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ELECTROCHEMICAL SYNTHESIS OF MERCURY(II) COMPLEXES WITH SOME HETEROCYCLIC THIONES: THE CRYSTAL AND MOLECULAR STRUCTURES OF BIS(6-TERTBUTYLDIMETHYLSILYL)2-PYRIDYL DISULPHIDE (6-Bu^tSidmepyS-Spy-6-Bu^tSidme) and Hg(6-Bu^tSidmepyS)$_2$

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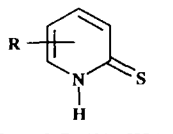
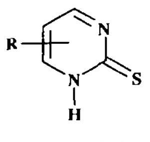
Abstract—A series of complexes of the type Hg(SR)$_2$ have been obtained by oxidation of the metal in an acetonitrile solution of the neutral heterocyclic thiones (RSH). The crystal and molecular structures of bis(6-tertbutyldimethylsilyl)2-pyridyl disulphide (6-Bu^tSidmepyS-Spy-6-Bu^tSidme) and of bis[(6-tertbutyldimethylsilyl) pyridyl-2-thionato] mercury(II), (Hg(6-Bu^tSidmepyS)$_2$), have been determined by single crystal X-ray diffraction. The structure the mercury complex consists of individual centrosymmetric monomeric molecules with linear two coordination, S—Hg—S and weak intramolecular Hg—N interactions. Vibrational and ^{1}H, ^{13}C and ^{199}Hg NMR spectral data of the complexes are discussed and related to the structure.

Current interest in the coordination chemistry of mercury complexes containing ligands bearing sulphur atoms is related to mercury–cysteine thionato interactions in toxicological behaviour of this metal,[1] in detoxification of the mercury by metallothioneins,[2] in a DNA-binding protein[3] and in mercury reductase and related proteins.[4]

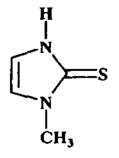
In previous papers, we have reported the direct electrochemical synthesis of metal thionato complexes by the oxidation of a sacrificial anode of zinc,[5–7] cadmium,[6–10] copper[9,11] or nickel[8–10,12] in a solution of the heterocyclic thione to produce the neutral M(SR)$_n$ compounds. Following a similar procedure we report here the synthesis of mercury(II) complexes with different heterocyclic thiones (see Scheme). Although Hg(6-Bu^tSidmepyS)$_2$ and Hg(3,6-Bu^tSidmepyS)$_2$ have been prepared by another method,[13] the other compounds reported in this article have not been synthesized previously. The crystal structures of bis(6-tertbutyldimethylsilyl)-2-pyridyl disulphide (6-Bu^tSidmepyS-Spy-Bu^tSidme) and the complex Hg(6-bu^{t}SidmepyS)$_2$ are also reported.



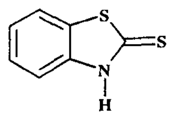
R = 3-Bu^tSi(CH$_3$)$_2$
(3-Bu^tSidmepySH)
R = 6-Bu^tSi(CH$_3$)$_2$
(6-Bu^tSidmepySH)
R = 3,6-(Bu^tSi(CH$_3$)$_2$)$_2$
(3,6-Bu^tSidmepySH)



R = H(pymSH)
R = 4,6-(CH$_3$)$_2$
(dmepymSH)



meimSH



bztSH

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EXPERIMENTAL

Acetonitrile and other solvents, chloro-tert-butyldimethylsilane, pyridine-2-thione, pyrimidine-2-thione, 4,6-dimethylpyrimidine-2-thione, 1-methylimidazoline-2-thione and benzothiazole-2-thione were commercial products and were used without further purification. *n*-Butyllithium and LDA (2 M) (lithium diisopropylamide) were purchased from Aldrich as a solution in hexane. The silylated ligands were prepared following a modified literature method.[13] A solution of LDA (11.45 g, 107 mmol) in dry THF (54 cm^3) was added dropwise under argon to a stirred THF (60 cm^3) solution of pyridine-2-thione (6 g, 54 mmol) at room temperature, and the stirring was kept for a further hour. The reaction flask was cooled to $-80^\circ C$ and then 22 cm^3 of *n*-butyllithium (2.5 M, 54 mmol) were added slowly with stirring. After addition of 40 cm^3 of dry THF, the cooling bath was removed, and the mixture was stirred at room temperature for 4 h. Chloro-tert-butyldimethylsilane (16 g, 106 mmol) was added to the vigorously stirred reaction mixture at $-80^\circ C$ and stirring was continued for 12 h at room temperature. Water (25 cm^3) was added slowly to the solution and the organic phase was concentrated in a rotevapour. The oily residue was dissolved in diethyl ether (250 cm^3) and then treated with water (300 cm^3). The reaction mixture was extracted with diethyl ether (3×50 cm^3); the organic phase was dried with Na_2SO_4, and concentrated in a rotevapour. The crude product was dissolved in a small amount of hexane, and subsequently chromatographed on silica gel (AcoEt, hexane) to give the compounds 3-(terbutyldimethylsilyl)pyridine-2-thione, 6-(tertbutyldimethylsilyl) pyridine-2-thione and 3,6-bis (tertbutyldimethylsilyl)pyridine-2-thione.

