23 Å.[32] Similar complexes having secondary bonding interactions have been reported, e.g. 3.08(2) Å for the Hg---O distance of [Hg(SC$_5$H$_9$NH(CH$_3$))$_2$][ClO$_4$]$_2$[30]

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and 2.878(4) Å for Hg[SSi(O-*t*-Bu)$_3$]$_2$.[33] Although the amide plane is positioned to conjugate with the aromatic ring, one of the CO groups coordinates to Hg(II) and retains a sterically unstable position in the amide plane against the aromatic ring (torsion angle 69(1)°). Such a preferable distortion toward a trigonal geometry by the intermolecular bonding interaction has been discussed for various two-coordinate Hg(II) thiolate complexes by Wright et al.[32]

The electronic effect of the amide group at the *o*- or *p*-position of the benzene ring is known not to be significant for organic disulfide molecules[34] but is for various [Mo^{V}O(2- or 4-(acylamino)benzenethiolato)$_4$]$^-$ complexes.[16] In the case of the Fe(II), Co(II), Mo(V), and Mo(IV) complexes, the local electron-withdrawing ability of the amide NH group through the NH---S hydrogen bond results in a decrease in the electron density of S(pπ).

On the other hand, the S → Hg(II) ligand-to-metal charge transfer in the bonding S(pπ)−Hg(pπ) LUMO contributes to the ^{199}Hg NMR chemical shift due to the paramagnetic character but only slightly to the Hg−S bonding in the heavy metal ion.

The present results suggest a function of the NH---S hydrogen bond in metalloproteins containing Hg(II), e.g. mercury reductase. The metal center of the Hg(II) metalloproteins possibly has a number of NH---S hydrogen bonds between the Cys thiolate and peptide amide NH groups. On the basis of the relationships between valence orbital bonding energies and crystal structure obtained by the multiple-scattering self-consistent-field Xα calculations, the decrease in the Hg−L(ligand) distance has been speculated to lead to a reduced Hg 5d−L p separation and a stronger destabilization associated with disproportionation to Hg(I) and Hg(II).[35] Actually, the positive shift of an Fe(II)/Fe(III) redox potential in [Fe(*o*-pabt)$_4$]$^{2-}$ and a Mo(IV)/Mo(V) redox potential in [Mo^{V}O(*o*-aabt)$_4$]$^-$ has been already observed.[16,19] Therefore, the NH---S hydrogen bonds could possibly be involved in the active center of the mercuric reductases and MerR and contribute to the regulation of the Hg−S bond and the structure.

IR Spectra of Hg(SAr)$_2$. The presence of an NH---S hydrogen bond was established by IR spectroscopy. Hg(*o*-aabt)$_2$ exhibits a hydrogen-bonding NH stretching band at 3228 cm^{-1} and free CO and hydrogen-bonding CO bands at 1672 and 1624 cm^{-1}, respectively. These bands are consistent with those of an inter- or intramolecular NH---O=C hydrogen bond which preferentially forms among the acetylamide groups.[36] Figure 4 shows the IR spectra of Hg(*o*-pabt)$_2$ and the corresponding disulfide, (*o*-pabt)$_2$, in the solid state. A disulfide, (*o*-pabt)$_2$, in the solid state exhibits a free NH and intermolecular NH---O=C hydrogen-bonding NH bands at 3389 and 3251 cm^{-1},[16] respectively, and a free CO and the corresponding intermolecular hydrogen-bonded CO bands at 1679 and 1644 cm^{-1}, respectively. These two pairs of bands correspond to each other as shown in Figure 4. Thus, the lack of an intermolecular NH---S hydrogen bond is suggested for the bulky disulfide in the solid state.

