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Symmetrisation, isomerism and structural studies on novel phenylmercury(II) thiosemicarbazonates: correlation of the energy barrier to rotation of the amino group with the bonding parameters of the thioamide group

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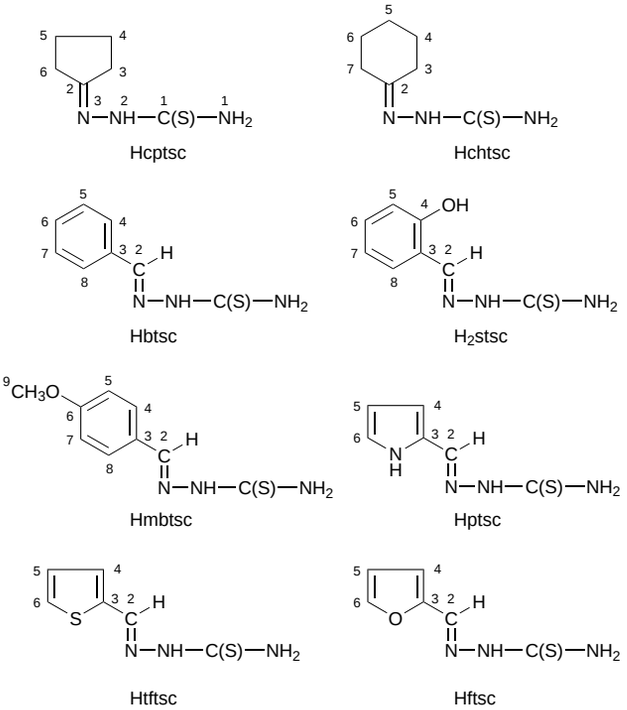
The reactions of phenylmercury(II) acetate with a series of alkyl, aryl and heterocyclic thiosemicarbazones in ethanol formed novel phenylmercury(II) derivatives of stoichiometry [HgPhL] [HL = R=$N^3N^2HC^1(S)N^1H_2$ = cyclopentanone **1**, cyclohexanone **2**, benzaldehyde **3**, 2-hydroxybenzaldehyde **4**, 4-methoxybenzaldehyde **5**, pyrrole-2-carbaldehyde **6**, thiophene-2-carbaldehyde **7** or furan-2-carbaldehyde **8** thiosemicarbazone], characterised with the help of analytical data, physical properties, IR, far-IR, multinuclear NMR (^{1}H, ^{13}C, ^{199}Hg) spectroscopy and X-ray crystallography of complexes **1**, **5** and **6**. The ^{1}H and ^{13}C NMR data suggest that the N^2H group is deprotonated during reaction with phenylmercury(II) acetate and co-ordination occurs *via* the N^3,S atoms in a chelating mode. The ^{199}Hg NMR data suggest symmetrisation phenomenon for complexes **3** and **5**, $2[HgPhL] \rightleftharpoons HgPh_2 + [HgL]$, which is supported also by ^{1}H and ^{13}C NMR data. The δ(Hg) values reveal that shielding of Hg with the change of organic group in the thiosemicarbazones decreases in the order: 2-hydroxybenzene ⋙ furan > benzene > 4-methoxybenzene ≫ thiophene ≈ cyclohexanone ≈ cyclopentanone > pyrrole and the Lewis basicity of the thiosemicarbazones varies in the opposite order. The ^{1}H and ^{13}C NMR data reveal that **7** and **8** show isomerism. There are two strong [Hg–C 2.063(7) **1**, 2.069(10) **5**, 2.049(11) **6**; Hg–S 2.382(2) **1**, 2.357(3) **5**, 2.377(3) Å **6**] and one weak bond [Hg–N^3 2.489(6) **1**, 2.611(7) **5**, 2.492(9) Å **6**], with C_{Ph}–Hg–S bond angles of 162.9(2), 174.2(3), 165.8(3)° respectively. The weak intermolecular interactions *via* Hg · · · N^2 [3.001(6) Å] in **1** and *via* Hg · · · S in **5** [3.518(3) Å] and **6** [3.528(3) Å] form centrosymmetric dimers and Hg formally acquires four-co-ordination with two strong (Hg–C, Hg–S), one weak (Hg · · · N^3) and one secondary (Hg · · · N^2 or S) bonds. The preferred dimer formation *via* N^2 nitrogen in **1**, rather than *via* sulfur atoms (**5** and **6**) despite Hg · · · S affinity represents an unusual bonding mode. From the low-temperature ^{1}H NMR studies of some selected complexes, the energy barrier (ΔG_{T_c}*, T_c is coalescence temperature) to rotation of the amino group about the C^1–N^1 bond was calculated and correlated with bonding parameters of the thioamide group in the solid state.

Heterocyclic thiones and thiosemicarbazones, which contain chemically active N(H)C(S) or =NN(H)C(S) chromophores, are useful model compounds for sulfur-containing analogues of purine and pyrimidine bases, and thus have invited considerable interest in their co-ordination behaviour.[1–6] These compounds as well as their metal derivatives have many biochemical and pharmacological properties.[1,5,7–10] The co-ordination chemistry of thiosemicarbazones with transition metals,[3–6,11–13] which began with Jensen's work,[14] has been more intensively investigated as compared to that of the main group elements.[15–17] Further, there is a continued interest in the binding properties of the organomercury(II) moiety RHg^+, particularly $HgMe^+$, with a variety of sulfur-containing ligands, both due to environmental concern ($HgMe^+$ is produced by bioconversion of metallic Hg in sludge) and to understand the stereochemical properties of RHg^+ moieties bonded to different ligands.[15,18] Further, it has recently been emphasised that activation of the Hg–C bond by co-ordination, followed by protonolysis, is a prerequisite step to detoxify organomercury(II) salts as is done by some bacteria through enzymatic processes.[19]

Only one derivative of thiosemicarbazones with $HgMe^+$, namely, HgMeL (HL = cyclopentanone thiosemicarbazone) has been reported[20] and there is no report of work on phenylmercury(II) [or arylmercury(II) in general] with thiosemicarbazones, though a few mercury(II) complexes with thiosemicarbazones or thiosemicarbazides are known.[21] The co-ordination chemistry of phenylmercury(II) explored with anions derived from aminophenol,[22] quinolinethiol,[23] xanthates,[24] dithiocarbamates,[24,25] dithiophosphinates or phosphates,[26,27] thiouracil [2,3-dihydro-2-thioxo-(1*H*)-pyrimidine-4-one],[28] benzenethiol,[29] dithizone (1,5-diphenylthiocarbazone),[30] thiocarbazonate,[31] pyridine-2-thione[32] and neutral triphenylphosphine[33] reveals the formation of one strong Hg–S (or P) bond with the C_{Ph}–Hg–S angle tending to be generally linear (*ca.* 165–170°). The second bond with N (or S, O) varies from medium to weak in strength.

In view of the pharmacological properties of thiosemicarbazones, and also due to the interest in Hg–C bond-activation properties,[19] in this paper we report the first examples of phenylmercury(II) derivatives of a series of thiosemicarbazones (Scheme 1) usually known to be chelating agents[34] and these are characterised using elemental analysis, IR, multinuclear NMR (^{1}H, ^{13}C, ^{199}Hg) and X-ray crystallography for some complexes. The investigations highlight the phenomena of symmetrisation and isomerism or polymerisation in the solution phase of some complexes. In addition, the barrier to rotation of the amino group (NH_2) about the C^1–N^1 bond is determined in some selected complexes, so as to correlate with the bonding parameters of the thioamide group.



Scheme 1

Experimental

Elemental analyses for C, H and N were obtained with a Carlo-Erba 1108 microanalyser. The melting points were determined with a Gallenkamp electrically heated apparatus. Infrared spectra were recorded in KBr pellets (4000–400 cm^{-1}) or Nujol mull in polyethene sheets (500–100 cm^{-1}) on a Bruker IFS 66V spectrometer, NMR spectra in $CDCl_3$ or $(CD_3)_2SO$ using a Bruker AMX 300 spectrometer at 300.14 and 75.48 MHz (^1H, ^{13}C) with $SiMe_4$ as the internal reference or a Bruker AMX 500 spectrometer at 89.51 MHz probe frequency (^{199}Hg) with $HgMe_2$ as the external reference.

Phenylmercury(II) acetate (Ventron, Karlsruhe), hydrazinecarbothioamide (commonly named thiosemicarbazide; Merck, München), benzaldehyde (Probus, Barcelona), salicylaldehyde (Merck, München), *p*-methoxybenzaldehyde (Ega-Chemie, Steinheim), furan-2-carbaldehyde (Probus, Barcelona), thiophene-2-carbaldehyde (Ega-Chemie, Steinheim), pyrrole-2-carbaldehyde (Aldrich-Chemie, Steinheim), cyclopentanone (Merck, München) and cyclohexanone (Merck, München) were used as received.