Preparation of the complexes

The electrochemical method used in the synthesis of the compounds is similar to that described by Tuck.[14] The cell was a 100 cm^3 tall-form beaker with a rubber bung through which the electrochemical leads entered into the cell. The mercury anode, in the bottom of the vessel, is connected through a platinum wire and the cathode was also a platinum wire. The thione ligand was dissolved in acetonitrile (*ca* 50 cm^3) and a small amount of tetraethylammonium perchlorate (*ca* 10 mg) was added to the solution. As electrolysis proceeded, the colour of the solution changed; at the end of the process the solution was filtered to remove any solid impurities, and the filtrate was slowly concentrated at room temperature to give solid products. Following a similar procedure but using a foil tin anode suspended from a platinum wire and a solution of 6-tertbutyldimethylsilylpyridine-2-thione in acetonitrile gives the ligand bis(6-terbutyldimethylsilyl) 2-pyridyl disulphide.

The cells can be summarized as $Pt(-)/CH_3CN+HL/Hg(+)$. Details of solution composition and electrochemical conditions are given in Table 1.

Physical measurement

Microanalyses were performed using a Carlo-Erba EA 1108 microanalyser and the results are given in Table 2. IR spectra were recorded in KBr mulls on a Perkin–Elmer 180 spectrophotometer. ^1H, ^{13}C and ^{199}Hg NMR spectra were recorded on a Bruker WN 250 MHz spectrometer using DMSO-d_6 as solvent; chemical shifts were determined against TMS as an internal standard.

Crystal structure determination

Crystal data for bis(6-tertbutyldimethylsilyl)2-pyridyldisulphide (**1**). $C_{22}H_{36}N_2S_2Si_2$; $M=448.8$, colourless block crystal of approximate dimensions $0.45\times0.50\times0.40$ mm, monoclinic space group $P2_{1/c}$, $a=7.775(2)$, $b=19.661(4)$, $c=17.392(3)$ Å, $\beta=97.18(3)^\circ$, $V=2637.8(13)$ Å^3, $Z=4$, $D_c=1.130$ gcm^{-3}, $F(000)=242$, $\lambda(Mo\text{-}K_\alpha)=0.71073$ Å, $\mu=0.303$ mm^{-1}.

Crystal data for [Hg (6-Bu^{t}Sidme-pyS)$_2$] (**2**). $C_{22}H_{36}HgN_2S_2Si_2$, $M=649.4$. Light yellow block [Hg(6-Bu^{t}Sidme-pyS)$_2$] of approximate dimensions $0.20\times0.12\times0.16$ mm, monoclinic space group, $P2_1/c$, $a=14.134(3)$, $b=13.604(3)$, $c=7.092(1)$ Å, $\beta=92.77(3)^\circ$, $V=1362.0(5)$ Å^3, $Z=2$, $D_c=1.583$ gcm^{-3} $F(000)=644$, $\lambda(Mo\text{-}K_\alpha)=0.71073$ Å, $\mu=5.903$ mm^{-1}.

Data collection and processing

Both compounds were mounted on glass fibres and data recorded on a Rigaku AFC5S diffractometer with graphite monochromated Mo-K_α radiation. The data for both crystals were collected at 213 K using the $\omega/2\theta$ scan technique with scan widths $(1.31+\tan\theta)^\circ$ and a scan of 2–8.00°m^{-1} (in omega) for the ligand and 8.00°m^{-1} (in omega) for the complex. The *hkl* range was $-18\leqslant h\leqslant18$, $-17\leqslant k\leqslant0$, $0\leqslant l\leqslant9$ for the complex and $0\leqslant h\leqslant8$, $0\leqslant h\leqslant21$, $-18\leqslant l\leqslant18$, for the ligand. 3458 reflections were measured for disulphide in the range 2θ = 2–45° and 3123 for the complex in the range $2\theta=0$–45°.