Hg(*o*-pabt)$_2$·$^1/_2$H$_2$O exhibits a broad NH band at 3345 cm^{-1} and three CO bands at 1685, 1665, and 1649 cm^{-1} as shown in Figure 4a. The two shifted CO bands observed at 1685 and 1649 cm^{-1} are tentatively assigned to those with two weak and strong Hg---O=C interactions detected by the X-ray analysis as illustrated in Figure 1b. The Δν(NH) for Hg(*o*-pabt)$_2$ can be estimated to be 44 cm^{-1} when the stretching of the free NH in the disulfide, (*o*-pabt)$_2$, is employed as a standard. A large Δν(NH) value (163 cm^{-1}) was found for a trigonal complex, [Cu^I(*o*-pabt)$_3$]$^{2-}$, in the solid state.[20] (NEt$_4$)$_2$[Co^{II}(*o*-pabt)$_4$] has been reported to give a strong hydrogen-bonding NH band at 3226 cm^{-1} in the solid state.[19] The weak hydrogen bonding in Hg(*o*-pabt)$_2$ is ascribed to a weak interaction between NH and S pπ against the strongly covalent Hg−S bond.

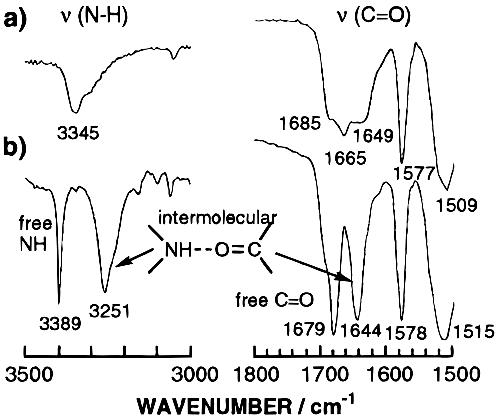

Figure 4. Amide NH and CO regions in the IR spectra of (a) Hg[2-(pivaloylamino)benzenethiolato]$_2$·$^1/_2$H$_2$O and (b) bis[2-(pivaloylamino)phenyl] disulfide.

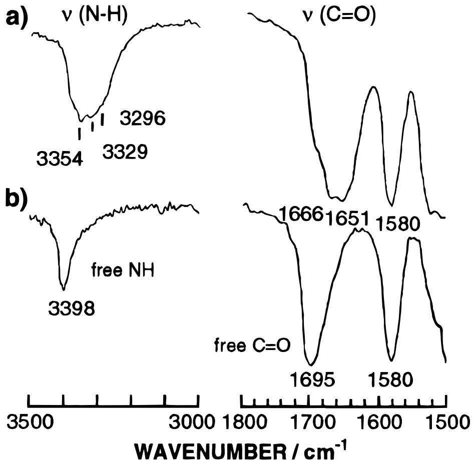

Figure 5. Amide NH and CO regions in the IR spectra of (a) Hg-[2,6-bis(pivaloylamino)benzenethiolato]$_2$ and (b) bis[2,6-bis(pivaloylamino)phenyl] disulfide.

The bands at 3256 and 1666 cm^{-1} (broad) for the largely shifted NH and slightly shifted CO stretchings of Hg(*o*,*o*′-daabt)$_2$ also indicate the presence of weak intramolecular NH---S hydrogen bonds. Hg(*p*-aabt)$_2$ shows almost non-hydrogen-bonded NH band at 3340 cm^{-1} and the CO band at 1665 cm^{-1}.

Crystalline Hg(*o*,*o*′-dpabt)$_2$ shows three NH bands at 3354, 3329, and 3296 cm^{-1} and two major CO bands at 1666 and 1651 cm^{-1} (Figure 5a). The crystallographic analysis indicates that the band shifted to 3296 cm^{-1} is assignable to that involved in the intermolecular NH---O=C hydrogen bond of which the corresponding CO band is observed at 1651 cm^{-1}. The NH and CO bands at 3354 or 3329 and 1666 cm^{-1} are due to those of the NH---S hydrogen bonding. The IR spectrum of the corresponding disulfide, (*o*,*o*-dpabt)$_2$, clearly indicates the free NH and free CO bands at 3398 and 1695 cm^{-1} as shown in Figure 5b. The two bulky *t*-Bu groups prevent the formation of an intermolecular NH---O=C hydrogen bond. Interestingly,