Synthesis of ligands

The ligands were prepared by the methods reported earlier.[34–39] One preparation as an example and some characteristics of the ligands are summarised below.

Benzaldehyde thiosemicarbazone (Hbtsc). To a solution of thiosemicarbazide (5.47 g, 0.06 mol) in hot distilled water (*ca.* 75 cm^3) was added slowly benzaldehyde (6 cm^3, 0.06 mol) dissolved in ethanol (70 cm^3). The mixture was refluxed for 6 h and the white product formed was filtered off and dried *in vacuo*. It was recrystallised from ethanol, yield 80%; m.p. 148–150 °C.

Other ligands, namely, 2-hydroxybenzaldehyde thiosemicarbazone (H_2stsc, m.p. 230–232 °C, white), 4-methoxybenzaldehyde thiosemicarbazone (Hmbtsc, m.p. 174–176 °C, white), furan-2-carbaldehyde thiosemicarbazone (Hftsc, 146–148 °C, brown), pyrrole-2-carbaldehyde thiosemicarbazone (Hptsc, 194–196 °C, brown), cyclopentanone thiosemicarbazone (Hcptsc, 150–151 °C, white) and cyclohexanone thiosemicarbazone (Hchtsc, 170–172 °C, light yellow) were prepared similarly. Thiophene-2-carbaldehyde thiosemicarbazone (Htftsc, m.p. 184–186 °C, light green) was prepared similarly, but for the addition of a few cm^3 of glacial acetic acid and refluxing for 1 h only.[39]

Synthesis of complexes

(Cyclopentanone thiosemicarbazonato-N^3,*S*)phenylmercury(II), [HgPh(cptsc)] 1. To a stirred solution of Hcptsc (0.186 g, 1.18 mmol) in ethanol (20 cm^3) was added a solution of phenylmercury(II) acetate (0.400 g, 1.18 mmol) in ethanol (20 cm^3). The mixture was stirred at room temperature (*ca.* 25 °C) for 4 h, concentrated under vacuum and left at room temperature to solidify. The light yellow solid was filtered off, crystallised from EtOH and dried *in vacuo*; m.p. 145–150 °C (decomp.), yield 60% (Found: C, 33.1; H, 3.43; N, 9.46. $C_{12}H_{15}HgN_3S$ requires C, 33.2; H, 3.45; N, 9.67%). It is soluble in $CHCl_3$, CH_2Cl_2, dimethyl sulfoxide (dmso), EtOH and MeOH. It decomposes slowly in dmso.

(Cyclohexanone thiosemicarbazonato-N^3,*S*)phenylmercury(II), [HgPh(chtsc)] 2. To a suspension of Hchtsc (0.152 g, 0.89 mmol) in ethanol (20 cm^3) was added a solution of phenylmercury(II) acetate (0.300 g, 0.89 mmol) in ethanol (20 cm^3). The mixture was stirred for 3 h at room temperature (20–25 °C), filtered and the filtrate left in a refrigerator. After 24 h very fine light yellow crystals of the complex formed and were dried at room temperature, m.p. 125–130 °C (decomp.), yield 52% (Found: C, 34.9; H, 3.60; N, 9.32. $C_{13}H_{17}HgN_3S$ requires C, 34.8; H, 3.79; N, 9.37%). It is soluble in $CHCl_3$, CH_2Cl_2, dmso, EtOH and MeOH. It decomposes slowly in dmso.

(Benzaldehyde thiosemicarbazonato-N^3,*S*)phenylmercury(II), [HgPh(btsc)] 3. To a stirred solution of Hbtsc (0.266 g, 1.48 mmol) in ethanol (20 cm^3) was added a solution of phenylmercury(II) acetate (0.500 g, 1.48 mmol) in ethanol (20 cm^3) at room temperature (20–25 °C). The mixture was stirred for about 2 h when a light green compound was formed. It was filtered off, washed with EtOH and dried *in vacuo*, m.p. 140–150 °C (decomp.), yield 77% (Found: C, 35.9; H, 2.70; N, 8.71. $C_{14}H_{13}HgN_3S$ requires C, 36.8; H, 2.85; N, 9.21%). It is partially soluble in $CHCl_3$, CH_2Cl_2, acetone, and poorly soluble in MeOH and EtOH. It decomposes in dmso.

(2-Hydroxybenzaldehyde thiosemicarbazonato-N^3,*S*)phenylmercury(II), [HgPh(Hstsc)] 4. To a stirred solution of H_2stsc (0.175 g, 0.90 mmol) in ethanol (30 cm^3) was added a solution of phenylmercury(II) acetate (0.300 g, 0.89 mmol) in ethanol (25 cm^3). The mixture was stirred for 2 h and the light creamy white solid formed was filtered off, washed with ethanol and dried *in vacuo*, m.p. 190–192 °C (decomp.), yield 83% (Found: C, 35.8; H, 2.71; N, 8.79. $C_{14}H_{13}HgN_3OS$ requires C, 35.6; H, 2.75; N, 8.90%). It is partially soluble in $CHCl_3$, CH_2Cl_2 and poorly soluble in EtOH and MeOH. It is stable in dmso for a few days.

(4-Methoxybenzaldehyde thiosemicarbazonato-N^3,*S*)phenylmercury(II), [HgPh(mbtsc)] 5. To a stirred solution of Hmbtsc (0.186 g, 0.89 mmol) in ethanol (25 cm^3) was added a solution of phenylmercury(II) acetate (0.300 g, 0.89 mmol) in ethanol (20 cm^3). The contents were stirred at room temperature (20–25 °C) for 5 h and the light yellow solid formed was filtered off, washed with ethanol and dried *in vacuo*, m.p. 135–140 °C (decomp.), yield 58% (Found: C, 36.8; H, 3.07; N, 8.65. $C_{15}H_{15}HgN_3OS$ requires C, 37.0; H, 3.09; N, 8.64%). It is partially soluble in $CHCl_3$, CH_2Cl_2, MeCN, poorly soluble in MeOH and EtOH. It decomposes in dmso.

Phenyl(pyrrole-2-carbaldehyde thiosemicarbazonato-N^3,*S*)-mercury(II), [HgPh(ptsc)] 6. To a stirred solution of Hptsc (0.150 g, 0.89 mmol) in ethanol (25 cm^3) was added a solution of phenylmercury(II) acetate (0.300 g, 0.89 mmol) in ethanol (25

cm^3). The mixture was stirred for 4 h and filtered and the filtrate left in a refrigerator for a few days. The light brown crystals formed were dried *in vacuo*, m.p. 150–155 °C (decomp.), yield 52% (Found: C, 32.6; H, 2.41; N, 12.29. $C_{12}H_{12}HgN_4S$ requires C, 32.4; H, 2.70; N, 12.58%). It is soluble in $CHCl_3$, CH_2Cl_2, EtOH, MeOH and dmso.

Phenyl(thiophene-2-carbaldehyde thiosemicarbazonato-*N*^{3},*S*)mercury(II), [HgPh(tftsc)] 7. To a stirred solution of Htftsc (0.165 g, 0.89 mmol) in ethanol (25 cm^3) was added a solution of phenylmercury(II) acetate (0.300 g, 0.89 mmol) in ethanol (25 cm^3). The mixture was stirred for 10 h at room temperature (20–25 °C) and the light yellow solid was filtered off, washed with ethanol and dried *in vacuo*, m.p. 130–135 °C (decomp.), yield 46% (Found: C, 31.3; H, 2.33; N, 9.06. $C_{12}H_{11}HgN_3S_2$ requires C, 31.2; H, 2.38; N, 9.09%). It is soluble in $CHCl_3$, CH_2Cl_2, acetone and dmso, and partially soluble in EtOH and MeOH.

(Furan-2-carbaldehyde thiosemicarbazonato-*N*^{3},*S*)phenylmercury(II), [HgPh(ftsc)] 8. To a stirred solution of Hftsc (0.200 g, 1.18 mmol) in ethanol (25 cm^3) was added a solution of phenylmercury(II) acetate (0.400 g, 1.18 mmol) in ethanol (20 cm^3). The mixture was stirred overnight at room temperature (20–25 °C) and the light yellow product formed was filtered off, washed with ethanol and dried *in vacuo*, m.p. 140–150 °C (decomp.), yield 76% (Found: C, 31.7; H, 2.16; N, 9.10. $C_{12}H_{11}HgN_3OS$ requires C, 32.3; H, 2.47; N, 9.42%). It is soluble in $CHCl_3$, CH_2Cl_2 and dmso, but partially soluble in MeOH or EtOH. It is relatively stable in dmso.