Table 1. Experimental conditions for the electronical synthesis

Compound	Amount of ligand (g)[a]	Initial Voltage (V)[b]	Time (h)	Metal dissolved (mg)	E_f (mol F^{-1})
[Hg(3-Bu^{t}SidmepyS)$_2$]	0.168	10	2	150	0.50
[Hg(6-Bu^{t}SidmepyS)$_2$]	0.168	10	2	152	0.51
[Hg(3,6-Bu^{t}SidmepyS)$_2$]	0.253	20	1	80	0.53
[Hg(pymS)$_2$]	0.168	20	2	156	0.52
[Hg(demepymS)$_2$]	0.104	20	1	75	0.50
[Hg(meimS)$_2$]	0.169	20	2	145	0.48
[Hg(bztS)$_2$]	0.249	20	2	155	0.52

[a] Plus Et_4NClO_4 (*ca* 20 mg).

[b] Voltage to produce a current of 20 mA.

Table 2. Analytical data

Complex	Found (Calc.)(%)			
	C	N	H	S
[Hg(3-Bu^{t}SidmepyS)$_2$]	40.6(40.7)	4.3(4.3)	5.6(5.6)	10.0(9.9)
[Hg(6-Bu^{t}SidmepyS)$_2$]	41.2(40.7)	4.3(4.3)	6.0(5.6)	9.8(9.9)
[Hg(3,6-Bu^{t}SidmepyS)$_2$]	46.5(46.5)	3.1(3.2)	7.3(7.3)	6.9(7.3)
[Hg(pymS)$_2$]	22.6(22.7)	12.5(13.3)	1.3(1.4)	14.8(15.1)
[Hg(demepymS)$_2$]	30.6(30.1)	12.4(11.7)	2.4(2.9)	13.2(13.4)
[Hg(meimS)$_2$]	22.9(22.5)	13.2(13.1)	2.4(2.3)	15.2(15.1)
[Hg(bztS)$_2$	30.7(31.5)	5.3(5.3)	1.3(1.5)	24.3(24.0)

Solution and refinement of the structures

For both compounds, full-matrix least-squares calculations were carried out on F, the function minimized being $\Sigma w(F_o - F_c)^2$. The structures were solved by direct methods. Refinements were carried out using 2502 for the ligand (**1**) and 2132 for the complex (**2**) with $F > 6.0\ \sigma(F)$. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions. For the ligand the final cycle of full-matrix least-squares, based on 143 variable parameters converged to $R = \Sigma(|F_o| - |F_c|)/\Sigma(F_o) = 0.069$ and $Rw = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.074$ with $w^{-1} = \sigma^2(F) + 0.0004F^2$. The maximum and minimum peaks on the final difference Fourier map were to 0.53 and -0.41 eÅ^{-3}, respectively. For the mercury complex, the final cycle of full-matrix least-squares, based on 133 variable parameters, converged to $R = \Sigma(|F_o| - |F_c|)/\Sigma(F_o) = 0.047$ and $Rw = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.059$ with $w^{-1} = \sigma^2(F) + 0.0010\ F^2$. The maximum and minimum peaks on the final difference Fourier map were 2.62 and -2.72 eÅ^{-3}, respectively. A Micro VAXII-based TEXRAY system,[15] which includes TEXSAN crystallographic software package, was used for diffractometer control and all calculations. Atomic scattering factors from *International Tables for X-ray Crystallography*.[16] The atomic positions full lists of bond lengths and angles and other crystallographic data have been deposited as Supplementary Publication No. CSD 58629. Copies can be obtained through the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlichtechnische Information mbH, D-7514 Eggenstein-Leopolshafen 2, Germany.

RESULTS AND DISCUSSION

Complexes of the type $Hg(SR)_2$ involving different heterocyclic thiones (RSH) have been prepared in high yield by an electrochemical method in a convenient one-pot process. The electrochemical efficiency defined as moles of metal dissolved per Faraday of charge is close to 0.5 mol F^{-1}. This value, together with the evolution of hydrogen gas at the cathode, is compatible with the following reaction scheme.

$$\text{Cathode}: RSH + e^- \longrightarrow 1/2\,H_2(g) + RS^-$$

$$\text{Anode}: 2\,RS^- + Hg \longrightarrow Hg(RS)_2 + 2\,e^-$$

Attempts to prepare tin complexes with these ligands using a tin anode and an acetonitrile solution of thiones were unsuccessful but in the case of the ligand 6-tertbutyldimethylsilylpyridine-2-thione crystals of bis(6-tertbutyldimethylsilyl) 2-pyridyl disulphide (6-Bu^{t}SidmepyS-Spy-6-Bu^t-Sidme) suitable for X-ray diffraction studies could be isolated. This compound is the result of an oxidation process of the ligand RSH to give the disulphide compound.