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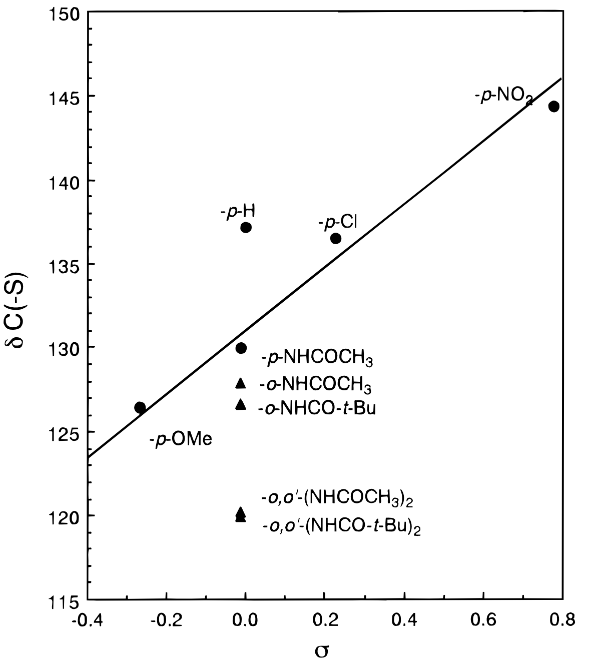

Figure 6. Correlation of ^{13}C chemical shifts of C(−S) in Me$_2$SO-d_6 with Hammett σ_p constants in Hg(SC$_6$H$_4$-*p*-X)$_2$ (X = OMe, H, NHCOCH$_3$, Cl, NO$_2$), Hg[2-(acetylamino)benzenethiolato]$_2$, Hg[2-(pivaloylamino)benzenethiolato]$_2$, Hg[2,6-bis(acetylamino)benzenethiolato]$_2$, and Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$.

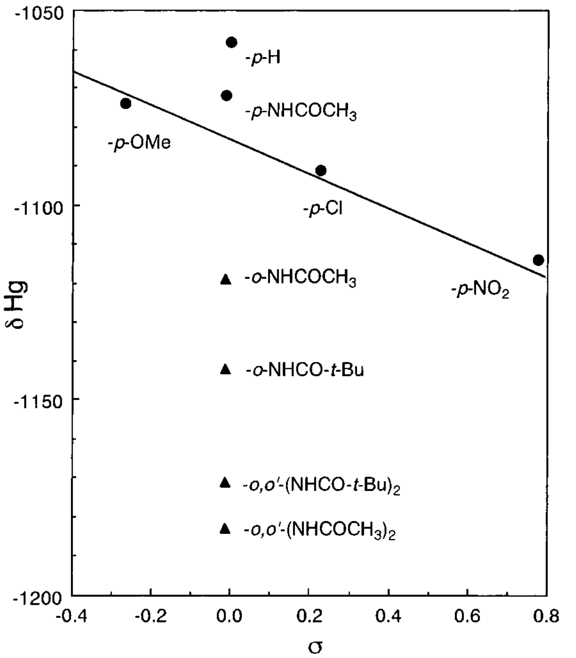

Figure 7. Correlation of ^{199}Hg chemical shifts in DMF with Hammett σ_p constants in Hg(SC$_6$H$_4$-*p*-X)$_2$ (X = OMe, H, NHCOCH$_3$, Cl, NO$_2$), Hg[2-(acetylamino)benzenethiolato]$_2$, Hg[2-pivaloylamino)benzenethiolato]$_2$, Hg[2,6-bis(acetylamino)benzenethiolato]$_2$, and Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$.