Crystallography

Table 1 contains crystal data and experimental conditions for all the three compounds (**1**, **5** and **6**). The intensities of reflections were measured at 293 K on a MACH 3 Enraf-Nonius diffractometer (Mo-Kα radiation, λ 0.710 93 Å) in the range θ 2–27° using the ω-scan technique. The intensities were corrected for Lorentz-polarisation factors. Empirical absorption corrections were applied.[40a]

The structures of the compounds were solved by the heavy atom method,[40b] the positions of the metal and sulfur atoms being deduced from a Patterson map; the other non-hydrogen atoms were located successively by repeated Fourier synthesis. Hydrogen atoms were included in the model at geometrically calculated positions.[40c] For compound **1** the analysis of variance indicated an extinction correction should be performed where the factor k refined at 0.0189(14) in the expression $F_c^* = kF_c(1 + 0.001F_c^2\lambda^3/\sin 2\theta)^{-\frac{1}{4}}$. Refinements on F^2 for all reflections with non-hydrogen atoms with individual anisotropic thermal parameters were performed with the weighting scheme $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$ and x, y are 0.0670, 0.9276; 0.0484, 8.6734; and 0.0669, 0.0000 for **1**, **5** and **6** respectively. Scattering factors, dispersion corrections and absorption coefficients were taken from the literature.[40d]

CCDC reference number 186/686.

Results and Discussion

Solid-state studies

Stoichiometry and general comments. The analytical and spectral data reveal that the reactions of phenylmercury(II) acetate with thiosemicarbazones in dry ethanol occur at room temperature (20–25 °C) involving deprotonation of the most acidic hydrazinic proton, N^{2}H and form phenylmercury(II) thiosemicarbazonates of general formula [HgPhL] [equation (1)]

$$[HgPh(O_2CMe)] + HL \xrightarrow{EtOH} [HgPhL] + MeCO_2H \quad (1)$$

where HL represents a thiosemicarbazone (Scheme 1). These

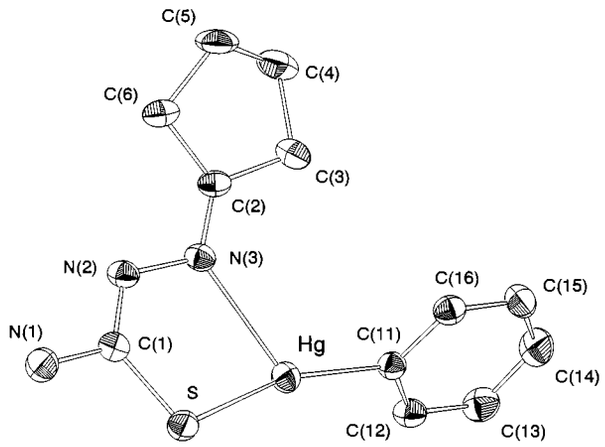


Fig. 1 An ORTEP[41] plot showing the molecular structure of [HgPh(cptsc)] **1** with the atom numbering scheme. The thermal ellipsoids correspond to 40% probability

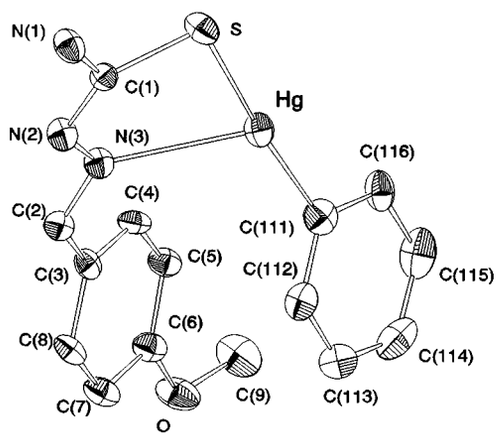


Fig. 2 An ORTEP plot showing the molecular structure of [HgPh(mbtsc)] **5**. Details as in Fig. 1

compounds vary in colour from creamy white to light yellow or light green, melt with decomposition (to black) in the temperature range 125–195 °C, have partial to complete solubility in the common organic solvents such as chloroform, dichloromethane, alcohols, dmso, *etc.*, are stable to light and moisture in solution and solid phases, more so in the latter, although generally decompose in dmso if left in solution for long and are thermally unstable. The crystal and molecular structures of the complexes **1**, **5** and **6**, and the IR spectroscopic properties of the products in the solid are now described.

Crystal and molecular structures. The atomic numbering schemes of [HgPh(cptsc)] **1**, [HgPh(mbtsc)] **5** and [HgPh(ptsc)] **6** are shown in Figs. 1–3; crystal data and bond lengths/angles are listed in Tables 1 and 2 respectively. Figs. 4–6 show the corresponding stereoscopic views of the unit cells of the three compounds. In all the compounds the ligands adopt the *Z* configuration and mercury is co-ordinated by the phenyl carbons, and by S and N^3 atoms of the thiosemicarbazonates, giving rise to a distorted T-shaped stereochemistry around the Hg centre.

The Hg–C bond distances 2.063(7), 2.069(10) and 2.049(11) Å in complexes **1**, **5** and **6** respectively are in the accepted range of unperturbed mercury–carbon bonds (2.05–2.09 Å).[42] All these Hg–C bonds are shorter than that in the analogous [HgMe(cptsc)] [Hg–C 2.09(1) Å].[20] This difference is attributed to the possibility of electron flow from mercury to π* orbitals of the phenyl group in the phenylmercury(II) complexes. The Hg–S bond distances, 2.382(2) **1**, 2.357(3) **5**, 2.377(3) Å **6** are similar to that in [HgMe(cptsc)] [2.380(3) Å],[20] though **5** shows the shortest distance among all these four compounds. The Hg–N^3 bond distances [2.489(6) **1**, 2.611(7) **5**, 2.492(9) Å **6**] are

Table 1 Crystallographic data for compounds **1**, **5** and **6**

	1	**5**	**6**
Formula	$C_{12}H_{15}HgN_3S$	$C_{15}H_{15}HgN_3OS$	$C_{12}H_{12}HgN_4S$
M	433.92	485.94	444.91
Crystal class	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	8.0457(11)	9.139(2)	13.619(2)
b/Å	8.7548(10)	10.2465(12)	5.4296(4)
c/Å	10.3494(11)	17.057(2)	18.410(2)
α/°	82.182(9)		
β/°	68.572(10)	101.824(13)	97.911(9)
γ/°	86.445(12)		
U/Å^3	672.24(14)	1563.4(4)	1348.4(2)
Z	2	4	4
D_c/g cm^{-3}	2.144	2.065	2.192
Crystal size/mm	0.15 × 0.30 × 0.40	0.40 × 0.40 × 0.25	0.40 × 0.15 × 0.10
Colour	White	Pale yellow	Brown
μ/mm^{-1}	11.585	9.979	11.556
F(000)	408	920	832
Transmission factor	0.386	0.326	0.284
θ Range/°	2.35–26.30	2.33–26.23	2.51–26.22
h,k,l Ranges	0, 10; −10, 10; −11, 12	−11, 11; 0, 12; −21, 0	−16, 16; −6, 0; 0, 22
Total no. reflections measured	2920	3280	2826
No. unique reflections, R_{int}	2719, 0.0323	3175, 0.0399	2733, 0.0557
No. reflections with $I > 2\sigma(I)$, parameters	2481, 155	2226, 197	1672, 164
R,[a] R' [b]	0.0364, 0.0950	0.0403, 0.0910	0.0423, 0.0984
S[c] on F^2	1.117	1.031	1.007
Peak, hole/e Å^{-3}	2.699, −2.079	1.730, −2.090	1.584, −0.843

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, where n = total number of reflections measured, p = number of parameters.

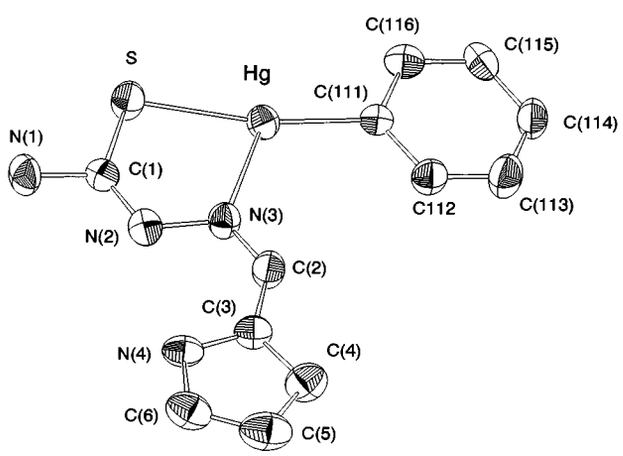


Fig. 3 An ORTEP plot showing the molecular structure of [HgPh(ptsc)] **6**. Details as in Fig. 1

comparable but lie on the two extremes of the distance [Hg–N^3 2.537(8) Å] shown by [HgMe(cptsc)],[20] with **5** showing the longest Hg–N^3 bond distance. All these distances are shorter than the usual lengths of so-called secondary bonds.[42] The co-ordination of nitrogen N^3 of the thiosemicarbazonates in **1**, **5** and **6** leads to the formation of five-membered chelate rings, necessitating deviation of C_{Ph}–Hg–S bond angles from linearity [162.9(2) **1**, 174.2(3) **5**, 165.8(3)° **6**], as shown by [HgMe(cptsc)] (C–Hg–S 167.7°).[20] It is interesting that the C–Hg–S bond angle increases with the increase in Hg–N bond length both being consequences of the steric demands of S,N chelation.