$$\text{Cathode}: 2\,RSH + 2\,e^- \longrightarrow H_2(g) + 2]\,RS^-$$

$$\text{Anode}: 2\,RS^- \longrightarrow RS\text{–}SR + 2\,e^-$$

A perspective view of the ligand bis(6-tertbutyldimethylsilyl)2-pyridyl disulphide is shown in Fig. 1; selected bond lengths and angles are given in Table 3. The torsion angle C1S1S2C12 of *ca* 90.0(4)° is within the range usually found in most aromatic disulphides (90 ± 10°) and the torsion angles X—C—S—S, where X = N or C, [N2C12S2S1 172.4(5); N1C1S2S1 177.7(4) and C13C12S2S1 6.0(7)°] are close to 0 or 180°, within the range found in other substituted aromatic disulphides with an equatorial conformation, following the Shefter classification[17] (*ca* 0 or 180° equatorial and 90° axial conformations). This means that both sulphur atoms lie approximately in the plane of the pyridine ring to which they are bound (0.036 Å). The average S—C distance, 1.791(9) Å, is likewise similar to those observed in other organic disulphides with an equatorial conformation[18] and is consistent with a single bond S—C. In addition and in accordance with the equatorial conformation the S—S bond distance, 2.302(3) Å, is shorter and the C—S—S angles, 106.3 and 105.2°, are larger than in other unsubstituted organic disulphides which show an axial conformation (2.060–2.108 Å and 100–103°).[18,19]

The pyridine rings are practically flat; the maximum deviation from a least squares plane is 0.0024 Å, with bond lengths are angles similar to those observed in other pyridinic systems. The angle N(1)—C(1)—C(2) is larger [123.9(7)°] than in pyridine-2-thione [115.2(2)°][20] and the angle between the pyridine rings is 91.2°.

The molecular structure of Hg(6-Bu^{t}SidmepyS)$_2$ is illustrated in Fig. 2; selected interatomic parameters and angles are listed in Table 4. The molecule is centrosymmetric and the Hg atom is bound to the sulphur atoms of two thiolate ligands with linear S—Hg—S bonding.

The Hg—S bond length, 2.344(2) Å, is very similar to those found in other mercury thionato complexes with linear geometry.[13,21] On the other hand, the thionato ligands are orientated so as to place the N(1) atom is close to the Hg atom with the Hg—N(1) separation of 2.793(1) Å. This distance is considerably longer than the shortest Hg—N distances observed in other mercury complexes involving heterocyclic nitrogen donor ligands for example in [Hg(pyS)(OAc)],[22] 2.210(2) Å and in [HgMe-py]NO$_3$,[23] 2.12(2) Å, but is shorter than 3.23 Å, the sum of the Van der Waals radii of the nitrogen (1.55 Å)[24] and mercury (1.73 Å)[25] and comparable to the distances characteristic of weak intramolecular Hg—N interactions in other mercury thiolate complexes (2.798–2.980 Å).[26] The pyridine rings are essentially planar, with the sulphur atoms lying approximately in the plane of the pyridine ring to which they are bound, and the Hg atom lying 0.1485 Å out of this plane as manifested in the torsion angle of 5.8(5)° for Hg—S—C—N. The S—C bound distance of 1.748(7) Å, is intermediate

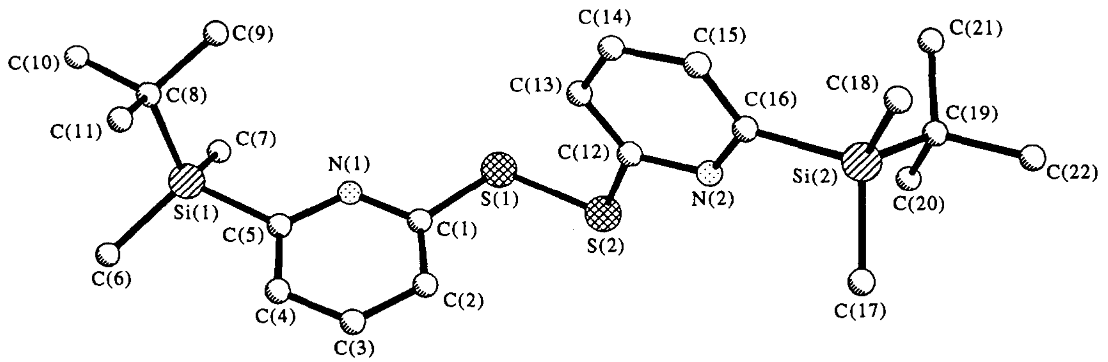


Fig. 1. The molecular structure of bis(6-tertbutyldimethylsilyl)2-pyridyl disulphide.