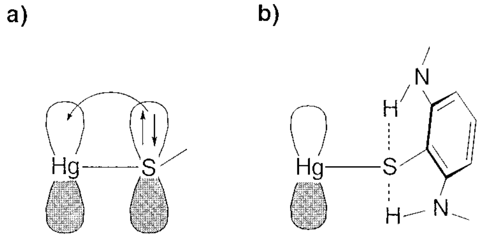

Figure 8. Schematic orbital drawing of (a) the paramagnetic contribution from the S *pπ* orbital to the empty Hg(II) *p* orbital and (b) the effect of NH- - -S hydrogen bonding.

no NH---S hydrogen bonding participates in the disulfide in spite of the location of the NH group close to a sulfur atom as described in the crystallographic analysis of the disulfide.[37]

^{13}C NMR and ^{199}Hg NMR Spectra of Hg(SAr)$_2$. The ^{13}C NMR chemical shifts of C(−S) on the benzenethiolate of various Hg(SAr)$_2$ complexes in Me$_2$SO-d_6 reflect the direct electronic effect of the *o*-, *m*-, or *p*-substituent on the benzene ring. Figure 6 shows the correlation of the ^{13}C NMR chemical shifts of aromatic C(−S) carbon with Hammett σ_p constants. The Hammett σ_p constants of the *p*-substituents, OMe, NHCOCH$_3$, Cl, and NO$_2$,[38] follow a straight line except those for the *p*-substituent, H. The deviation of Hg(SPh)$_2$ from the line with a high-field chemical shift is probably ascribed to the contamination of polymeric structures of tri- or tetracoordinate geometry with intermolecular associations in Me$_2$SO-d_6 solution. The polymeric structure for the complexation between Hg(II) and thiophenolate has been discussed using IR and Raman spectroscopies.[39] The ^{13}C NMR spectrum of the tricoordinate complex [(*n*-Bu)$_4$N)[Hg(SPh)$_3$]^{23} indicates a high-field shifted C(−S) signal at 143.6 ppm in Me$_2$SO-d_6.

The differences in the ^{13}C chemical shift of each C(−S) carbon between the *o*-acylamino-substituted Hg(SAr)$_2$ complexes and Hg(*p*-aabt)$_2$ were estimated as 2.0 ppm for Hg(*o*-aabt)$_2$ and 9.7 ppm for Hg(*o,o*′-daabt)$_2$ as shown in Figure 6. This result demonstrates the additivity of a NHCOCH$_3$ substituent effect on the *o*-positions of the benzene ring.

The electronic contribution of the amide group at the *o*-position is negligible (σ_p = ca. 0 for NHCOCH$_3$), or a rather slightly electron-donating effect was observed (Figure 6). The results of the C(−S) chemical shifts for Hg(*o*-aabt)$_2$ and Hg(*o,o*′-daabt)$_2$ indicates the direct NH---S hydrogen bonding effect of one or two NHCOCH$_3$ groups at the *o*- or *o,o*′-positions to the benzene ring.

Figure 7 plots the chemical shifts of the ^{199}Hg signals in DMF solution of Hg(SAr)$_2$ with Hammett σ_p constants. The plots of the *p*-substituents, OMe, NHCOCH$_3$, Cl, and NO$_2$, follow a straight line with similar behaviors as observed for the chemical shifts of the ^{13}C(−S) signal described above. Hg(SPh)$_2$ also deviates from the line for the same reason as the high-field shift of the ^{13}C(−S) signal due to the formation of a polymeric structure, because the relatively long Hg−S bond distance of [Hg(SPh)$_3$]$^-$ in the tricoordinate structure results in a decrease of the electron-donating contribution from S to Hg(II).

The introduction of amide groups at the *o*-position of the benzene ring results in a high-field shift of the ^{199}Hg signals for Hg(*o*-aabt)$_2$. When the chemical shift (δ ^{199}Hg) of the *p*-substituted complex, Hg(*p*-aabt)$_2$, at 30 °C is employed as a standard, the difference in the high-field shift is 47 ppm for Hg(*o*-aabt)$_2$ and 111 ppm for Hg(*o,o*′-daabt)$_2$. The effect of two amide groups at the *o,o*′-positions clearly shows additivity for the ^{199}Hg signal shift. The direct hydrogen-bonding effect of Hg(*o*-aabt)$_2$ and Hg(*o,o*′-daabt)$_2$ shows a similar magnitude for the electron-withdrawing NO$_2$ substituent shown in Figure 7.