Compound **5** shows relatively the longest C(1)–S bond distance as compared to that in **1** or **6** (Table 2). Further, all these bonds are shorter than a C–S single bond (1.81 Å) but longer than a C–S double bond (1.62 Å),[43] suggesting partial double-bond character in the complexes, similar to related thiosemicarbazonates of methylmercury(II) and dimethylthallium(III).[20,38] The C^2–N^3 bond distances conform with the double-bond distances [d(C=N) 1.28 Å][43] and deprotonation of the hydrazinic N^{2}H proton induces double-bond character with the result that the C^1–N^2 bond lengths are close to those of C–N double bonds (Table 2).[20,38] It also suggests that the thiosemicarbazones in these three and other complexes are acting as uninegative chelating ligands. The substituents at C(2) affect the C(2)–N(3) bond distance marginally, more so in the case of **5**. The amidic C^1–N^1 bonds have similar lengths to C–N double bonds,[43] suggesting considerable double-bond character induced by electron delocalisation of the lone pair on the NH_2 group along the C^1–N^1 bond; this bond is somewhat shorter in **5** than in **1** and **6**.

The *endo*-metallacyclic bond angles do not differ significantly except for the N^2–N^3–Hg bond angle [111.0(5) **5**, 115.4(4) **1**, 117.5(7)° **6**]. Nearly the same bite angle S–Hg–N^3 in all these cases and the narrowest *exo*-metallacyclic C_{Ph}–Hg–N^3 bond angle in **5** [109.9(3) **5**, 120.3(2) **1**, 118.4(4)° **6**] suggest that the phenyl bonded to Hg shifts towards the HgN^{3}C^2 moiety, thus increasing the C_{Ph}–Hg–S bond angle. Except for Hg–N^3–C^2, the *exo*-metallacyclic bond angles [127.2(8) **6**, 130.0(5) **1**, 129.0(6)° **5**], the other bond angles differ marginally.

From the above discussion on bond lengths and angles the following conclusions are worthy of mention: (*i*) *p*-methoxybenzene substituent at C^2 carbon causes the most pronounced structural changes among all the three complexes; (*ii*) low thermal or solution-phase stability is due to the weakest N^2–N^3 bond in the Hg–S–C^1–N^2–N^3 metallacyclic ring; (*iii*) except for the N^2–N^3–Hg bond angle of this ring, other *endo*-metallacyclic bond angles do not change significantly, and (*iv*) the *exo*-metallacyclic bond angles, C^2–N^3–Hg, N^3–Hg–C_{Ph} and C_{Ph}–Hg–S, are most susceptible to changes with the nature of the ligand and major variations are observed in case of **5**, among the complexes characterised crystallographically.

All the three compounds (**1**, **5** and **6**) exist as centrosymmetric dimers in the solid state. In **1** the dimerisation involves interaction of the N^2 pair with the Hg atom of a second molecule (Fig. 4), while in **5** and **6** it occurs *via* sulfur atoms (Figs. 5 and 6). In **1** the Hg · · · N^2 bond distance of 3.001(6) Å is somewhat less than the sum of van der Waals radii (1.73 + 1.55 = 3.28 Å)[44] and the S · · · Hg distances of 3.518(3) and 3.528(3) Å in **5** and **6** respectively are close to or more than the sum of the van der Waals radii (3.5 Å).[44b]

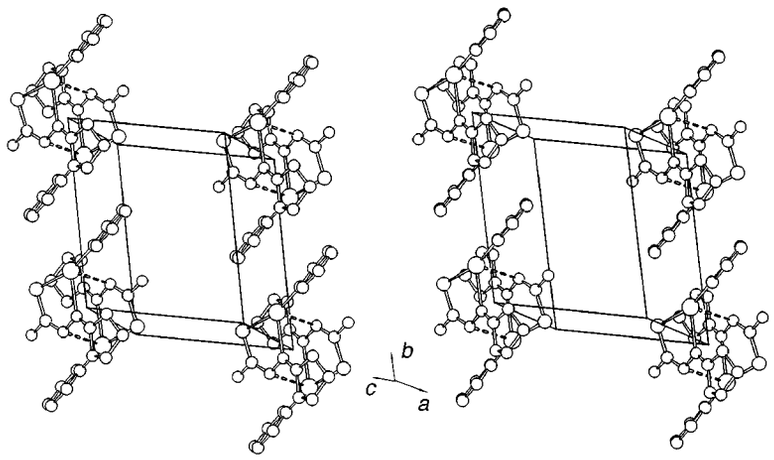


Fig. 4 Stereoview of the structure of [HgPh(cptsc)] **1** showing weak intra- and inter-molecular interactions

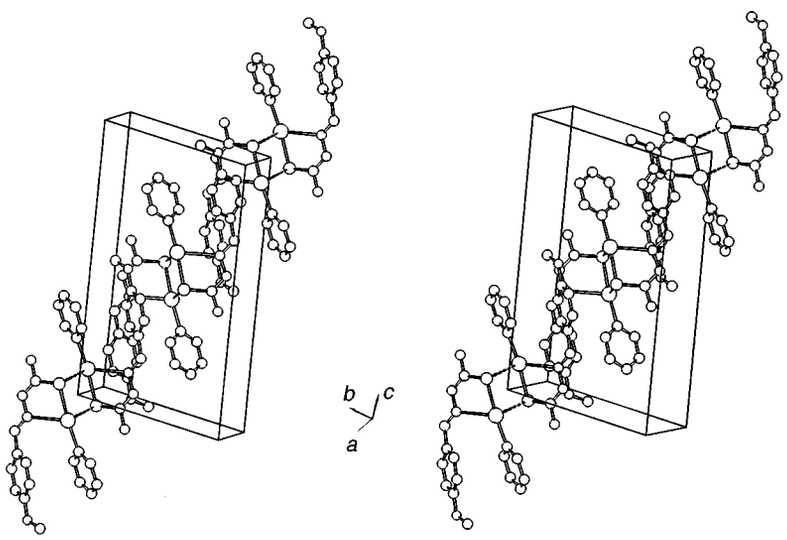


Fig. 5 Stereoview of the structure of [HgPh(mbtsc)] **5**. Details as in Fig. 4

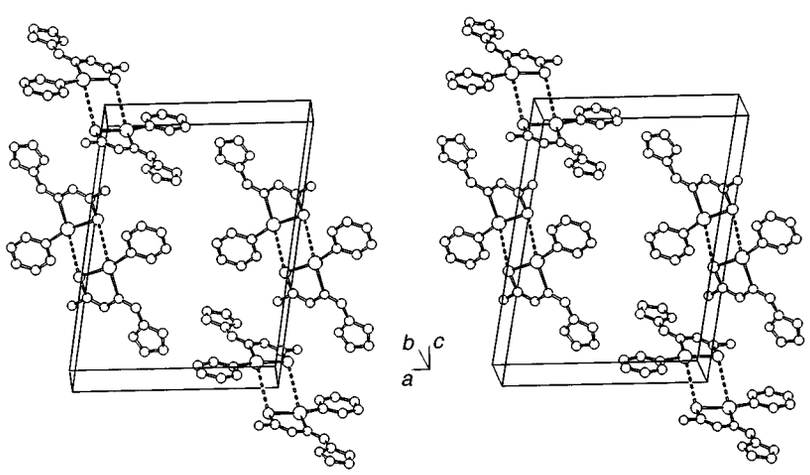


Fig. 6 Stereoview of the structure of [HgPh(ptsc)] **6**. Details as in Fig. 4

Infrared spectra. Table 3 shows the main IR bands for the ligands and their complexes. The bands assigned to ν(N–H) in the ligands thiosemicarbazones [for H_2stsc contributed to by ν(OH)] can be split into two classes: (*i*) those located between 3450 and 3200 cm^{-1}, due to the NH_2 group, and (*ii*) two or a broad band close to 3150 cm^{-1} due to the NH group. As a consequence of the deprotonation, this last band disappears in the spectra of the complexes, although for the Hchtsc, Hbtsc and Hftsc derivatives a medium band remains around 3100 cm^{-1} and a detailed inspection reveals that it is due to the substituent at C(2). The position of the NH_2 bands in the spectra of all the complexes is indicative [38a] of non-participation of this group in the co-ordination to the Hg^{II} as was shown by X-ray diffraction studies for **1**, **5** and **6** (see above) and solution-phase studies (see below).