Table 3. Selected bond lengths (Å) and bond angles (°) for bis(6-tertbutyldimethylsilyl)2-pyridyl disulphide

S(1)—S(2)	2.032(3)	S(1)—C(1)	1.788(8)
S(2)—C(12)	1.795(7)	N(1)—C(1)	1.328(9)
N(1)—C(5)	1.350(10)	N(2)—C(12)	1.337(8)
N(2)—C(16)	1.361(9)	C(1)—C(2)	1.374(11)
C(2)—C(3)	1.351(13)	C(3)—C(4)	1.372(13)
C(4)—C(5)	1.389(12)	C(13)—C(14)	1.367(10)
C(14)—C(15)	1.378(10)	C(15)—C(16)	1.372(11)

S(2)—S(1)—C(1)	106.3(3)	S(1)—S(2)—C(12)	105.2(3)
C(1)—N(1)—C(5)	118.6(6)	C(12)—N(2)—C(16)	117.7(6)
S(1)—C(1)—N(1)	109.7(5)	S(1)—C(1)—C(2)	126.4(6)
N(1)—C(1)—C(2)	123.9(7)	C(1)—C(2)—C(3)	117.5(8)
C(2)—C(3)—C(4)	120.4(9)	C(3)—C(4)—C(5)	119.5(8)
S(2)—C(12)—N(2)	109.8(5)	S(2)—C(12)—C(13)	125.3(5)
N(2)—C(12)—C(13)	124.9(6)	C(12)—C(13)—C(14)	117.6(7)
C(13)—C(14)—C(15)	118.5(7)	C(14)—C(15)—C(16)	121.8(7)
N(2)—C(16)—C(15)	119.5(6)		

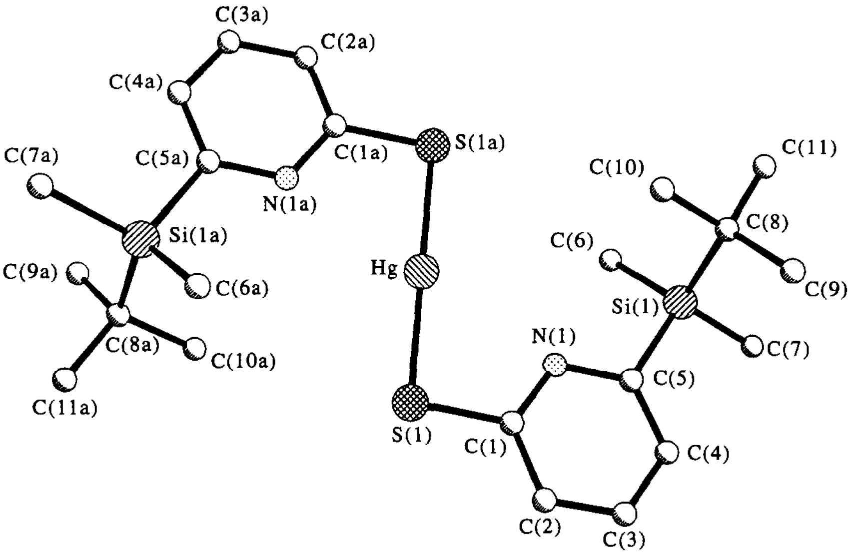


Fig. 2.The molecular structure of bis[(6-tertbutyldimethylsilyl)pyridyl-2-thionato]mercury(II).

between the value of 1.68 Å found in free pyridine-2-thione,[27] which exists as an thione form in the solid state, and the average value of 1.791(9) Å in bis(6-tertbutyldimethylsilyl) 2-pyridyl disulphide, in which there is a single C—S bond. This observation suggest that the ligand is coordinated in a form that is closer to thionato ligand than to the thione form of the free ligand.

Vibrational spectra

The infrared spectra of the compounds show no bands assignable to ν(N—H) (3200–3050 cm^{-1} for the free ligands), suggesting that deprotonation of the HN group has occurred during electrosynthesis and therefore that the ligand is coordinated in the thionato form.