The combined results indicate that the *o*- and *o,o*′-NHCOCH$_3$ groups act as electron-withdrawing ones toward the Hg−S bond, even though the electron-donating effect of the *o*- and *o,o*′-NHCOCH$_3$ substituents operates through the aromatic ring. The observed high-field shift of the ^{199}Hg signal is explained by lowering of the unpaired electron density with the decrease in

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the S → Hg(II) ligand-to-metal charge transfer in the LUMO upon formation of the NH---S hydrogen bonding as illustrated in Figure 8.

Thus, it is interesting that single and double NH---S hydrogen bonds affect the Hg−S bond character more than the expected effect of the *p*-substituent on the benzenethiolate ligand. Only the small change in Hg−S bond characters has been observed in various mercury thiolate complexes, $Hg(SR)_2$ (R = CH_2CH_2-OH, *i*-Pr, CH_2CH_2COOH, CH_2COOH, Ph), where the electronic effects of the R groups were reported using ^{199}Hg NMR.[26] The reported high-field shift of ^{199}Hg signals is interpreted as due to the increase in Hg−S ionicity of the Hg−S bonding. The chemical shift of the ^{113}Cd signals of CdL_2 complexes (L = Cl, CN, CH_3) having a d^{10} configuration have been predicted by the estimation of the paramagnetic contribution from the S atom to the Cd(II) hole using *ab initio* calculations, as well as for the Hg(II) complexes.[40,41] The present results of the ^{199}Hg chemical shifts in $Hg(SAr)_2$ strongly suggest that the NH group attracts the S(pπ) electron involved in the NH---S hydrogen bonding to decrease the paramagnetic contribution from the S atom to Hg(II) in the bonding LUMO as shown in the schematic drawing of Figure 8b.

Conclusions

Hg[2-(pivaloylamino)benzenethiolato]$_2\cdot{}^1/_2H_2O$ exhibits the presence of two distinct conformers with different C−S−(Hg)−S−C torsion angles (81.7 and 176.6°) in the crystal. The NH---S hydrogen bond weakens the Hg(pπ)−S(pπ) bonding HOMO and increases the dominant contribution of the Hg(dπ)−S(pπ) antibonding, which stabilizes the extended conformer with a 180° C−S−(Hg)−S−C torsion angle. Hg[2,6-bis(pivaloylamino)benzenethiolato]$_2$ has ordinary Hg−S bonds (2.335(2) and 2.342(2) Å) and a linear S−Hg−S bond (174.7(1)°) having a weak interaction of one of the amide CO groups with Hg(II).

The presence of a weak NH---S hydrogen bond in both complexes is established by the observation of the shifted NH stretching of the amide groups in the IR spectra in the solid state. The ^{199}Hg NMR spectra show the high-field shift with a decrease in the S → Hg(II) ligand-to-metal charge transfer due to the NH---S hydrogen bonding. The high-field shift by the double NH---S hydrogen bond is far greater than that due to the *p*-substituent effect of the electron-withdrawing groups on benzenethiolate.

Mercury-containing proteins have thiolate−metal bonds which are expected to be surrounded by peptide amide groups to form NH---S hydrogen bonds. Our results suggest that the NH---S hydrogen bonding regulates the properties of the S−Hg−S bond and also slightly affects the geometry.

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Supporting Information Available: Tables of non-hydrogen anisotropic thermal parameters, hydrogen isotropic thermal parameters, atomic coordinates and *B*(eq) values, and intramolecular distances and angles (19 pages). Ordering information is given on any current masthead page.

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