This study shows that in the three complexes mentioned above the co-ordination of the thiosemicarbazone moiety is *via* the S and N(3) atoms. The co-ordination by S induces changes in the bands around 1100 and 800 cm^{-1}, which disappear for the complexes [since close to these positions the complexes

Table 2 Selected bond lengths (Å) and angles (°)

(*a*) [HgPh(cptsc)] **1**

Hg–C(11)	2.063(7)	N(2)–C(1)	1.302(9)
Hg–S	2.382(2)	N(2)–N(3)	1.403(8)
Hg–N(3)	2.489(6)	N(3)–C(2)	1.264(9)
S–C(1)	1.751(7)	Hg · · · N(2′)	3.001(6)
N(1)–C(1)	1.348(9)		
C(11)–Hg–S	162.9(2)	C(2)–N(3)–Hg	130.0(5)
C(11)–Hg–N(3)	120.3(2)	N(2)–N(3)–Hg	115.4(4)
S–Hg–N(3)	75.69(13)	N(2)–C(1)–N(1)	116.8(7)
C(11)–Hg–N(2′)	93.3(2)	N(2)–C(1)–S	129.1(6)
S–Hg–N(2′)	96.86(12)	N(1)–C(1)–S	114.0(5)
N(3)–Hg–N(2′)	76.6(2)	N(3)–C(2)–C(6)	127.9(7)
C(1)–S–Hg	101.4(2)	N(3)–C(2)–C(3)	122.3(7)
C(1)–N(2)–N(3)	114.5(6)	C(12)–C(11)–Hg	121.9(5)
C(2)–N(3)–N(2)	114.6(6)	C(16)–C(11)–Hg	120.9(5)

(*b*) [HgPh(mbtsc)] **5**

Hg–C(111)	2.069(10)	N(2)–C(1)	1.296(11)
Hg–S	2.357(3)	N(2)–N(3)	1.384(10)
Hg–N(3)	2.611(7)	N(3)–C(2)	1.292(11)
S–C(1)	1.781(9)	S · · · Hg′	3.518(3)
N(1)–C(1)	1.339(11)		
C(111)–Hg–S	174.2(3)	C(2)–N(3)–Hg	129.0(6)
C(111)–Hg–N(3)	109.9(3)	N(2)–N(3)–Hg	111.0(5)
S–Hg–N(3)	75.4(2)	N(2)–C(1)–N(1)	117.4(8)
C(1)–S–Hg	100.6(3)	N(2)–C(1)–S	130.0(7)
C(1)–S–Hg′	84.7(3)	N(1)–C(1)–S	112.6(7)
Hg–S–Hg′	89.90(8)	N(3)–C(2)–C(3)	121.1(8)
C(1)–N(2)–N(3)	115.7(7)	C(112)–C(111)–Hg	118.3(8)
C(2)–N(3)–N(2)	113.2(7)	C(116)–C(111)–Hg	121.2(8)

(*c*) [HgPh(ptsc)] **6**

Hg–C(111)	2.049(11)	C(4)–C(3)	1.37(2)
Hg–S	2.377(3)	C(4)–C(5)	1.38(2)
Hg–N(3)	2.492(9)	C(2)–C(3)	1.43(2)
S–C(1)	1.742(11)	C(3)–N(4)	1.351(14)
N(1)–C(1)	1.36(2)	N(4)–C(6)	1.33(2)
N(2)–C(1)	1.30(2)	C(6)–C(5)	1.37(2)
N(2)–N(3)	1.400(12)	S · · · Hg′	3.528(3)
N(3)–C(2)	1.28(2)		
C(111)–Hg–S	165.8(3)	N(2)–C(1)–S	130.6(9)
C(111)–Hg–N(3)	118.4(4)	N(1)–C(1)–S	112.2(9)
S–Hg–N(3)	75.8(2)	N(3)–C(2)–C(3)	132.7(12)
C(1)–S–Hg	102.4(4)	N(4)–C(3)–C(4)	107.0(11)
C(1)–S–Hg′	125.7(4)	N(4)–C(3)–C(2)	125.8(11)
Hg–S–Hg′	96.86(10)	C(4)–C(3)–C(2)	127.2(12)
C(1)–N(2)–N(3)	113.4(9)	C(6)–N(4)–C(3)	110.9(12)
C(2)–N(3)–N(2)	115.2(10)	N(4)–C(6)–C(5)	107.1(14)
C(2)–N(3)–Hg	127.2(8)	C(6)–C(5)–C(4)	108.1(14)
N(2)–N(3)–Hg	117.5(7)	C(112)–C(111)–Hg	121.7(8)
C(3)–C(4)–C(5)	106.9(14)	C(116)–C(111)–Hg	121.6(9)
N(2)–C(1)–N(1)	117.2(10)		

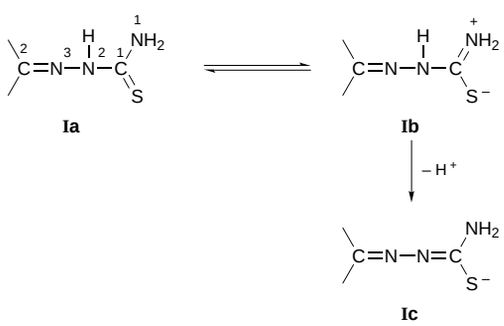
Primed atoms are related to unprimed ones by the symmetry transformations $-x$, $-y$, $-z$.

show bands due to the phenyl ring (see below), the possibility that these bands involve ν(C=S) cannot be excluded] and nitrogen co-ordination shifts ν(C=N) slightly to higher wavenumbers, which led to a spectroscopic pattern similar to those previously found for compounds with a similar co-ordination mode.[38a,45] The similarity of this pattern for all the complexes prepared in this work suggests also a similar S,N co-ordination mode. This mode is compatible with the presence of a medium band around 350 cm^{-1} assigned as ν(Hg–S), however a rigorous assignment of ν(Hg–N) was not possible. We have not found significant spectroscopic differences in the thiosemicarbazone ligand pattern which are indicative of the two different structural arrangements in the solid, namely Hg–N(2) (*e.g.* **1**) or Hg–S (*e.g.* **5** and **6**) secondary interactions. Besides the bands shown in Table 3, we found other bands, not shown, due to the phenylmercury ring[46] [for instance, 1590 (sh), 1477m, 1430m, 1020m, 998m, 729vs, 700vs, 451s, 237w, 201s and 180 (sh) for **1**] which are practically at the same position for all the complexes, and others from the substituent at C(2) [for instance, 1283s, 1267s, ν(C–O), for H_2stsc and 1283s, 1265s for **4**] that in all cases, where it is possible, reveal non-participation of this substituent in the mercury co-ordination.

Solution-phase studies

N^3,S-Co-ordination mode of thiosemicarbazones (^{1}H and ^{13}C NMR spectra). The hydrazinic group N^2H of the free thiosemicarbazones shows a strong and generally broad peak in the range δ 8.42–11.43 (Table 4) and the absence of this signal for all the phenylmercury(II) thiosemicarbazonates reveals deprotonation. Also, the signals of the OH group of H_2stsc shift to low field for compound **4** and there is no deprotonation; similarly, the N^4H group of the pyrrole ring of Hptsc is not deprotonated and shows slight changes in its peak position. Thus, the thiosemicarbazones co-ordinate to $PhHg^{II}$ as singly charged anionic ligands.

The N^1H_2 protons of the thioamide in the free thiosemicarbazones show two broad peaks in ranges δ 7.17–8.12 and 6.29–7.97 respectively at room temperature which are attributed to the restricted rotation of this group about the C^1–N^1 bond axis due to the delocalisation of the lone pair on the N^1H_2 nitrogen (**Ia**,**Ib**). These protons generally show a single broad signal for the complexes (at high-field positions in the range δ 4.9–5.92, Table 4) because deprotonation of N^2H groups leads to the structure **Ic** and reduction in the double-bond character of the C^1–N^1 bond makes possible free rotation of the NH_2 group about the C–N bond at room temperature. The appearance of more than one N^1H_2 proton signal for some complexes suggests more than one species in the solution phase (see below).