The strong bands for ν(C═C) and ν(C═N) at 1600 and 1570 cm^{-1} in the silylated ligand spectra are shifted to smaller wavenumbers in their complexes; in the case of $Hg(6\text{-}Bu^tSidmepyS)_2$, these are close to those observed in the disulphide. This is the behaviour expected for aromatic stretching vibrations, and it supports the notion that the ligand is coordinated in the thionato form. The IR spectra of these compounds show a strong band at 840 cm^{-1} which can be attributed to ν(Si—C).[28]

When the ligands are pymS and dmepymS the

Table 4. Bond lengths (Å) and bond angles (°) of bis[(6-tertbutyldimethylsilyl)pyridyl-2-thionato]mercury(II)

Hg—S(1)	2.344(2)	Hg—S(1A)	2.344(2)
S(1)—C(1)	1.748(7)	Si(1)—C(5)	1.891(6)
Si(1)—C(6)	1.852(7)	Si(1)—C(7)	1.867(9)
Si(1)—C(8)	1.888(8)	N(1)—C(l)	1.349(8)
N(1)—C(5)	1.354(8)	C(1)—C(2)	1.410(10)
C(2)—C(3)	1.370(10)	C(3)—C(4)	1.389(10)
C(4)—C(5)	1.385(9)	C(8)—C(9)	1.543(12)
C(8)—C(10)	1.535(12)	C(8)—C(11)	1.524(12)
S(1)—Hg—S(lA)	180.0(1)	Hg—S(1)—C(1)	93.7(2)
C(5)—Si(1)—C(6)	107.8(3)	C(5)—Si(1)—C(7)	108.1(3)
C(6)—Si(1)—C(7)	108.5(4)	C(5)—Si(1)—C(8)	109.7(3)
C(6)—Si(1)—C(8)	111.6(4)	C(7)—Si(1)—C(8)	111.0(4)
C(1)—N(1)—C(5)	119.2(5)	S(1)—C(1)—N(1)	118.3(5)
S(1)—C(1)—C(2)	119.9(5)	N(1)—C(1)—C(2)	121.8(6)
C(1)—C(2)—C(3)	118.6(6)	C(2)—C(3)—C(4)	119.3(6)
C(3)—C(4)—C(5)	120.0 (6)	Si(1)—C(5)—N(1)	116.1(4)
Si(1)—C(5)—C(4)	122.9(5)	N(1)—C(5)—C(4)	121.0(6)
Si(1)—C(8)—C(9)	108.5(6)	Si(1)—C(8)—C(10)	110.1(5)
C(9)—C(8)—C(10)	108.8(7)	Si(1)—C(8)—C(11)	110.5(6)
C(9)—C(8)—C(11)	109.8(7)	C(10)—C(8)—C(11)	109.1(7)

shifts observed by the ring stretching, C—H in-plane deformation and ring breathing ligands bands indicate that in the complexes these ligands are in the thiol form.[29]

In the IR spectrum of $Hg(meimS)_2$, the band at 530 cm^{-1} assignable to $\nu(C{=}S)$ is shifted to lower frequency and the band arising from C—N stretching at 1460 cm^{-1} is shifted towards higher frequency on complexation, indicating a reduction of the double bond character of the C=S bond and a higher double bond order of the C=N bond, in accordance with the ligand being coordinated in the thionato form.[30]

In $Hg(bztS)_2$ of the bands with the greatest $\nu(C{=}S)$ character, only the ligand band at 1030 cm^{-1} appears in the spectrum of the complex, the shift to smaller wavenumbers resulting from reduction of the C—S bond order, suggesting that the ligand has a greater contribution from the thionate form in the complex.[31]

NMR studies

The ^{1}H NMR spectra of the complexes (Table 5) show signals for all the ligand hydrogen atoms except the NH proton, which in the spectra of the free ligands appears as a broad signal between 12.03 and 14.42 ppm. This confirms that in the complexes the ligands are deprotonated and coordinate in the thionato form.

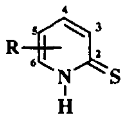
In the ^{13}C NMR spectra of the complexes (Table 6) also show all of the expected signals and the upfield shift of the C_2 signal is probably due to a reduction in the order of the C—S bond,[32] and this is further evidence of the predominance of the thionato form of the ligands in these complexes.

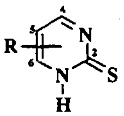
In the ^{13}C NMR spectra of silylated complexes, the C_2, C_3 and C_4 resonances are shifted upfield whereas C_5 and C_6 are shifted downfield compared with the corresponding free ligand. These data are similar to those observed in other complexes where a weak intramolecular coordination of the heterocyclic nitrogen in solution is postulated.

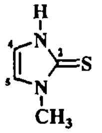
The ^{1}H NMR spectrum of the complex $Hg(pymS)_2$ in DMSO shows two signals, one a doublet that integrates for two protons at about 8.47 ppm attributable to hydrogens H_4 and H_6, and the other a triplet that integrates for one at about 7.15 ppm attributable to hydrogen H_5. However, if the structure of this compound is similar to the compound $Hg(6\text{-}Bu^tSiMe_2pyS)_2$, whose structure has been determined by X-ray diffraction, the hydrogens H_4 and H_6, of the pymt ring are not equivalent, and the NMR spectrum should consequently show two different signals for them; their equivalence would be explained if coordination to the metal alternates between nitrogens N_1 and N_3,[7,8] or if there is free rotation about the S—C bond in solution, in contrast to the solid state structure of $Hg(6\text{-}Bu^tSiMe_2pyS)_2$. The ^{13}C NMR spectrum is consistent with these data and exhibits only a signal attributable to C_4 and C_6 at 157.79 ppm.

Table 5. ^1H NMR data for complex(ppm)

3-Bu^{t}SidmepySH	13.22 s (NH) ;	7.58 d (H_6) ; 7.52 dd (H_4) ; 6. 70 t (H_5) ; 0.92 s (C—CH_3) ; 0.31 s (Si—CH_3)
[Hg(3-Bu^{t}SidmepyS)$_2$]		7.67 d (H_6) ; 7.44 dd (H_4) ; 7.05 t (H_5) ; 0.94 s (C—CH_3) ; 0.43 s (Si—CH_3)
6-Bu^{t}SidmepySH	12.84 s (NH) ;	7.29 d (H_3) ; 7.27 d (H_4) ; 6.84 d (H_5) ; 0.87 s (C—CH_3) ; 0.34 s (Si—CH_3)
[Hg(6—Bu^{t}SidmepyS)$_2$]		7.43 dd (H_3) ; 7.25 d (H_4), 7.20 d (H_5) ; 0.73 s (C—CH_3) ; 0.15 s (Si—CH_3)
3,6-Bu^{t}SidmepySH	12.41 s (NH) ;	7.43 d (H_3) ; 6.82 d (H_4) ; 0.93 s, 0.87 s (C—CH_3) ; 0.33 s, 0.31 s (Si-CH_3)
[Hg(3,6-Bu^{t}SidmepyS)$_2$]		7.45 d (H_3) ; 7.10 d (H_4) ; 0.96 s, 0.80 s (C—CH_3) ; 0.41 s, 0.17 s (Si—CH_3)
pymSH		8.28 d (H_4)/(H_6) ; 6.83 dd (H_5)
[Hg(pymS$_2$]		8.47 d (H_4)/(H_6) ; 7.15 t (H_5)
dmepymSH	13.49 s (NH) ;	6.62 s (H_5) ; 2.24 s ($H_{4'}/H_{6'}$)
[Hg(dmepymS)$_2$]		6.91 s (H_5) ; 2.17 s ($H_{4'}/H_{6'}$)
meimSH	12.03 s (NH) ;	7.03 d (H_5) ; 6.85 d (H_4) ; 3.40 s (NCH_3)
[Hg(meimS)$_2$]		7.05 d (H_5) ; 6.76 d (H_4) ; 3.42 s (NCH_3)
bztSH	13.4 s (NH) ;	7.69 d (H_4) ; 7.34 m ($H_{5,6,7}$)
[Hg(bztS)$_2$]		7.88 d (H_4) ; 7.35 d, 7.26 d ($H_{5,6}$) ; 7.60 d (H_7)







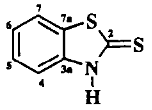


Table 6. ^{13}C and ^{199}Hg NMR data for complexes (ppm)