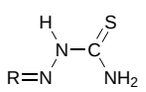
The upfield shifts of N^1H_2 protons are also consistent with the formation of species **Ic**. On the other hand, low-temperature ^{1}H NMR studies (see below) clearly demonstrate the presence of an unco-ordinated N^1H_2 group. So, it appears that co-ordination by the N^3,S donor atoms forming stable five-membered chelate rings is favoured over N^2,S and N^1,S which form relatively less stable four-membered chelate rings. The N^2,S mode of binding is rare,[34] but there is no evidence for the N^1,S binding mode.[3–6]

The azomethine proton, C^2H, does not show a regular trend in the complexes and the variations of the position of its signal are more complicated. For instance, compounds **3**, **4** and **6** showed upfield shifts while **5**, **7** and **8** showed low-field shifts relative to the free thiosemicarbazones. The ligand ring protons reveal small low-field shifts in the complexes and unresolved multiplets for the free thiosemicarbazones are resolved for some of the complexes (Table 4). Finally, HgPh protons are assigned in compounds **1**, **2**, **4**–**6**, but in **3**, **7** and **8** these are obscured by the ligand ring protons.

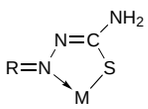
The ^{13}C NMR data reveal that phenylmercury(II)–thiosemicarbazone interactions affect mainly C^1 and C^2 carbons; other ligand ring or HgPh carbons are either marginally affected or remain unchanged in several cases (Table 5). The deprotonation

Table 3 Main IR bands (cm^{-1}) for phenylmercury(II) thiosemicarbazonates

Compound	ν(N–H)	δ(NH_2)	ν(C=N)	ν(C=S)	ν(Hg–S)
1	3449s, 3338s	1640m	1591m	1065w	373 (sh), 353m
2	3445m, 3281m, 3163m	1624s	1605s	1070w	335m
3	3439m, 3268s, 3105m (br)	1623m	1592m		337m (br)
4	3486m, 3383m	1622 (sh), 1600 (sh)	1595s, 1567m		323m (vbr)
5	3435m, 3274m	1629m	1606s, 1590m		336w
6	3454m, 3364s, 3340s	1630 (sh)	1606s, 1575m		
7	3436m, 3340m, 3268m	1622m	1582s, 1573s		345m (br)
8	3429m, 3264m, 3117m (br)	1622s (br)	1622s (br), 1574m		331m
Hcptsc	3382s, 3234s, 3184s, 3144s	1662m	1589s	1079s, 1035m, 822m	
Hchtsc	3381s, 3217s, 3145s	1643m	1586s	1084s, 1075s, 833s	
Hbtsc	3423s, 3253s, 3156s	1591s (br)	1591s (br)	1102m, 1058m, 817m	
H_2stsc	3446m, 3321s, 3175m (br)	1616s	1605s	1062m, 1036m, 830m	
Hmbtsc	3406m, 3291m, 3152m	1606s (br)	1606s (br)	1088s, 1057m, 815m	
Hptsc	3449m, 3303s, 3273s, 3152m (br)	1670m	1590s	1124m, 836m	
Htftsc	3415m, 3235m, 3150s (br)	1611s	1596m, 1580m	1103m, 1062m, 837m	
Hftsc	3413m, 3400m, 3220m	1617m	1590s	1124m, 836m	



II, *E*



III, *Z*

of N^2H protons of thiosemicarbazones and upfield shift of C^1 carbons in the complexes suggest the electron delocalisation in **Ia–Ic**.[34,38,45]

The accumulation of negative charge density on sulfur, the low-field shift of C^2 relative to that of the ligands and the affinity of sulfur for Hg^{II} all suggest co-ordination *via* N^3 and S. Thus, the thiosemicarbazones are acting as N^3,S-chelating agents and change from an *E* (**II**) to a *Z* configuration (**III**) in the complexes.[38,45] Hence, the N^3,S-chelating mode of the thiosemicarbazonates found in the solid state is retained in solution.

^{199}Hg NMR spectra and symmetrisation. Table 6 contains ^{199}Hg NMR data for phenylmercury(II) thiosemicarbazonates. Except for **3** and **5**, all compounds showed one signal each indicating the presence of only one type of chemical environment about the Hg^{II}. The δ(Hg) values suggest that the shielding of Hg with the change of the R group in thiosemicarbazones varies in the sequence: 2-hydroxybenzene ⋙ furan > benzene > 4-methoxybenzene ⩾ thiophene ≈ cyclohexanone ≈ cyclopentanone > pyrrole. It is known that ligands which more effectively donate electrons to Hg^{II} are expected to show lower shielding.[47] Thus, the Lewis basicity of the present thiosemicarbazones varies in the sequence: Hptsc > Hcptsc ≈ Hchtsc ≈ Htftsc ⩾ Hmbtsc > Hbtsc > Hftsc ⋙ H_2stsc. The chemical shift values δ(Hg) of phenylmercury(II) thiosemicarbazonates are similar to those of phenylmercury(II) dithiophosphinates,[26] [$HgPh(S_2PR_2)$] [δ(in $CDCl_3$): R = Et, −898; C_6H_{11}, −871; Ph, −926] having one strong Hg–S (2.375 Å), two weak intra- and inter-molecular Hg–S bonds (*ca.* 3.182 Å) and a C_{Ph}–Hg–S bond angle of 177.0°. The range of δ(Hg), −672 to −953 (Table 6), is fairly wide due to the variety of substituents. A comparison of the δ(Hg) values with those of phenylmercury(II) halides/acetate, [HgPhX] [δ(dmso): X = Cl, −1187; Br, −1287; I, −1459; O_2CMe, −1365] or related [HgMe(SR)] derivatives [δ($CDCl_3$): R = Ph, −553; $C_6H_4SSiMe_3$, −566][48] suggest that the shielding of Hg in thiosemicarbazonates lies between these two extremes, keeping in mind the effect of the solvent.

For compounds **3** and **5**, the signals at δ −749 and −750 respectively correspond to the formation of $HgPh_2$ in $CDCl_3$ solution[49] (Fig. 7), equation (2) (HL = Hbtsc or Hmbtsc). This

$$\underset{\mathbf{A}}{2[HgPhL]} \rightleftharpoons \underset{\mathbf{B}}{[HgL_2]} + \underset{\mathbf{C}}{HgPh_2} \qquad (2)$$

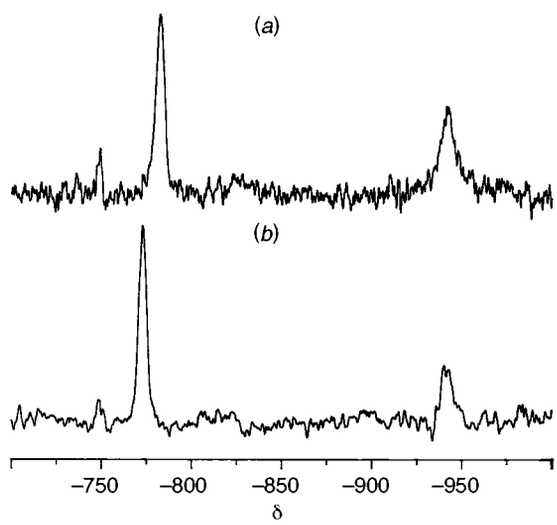


Fig. 7 The ^{199}Hg NMR spectra (297 K) of (*a*) [HgPh(btsc)] **3** and (*b*) [HgPh(mbtsc)] **5**

shows that **3** and **5** undergo symmetrisation.[49–52] The signals at δ −783 and −773 of **3** and **5** respectively are due to the unsymmetrised [HgPhL] moiety (species **A**), and obviously the signals at δ −941 and −942 are assigned to the second symmetrised product (species **B**).

The integrals of the N^1H_2 proton signals for compound **3** reveal the presence of 40 and 60% of species **A** and **B** respectively in solution; **5** showed slightly different percentages, 38 and 62%, of similar species. Further, **5** showed three N^1H_2 proton signals unlike two shown by **3** (probably, species **B** of **5** shows two signals) (Table 4). Separate signals for azomethine (C^2H) protons, most of the ligand ring protons (Table 4), as well as ^{13}C NMR signals for C^1, C^2 and ligand ring carbons for **A** and **B** species were obtained (Table 5).

From the observation that symmetrisation occurred when the organic group was benzaldehyde (**3**) or 4-methoxybenzaldehyde (**5**) and not in other cases, it is inferred that organic groups of thiosemicarbazones have some role in this phenomenon.