		$\delta(^{199}Hg)$
3-Bu^{t}SidmepySH	182.75(C_2) ; 138.60(C_3) ; 140.87(C_4) ; 112.24(C_5) ; 146.01(C_6) ; 18.04, 18.75(C*—CH_3) ; 28.25(C—C*H_3) ; −3.30(Si—CH_3)	
[Hg(3-Bu^{t}SidmepyS)$_2$]	175.62(C_2) ; 132.55(C_3) ; 138.24(C_4) ; 118.76(C_5) ; 157.1(C_6) ; 18.35(C*—CH_3) ; 27.7(C—C*H_3) ; −3.30(Si—CH_3)	—
6-Bu^{t}SidmepySH	180.12(C_2) ; 134.1(C_3) ; 135.0(C_4) ; 121.2(C_5) ; 152.7(C_6) ; 16.7(C*—CH_3) ; 26.60(C—C*H_3) ; −6.15(Si—CH_3)	
[Hg(6-Bu^{t}SidmepyS)$_2$]	166.4(C_2) ; 127.0(C_3) ; 135.2(C_4) ; 120.9(C_5) ; 160.3(C_6) ; 16.81(C*—CH_3) ; 26.50(C—C*H_3) ; −6.30(Si—CH_3)	−1185.7
3,6-Bu^{t}SidmepySH	184.72(C_2) ; 141.8(C_3) ; 143.4(C_4) ; 120.3(C_5) ; 153.2(C_6) ; 18.04, 16.77(C*—CH_3) ; 28.33, 26.72(C—C*H_3) ; −3.22, −6.29(Si—CH_3)	
[Hg(3,6-Bu^{t}SidmepyS)$_2$]	170.60(C_2) ; 131.6(C_3) ; 142.2(C_4) ; 123.4(C_5) ; 163.9(C_6) ; 18.40, 16.78(C*—CH_3) ; 27.4,26.5(C—C*H_3) ; −3.34, −6.38(Si—CH_3)	−1185.1
pymSH	181.4(C_2) ; 158.6(C_4, C_6) ; 119.1(C_5)	
[Hg(pymS)$_2$]	176.0(C_2) ; 157.8(C_4, C_6) ; 117.2(C_5)	—
dmepymSH	181.2(C_2) ; 165.0(C_4, C_6) ; 109.8(C_5) ; 21.76($C_{4'}$, $C_{6'}$)	
[Hg(dmepymS)$_2$]	172.5(C_2) ; 164.3(C_4, C_6) ; 113.2(C_5) ; 21.02($C_{4'}$, $C_{6'}$)	−1218.0
meimSH	161.28(C_2) ; 114.25(C_4) ; 119.65(C_5) ; 33.67(CH_3)	
[Hg(meimS)$_2$]	147.4(C_2) ; 123.60(C_4) ; 118.44(C_5) ; 35.07(CH_3)	−1059.8
bztSH	189.9(C_2) ; 141.3(C_{3a}) ; 121.7(C_4) ; 127.1(C_5) ; 124.2(C_6) ; 112.4(C_7) ; 129.4(C_{7a})	
[Hg(bztS)$_2$]	168.1(C_2) ; 153.3(C_{3a}) ; 121.7(C_4) ; 126.5(C_5) ; 124.4(C_6) ; 120.5(C_7) ;137.5(C_{7a})	−1211.8

The ^1H NMR spectrum of $Hg(dmepymS)_2$ exhibits a singlet that integrates as one proton at 6.91 ppm attributed to the CH, and one signal that integrates for six protons at about 2.17 ppm for the methyl protons of $dmpymt^-$. This shows that at room temperature both methyl groups are chemically equivalent, a feature consistent with the ^{13}C NMR spectrum where only a signal assigned to $C_{4'}$ and $C_{6'}$ of the methyl groups is observed at 21.02 ppm. As in the corresponding $Hg(PymS)_2$, this equivalency is tentatively assigned to the same behaviour.

As expected, for the $Hg(meimS)_2$ complex, the C_2 carbon is shifted upfield by about -6.30 ppm. This shift for the C_2 resonance is due to the decrease in the double bond character of the thione group. The C_4 and C_5 resonances are shifted downfield because of the increase in the double bond character of the $C{=}N$ groups.

The ^1H NMR spectrum of the $Hg(bztS)_2$ complex has four signals well differentiated with the expected multiplicities. These signals have been attributed to the H_4 at 7.88, H_7 7.60 and H_5 and H_6 at 7.35 and 7.26 ppm. The ^{13}C NMR spectrum shows the expected signals, of which those for C_{3a}, C_4 and C_{7a} are shifted downfield as a result of deshielding due to coordination to the metal in the thionato form.

These complexes exhibit $\delta(^{199}Hg)$ in the -1060 to -1218 ppm range. These values are close to those found in other mercury(II) bis thionato complexes where some intramolecular interaction between the heterocyclic nitrogen and mercury in solution can be inferred.[13]

These data suggest that the complexes have a structure similar to that found for $Hg(6\text{-}Bu^tSiMe_2pyS)_2$ by X-ray diffraction.

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