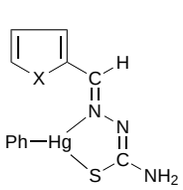
Isomerism or dimerisation in phenylmercury(II) thiosemicarbazonates. It is interesting that the ^{199}Hg NMR spectrum of compound **7** showed one signal indicating one type of chemical environment about Hg^{II}; however, the ^{1}H NMR as well as the ^{13}C NMR data reveal three peaks each for N^1H_2, C^2H and for most of the ligand ring protons, except those obscured by HgPh and chloroform protons (Tables 4 and 5). These data suggest three different chemical environments affecting various protons

Table 4 The ^{1}H NMR spectral data (δ)[a] for phenylmercury(II) thiosemicarbazonates

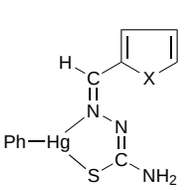
Compound	N^1H_2	N^2H (OH, N^4H)	C^2H	Ligand ring protons	PhHg protons
1[b]	5.00s (br)	—	—	2.60 (t, $C^{3,6}H_2$)	7.44 (m, *o*)
				2.45 (t, $C^{3,6}H_2$)	7.36 (m, *m*)
				1.72 (m, $C^{4,5}H_2$)	7.25 (m, *p*)
2[b]	4.94s (br)	—	—	2.77 (t, $C^{3,7}H_2$)	7.44 (m, *o*)
				2.45 (s br, $C^{3,7}H_2$)	7.38 (m, *m*)
				1.67 (t, $C^{4,5,6}H_2$)	7.24 (m, *p*)
				1.60 (t, $C^{4,5,6}H_2$)	
3[b]	5.91 (s vbr, **A**)[c]	—	8.40 (s, **A**)	7.91 (d, **A**, $C^{4,8}H$)	7.51 (m)[d]
	5.10 (s br, **B**)[c]		8.81 (s, **B**)	7.80 (d, **B**, $C^{4,8}H$)	
				7.51 (m, $C^{5,6,7}H$)[c]	
4[b]	5.49 (s br)	11.12 (OH)	8.26 (s)	7.43 (s br, C^5H)	7.40 (s br, *o*)
				7.23 (t, C^6H)	7.33 (m, *m*)
				6.97 (d, C^8H)	7.26 (m, *p*)[e]
				6.90 (t, C^7H)	
5[b]	5.92 (s vbr, **A**)[c]	—	8.11 (**A**)	8.16 (d, **A**, $C^{5,7}H$)	7.50 (m, *o*)
	5.07 (s br, **B**)[c]		8.54 (**B**)	7.62 (d, **B**, $C^{5,7}H$)	7.43 (m, *m*)
	5.28 (s br, **B**)[c]			6.54 (m, **A**, $C^{4,8}H$)	7.30 (m, *p*)[e]
				6.91 (d, **B**, $C^{4,8}H$)	
				3.70 (s, **A**, C^9H_3)	
				3.85 (s, **B**, C^9H_3)	
6[b]	5.21 (s br)	11.27 (N^4H)	7.46 (s)	7.01 (d, C^6H)	7.41 (m, *o*)
				6.57 (s br, C^4H)	7.35 (m, *p*)
				6.27 (dd, C^5H)	7.22 (m, *m*)
7[b,f]	5.86 (s vbr, **i**)	—	8.27 (s, **i**)	7.45 (d, **i**, C^6H)	7.35 (m)[e,g]
	5.32 (s br, **ii**)		8.66 (s, **ii**)	7.58 (d, **ii**, C^6H)	
	5.09 (s br, **iii**)		7.78 (s, **iii**)	7.22 (d, **i**, C^4H)	
				7.17 (d, **iii**, C^4H)	
				7.03 (t, **i**, C^5H)	
				7.08 (t, **ii**, C^5H)	
				6.92 (t, **iii**, C^5H)	
8[b,f]	5.11 (s br, **i**)	—	8.24 (s, **i**)	6.27 (s br, C^4H)	7.42 (m)[e]
	5.33 (s br, **ii**)		8.00 (s, **i**)	6.57 (m, $C^{5,6}H$)	
Hcptsc[b]	7.18 (s)	8.42 (s)	—	2.40 (t, $C^{3,6}H_2$)	
	6.41 (s)			2.29 (t, $C^{3,6}H_2$)	
				1.89 (m, $C^{4,5}H_2$)	
				1.78 (m, $C^{4,5}H_2$)	
Hchtsc[b]	7.25 (s)	8.74 (s)	—	2.31 (m, $C^{3,7}H_2$)	
	6.37 (s br)			2.29 (m, $C^{3,7}H_2$)	
				1.67 (m, $C^{4,5,6}H_2$)	
Hbtsc[b]	7.27 (s br)	10.22 (s br)	9.26 (s)	7.69 (m, $C^{4,8}H$)	
	6.60 (s br)			7.43 (m, $C^{5,6,7}H$)	
H_2stsc[h]	8.12 (s br)	11.38 (s br)	8.36 (s)	7.91 (s br, C^5H)	
	7.89 (s br)	9.87 (s br) (OH)		7.19 (m, C^6H)	
				6.86 (m, $C^{7,8}H$)	
Hmbtsc[b]	7.18 (s br)	9.31 (s br)	7.78 (s)	7.61 (d, $C^{5,7}H$)	
	6.29 (s br)			6.94 (d, $C^{4,8}H$)	
				3.86 (s, C^9H_3)	
Hptsc[h]	8.08 (s br)	11.28 (s)	7.82 (s)	6.95 (d, C^6H)	
	7.97 (s br)	11.34 (s) (N^4H)		6.37 (d, C^4H)	
				6.08 (dd, C^5H)	
Htftsc[b]	7.17 (s br)	9.45 (s)	8.01 (s)	7.30 (d, C^4H)	
	6.30 (s br)			7.08 (dd, C^5H)	
				7.41 (d, C^6H)	
Hftsc[b]	7.31 (s)	10.60 (s br)	7.78 (s)	6.76 (d, C^4H)	
	6.40 (s)	9.94 (s br)	7.00 (s)	6.53 (dd, C^5H)	
				7.60 (dd, C^6H)	
Hftsc[h]	8.22 (s br)	11.43 (s br)	7.95 (s)	6.95 (d, C^4H)	
	7.63 (s br)			6.62 (dd, C^5H)	
				7.79 (d br, C^6H)	

[a] s = Singlet, d = doublet, t = triplet, m = multiplet. [b] Solvent $CDCl_3$. [c] **A**, **B** refer to [HgPhL] and HgL_2 respectively in equation (2). [d] Obscured by ligand bands. [e] Includes $CHCl_3$ peak. [f] **i**, **ii**, **iii** refer to isomers. [g] Includes C^6H (**C**) and C^4H (**B**) protons of isomers. [h] Solvent $(CD_3)_2SO$.

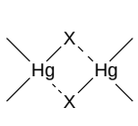
and carbons, but not affecting the mercury environment or that the variations about Hg are so small that they are not discriminated in ^{199}Hg NMR spectroscopy on account of the large linewidth of the ^{199}Hg NMR signals. The three species labelled **i**, **ii** and **iii** have approximate contributions 44, 28 and 28% respectively (*cf.* based on integral heights of C^2H proton signals). The precise nature of these species is difficult to establish with the available data (*cf.* low-temperature NMR studies, see below). Compound **8** also showed separate signals for N^1H_2 and C^2H protons as well as C^1, C^2 carbons, suggesting more than one species (**i**, 85; **ii**, 15%).



i X = O, S



ii X = O, S



iii X = O, N, S

For complexes **7** and **8**, the presence of thiophene and furan containing S or O donor atoms appears to play a significant role in giving rise to isomeric and dimeric species.

Table 5 The ^{13}C NMR spectral data (δ) for phenylmercury(II) thiosemicarbazonates[a]

Compound	C^1	C^2	Ligand ring carbons	PhHg carbons
1	176.23	167.00	34.37, 31.52, 31.32 ($C^{3,6}$)	158.30 (C_i)
			25.33, 20.05 ($C^{4,5}$)	137.56 (C_o)
				129.20 (C_m)
				128.29 (C_p)
2	169.34, 170.91	165.74	26.52, 25.90 ($C^{3,7}$)	158.69 (C_i)
			29.94, 27.59 ($C^{4,6}$)	137.48 (C_o)
			34.92 (C^5)	129.21 (C_m)
				128.31 (C_p)
3[b]	166.10 (**A**)[c]	150.76 (**A**)	134.90 (**A**), 133.31 (**B**) (C^3)	157.18 (C_i)
	170.14 (**B**)[c]	155.80 (**B**)	128.55 (**A**), 128.67 (**B**) ($C^{4,8}$)	137.58 (C_o)
			129.81 (**A**), 130.16 (**B**) (C^6)	128.30 (C_m)
			127.51 (**A**), 128.26 (**B**) ($C^{5,7}$)	131.88 (C_p)
4	167.04	156.21	158.90 (C^4), 131.86 (C^3)	131.75 (C_o)
			129.32 (C^5), 119.94 (C^6)	129.54 (C_m)
			119.67 (C^7), 116.84 (C^8)	128.79 (C_p)
5[b]	169.46 (**A**)[c]	165.48 (**A**)	161.81, 161.51 (C^6, **A**)	138.06 (C_o)
	170.87 (**B**)[c]	156.06 (**B**)	150.88, 149.89 (C^6, **B**)	130.62 (C_m)
			134.45 (**A**), 129.49 (**B**) (C^3)	129.23 (C_p)
			129.13, 128.76 ($C^{5,7}$, **A**, **B**)	
			114.50, 114.14, 114.11 ($C^{4,8}$, **A**, **B**)	
6	168.93	156.58	138.05 (C^3), 110.35 (C^5)	137.70 (C_o)
			117.14 (C^6), 123.06 (C^4)	129.38 (C_m)
				127.90 (C_p)
7[d]	169.69 (**i**)	145.49 (**i**)	138.05 (**i**), 140.69 (**ii**), 137.19 (**iii**) (C^3)	134.45 (C_o)[e]
	169.25 (**i**)	149.29 (**ii**)	130.21 (**i**), 131.00 (**ii**), 133.22 (**iii**) (C^6)[e]	134.32 (C_o)[e]
	166.14 (**ii**)	144.34 (**iii**)	129.32 (**i**), 129.13 (**ii**), 128.76 (**iii**) (C^4)[e]	129.32 (C_m)[e]
	170.87 (**iii**)		127.94 (**i**), 127.97 (**ii**), 127.90 (**iii**) (C^5)[e]	129.11 (C_m)[e]
				126.79 (C_p)[e]
8[d]	167.65 (**i**)	142.27 (**i**)	148.66 (C^3)	136.81 (C_o)
	164.12 (**ii**)	141.0 (**ii**)	144.74 (C^6)	128.57 (C_m)
			115.65 (C^4)	127.79 (C_p)
			111.68 (C^5)	
Hcptsc	178.83	163.43	33.23, 27.68 ($C^{3,6}$)	
			24.76, 24.57 ($C^{4,5}$)	
Hchtsc[f]	178.71	157.22	25.74, 25.06 ($C^{3,7}$)	
			27.72, 26.93 ($C^{4,6}$)	
			34.92 (C^5)	
Hbtsc	178.86	143.94	133.99 (C^3), 130.87 (C^6)	
			128.96 ($C^{4,8}$), 127.54 ($C^{5,7}$)	
H_2stsc[f]	177.87	139.98	155.49 (C^4), 120.35 (C^6)	
			131.14 (C^3), 119.34 (C^7)	
			126.91 (C^5), 116.12 (C^8)	
Hmbtsc	178.50	143.64	161.95 (C^6), 125.49 (C^3)	
			114.48 ($C^{4,8}$), 129.16 ($C^{5,7}$)	
			55.4 (C^9)	
Hptsc[f]	177.40	133.80	127.63 (C^3), 121.76 (C^4)	
			112.82 (C^6), 109.20 (C^5)	
Htftsc[f]	177.72	137.70	138.64 (C^3), 130.54 (C^6)	
			129.93 (C^5), 128.83 (C^4)	
Hftsc[f]	177.93	132.56	149.44 (C^3), 144.96 (C^6)	
			112.73 (C^4), 112.28 (C^5)	

[a] In $CDCl_3$ solvent. [b] **A**, major isomer; **B**, minor isomer. [c] **A**, **B** refer to [HgPhL] and [HgL_2] respectively in equation (2). [d] **i** = Major isomer, **ii** = medium isomer, **iii** = minor isomer. [e] Uncertainty in assignment. [f] In $(CD_3)_2SO$.

Low-temperature ^1H NMR studies. Low-temperature studies were carried out for selected complexes (**1**, **2**, **5**–**7**). Complex **1** shows one ^1H NMR signal due to the N^1H_2 group at room temperature (Table 4) and on lowering the temperature to 223 K the signal shifts to low field, splits into two at 203 K ($\delta_{203\ K}$ *ca.* 6.7 and 5.1) and the two signals coalesce at 207 K ($\delta_{c207\ K}$ *ca.* 5.7). The behaviour of **2** and **6** is similar (**2**, $\delta_{c198\ K}$ *ca*. 5.3; $\delta_{193\ K}$ *ca.* 5.9 and 4.9; **6**, $\delta_{c202\ K}$ *ca*. 5.5; $\delta_{193\ K}$ *ca.* 5.7 and 5.1). The N^1H_2 signals of **5** at δ 5.92 [Table 4, species **A**, equation (2)] at room temperature showed coalescence temperature, T_c, at 217 K with two split peaks appearing at $\delta_{194\ K}$ *ca.* 5.0 and 6.1.

The above studies reveal that the free rotation of the N^1H_2 group about the C^1–N^1 bond at room temperature is slowed initially and finally stopped at low temperature and the N^1H_2 protons become magnetically non-equivalent giving rise to two signals. Owing to some residual double-bond character of the C^1–N^1 bond, there is insufficient thermal energy at low temperature to rotate the N^1H_2 group. On raising the temperature the two peaks coalesce and thus coalescence temperatures and linewidths were obtained from the low-temperature experiments. The energy barrier to rotation of the N^1H_2 group has been calculated from equation (3) which is a modified form

$$\Delta G_{T_c}^{*} = T_c[0.191 - 0.019 \log(\Delta\nu/T_c)]\ \text{kJ mol}^{-1} \quad (3)$$

of the Gutowsky–Holm equation,[53] where ΔG^* = free energy of activation, T_c the coalescence temperature in K and Δν the linewidth in Hz at the half-height of the coalescence peak. Table 7 shows the calculated values of ΔG^* which fall in the range 36–42 kJ mol^{-1}. Complex **5** shows the largest ΔG^* value in accordance with its shortest C^1–N^1 and longest C^1–S bonds.

Finally, compound **7** which showed three N^1H_2 signals was examined to determine the coalescence temperatures for the

Table 6 The ^{199}Hg NMR data (δ, *J*/Hz) for phenylmercury(II) thiosemicarbazonates[a]

Compound	δ(Hg)	^3J(Hg–H)	Comment
1	−687		Single component
2	−693	156.0	Single component
3	−783 (A)[b]		Due to [HgPh(btsc)]
	−941 (B)[b]		Due to [Hg(btsc)$_2$]
	−749 (C)[b]		Due to $HgPh_2$
4	−953		Single component
5	−773 (A)[b]		Due to [HgPh(mbtsc)]
	−942 (B)[b]		Due to [Hg(mbtsc)$_2$]
	−750 (C)[b]		Due to $HgPh_2$
6	−672	170.1	Single component
		161.1	
7	−695	155.9	Single component
8	−800		Single component

[a] δ Values relative to $HgMe_2$; increasing negative values indicate higher field (low frequency); solvent $CDCl_3$ in all cases. [b] See text, equation (2).

Table 7 Calculated barrier to rotation of the N^1H_2 group about the C^1–N^1 bond of selected complexes

Complex	T_c/K	Δν/Hz	ΔG_{T_c}*/kJ mol^{-1}	d(C^1–S)/Å	d(C^1–N^1)/Å
1	207	687.7	37.49	1.751(7)	1.348(9)
2	198	508.0	36.28	—	—
5	217	192.0	41.67	1.781(9)	1.339(11)
6	202	326.2	37.78	1.742(11)	1.360(20)

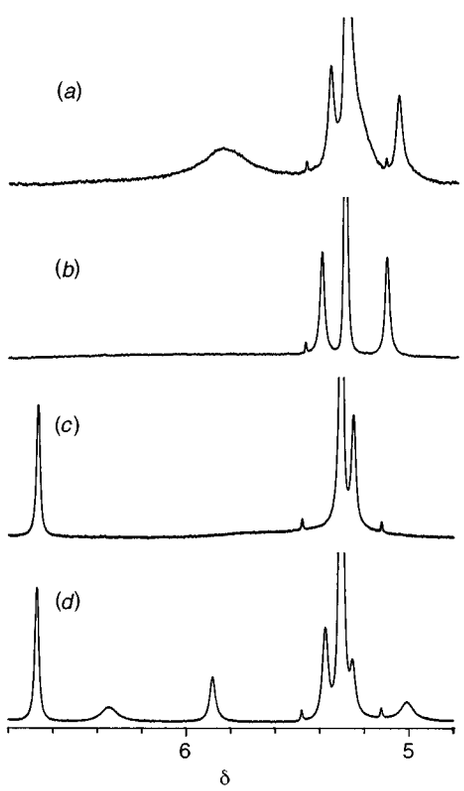


Fig. 8 The ^{1}H NMR spectra of [HgPh(tftsc)] **7** in CD_2Cl_2 at (*a*) 297, (*b*) 277, (*c*) 220 and (*d*) 193 K (spectra contain additional solvent peaks)

isomers suggested earlier, but on lowering the temperature the variations in their positions and intensities are random and no coalescence value for any isomer could be determined. Fig. 8 shows ^{1}H NMR spectra of **7** for selected temperatures. At the lowest temperature achieved, six signals are clearly seen, but on raising the temperature the peak intensities interchange in a non-systematic manner suggesting that probably the isomers interchange.

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