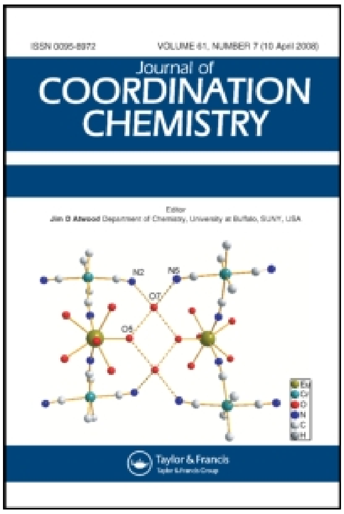

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Crystal structures of organomercury(II) derivatives of cyclohexanone and benzaldehyde thiosemicarbazones

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Crystal structures of organomercury(II) derivatives of cyclohexanone and benzaldehyde thiosemicarbazones

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The crystal and molecular structures of the organomercury(II) complexes [Hg(C_6H_5)(chtsc)], **1**, and [Hg($C_6H_5C_5H_4N$)(btsc)], **2**, obtained from the reaction of phenylmercury(II) acetate with cyclohexanone thiosemicarbazone (Hchtsc) and that of [2-(pyridin-2′-yl)]phenyl]mercury(II) acetate with benzaldehyde thiosemicarbazone (Hbtsc), respectively, are described. Both **1** and **2** are monoclinic, space group *C*2/*c*. Complex **1** has a distorted T-shaped geometry {C-Hg-S, 161.91(10)°} and **2** can be considered to have a distorted seesaw geometry {C-Hg-S, 171.2(10)°}. In both complexes the ligands act as bidentate chelating anions bonding through azomethine N^1 and thiolato S atoms.

Keywords: Organomercury(II); Thiosemicarbazone; T-shaped; X-ray structures

1. Introduction

Mercury has a detrimental effect on the living organism and its environment [1]. Being a soft Lewis acid, it forms strong bonds with sulfur-containing ligands such as heterocyclic thioamides, thiosemicarbazones, etc. [1–16]. There are efforts to detoxify organomercury(II) by activation of Hg-C bonds using coordination, followed by treatment with an acid, to generate parent hydrocarbon (RH) and inorganic mercury(II) salts [17, 18]. Coordination of organomercury(II) by thiosemicarbazones has been reported by Casas *et al*. [14, 15].

In this paper, we report the crystal and molecular structures of the organomercury(II) compounds [Hg(C_6H_5)(chtsc)], **1**, and [Hg($C_6H_5C_5H_4N$)(btsc)], **2**, obtained from the reaction of phenylmercury(II) acetate with cyclohexanone thiosemicarbazone (Hchtsc), and that of [2-(pyridin-2′-yl)]phenyl]mercury(II) acetate with benzaldehyde thiosemicarbazone (Hbtsc), respectively. Scheme 1 shows the ligands

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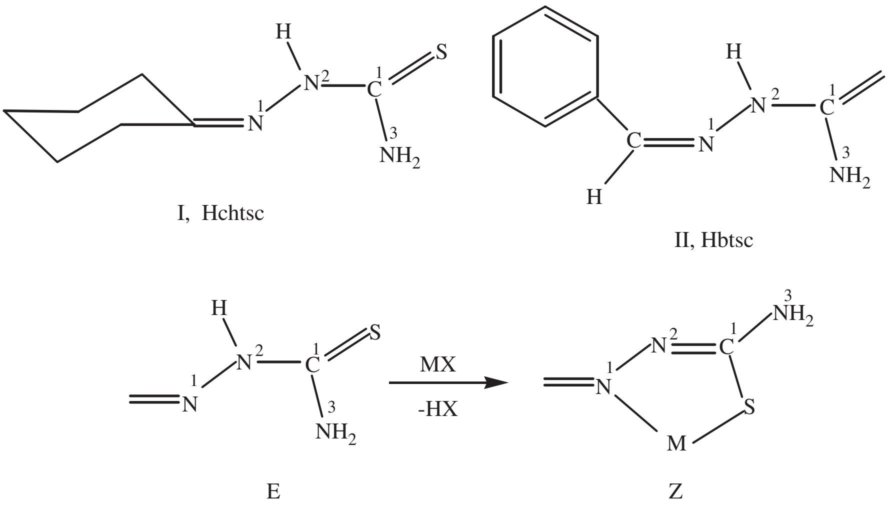


Scheme 1.

used, and after deprotonation of the N^2H proton, the neutral ligand adopts the *Z*-configuration in its compounds.

2. Experimental

2.1. *Materials*

Benzaldehyde, cyclohexanone and phenylmercury(II) acetate were procured from Aldrich Sigma Ltd. The ligands cyclohexanone thiosemicarbazone (Hchtsc, I), benzaldehyde thiosemicarbazone (Hbtsc, II), were prepared by reported methods [19]. [2-(Pyridin-2′-yl)phenyl]mercury(II) acetate was prepared by the mercuration of 2-pyridylbenzene using mercury(II) acetate, by a reported method [20].

2.2. *[Hg(C_6H_5)(chtsc)] (1)*

The complex was prepared by following a modified procedure to that reported in the literature [14]. To a solution of Hchtsc (0.013 g, 0.076 mmol) in methanol (10 cm^3) was added solid phenylmercury(II) acetate (0.025 g, 0.076 mmol) and the mixture stirred for 10 min. The resulting clear solution was kept at room temperature (25 ± 2°C). After about 12 h, light yellow crystals of **1** were obtained.

2.3. *[Hg($C_6H_5C_5H_4N$)(btsc)] (2)*

The complex was prepared by following a modified procedure to that reported in the literature [15]. To a solution of Hbtsc (0.011 g, 0.061 mmol) in methanol (10 cm^3) was added solid 2-pyridylphenylmercury(II) acetate (0.025 g, 0.061 mmol) and the mixture stirred for 10 min. The resulting clear solution was kept at room temperature (25 ± 2°C). After about 10 h, light yellow crystals of **2** were obtained.

2.4. *X-ray crystallography*

A prismatic crystal of **1** was mounted on an automated Enfra-Nonius CAD-4 diffractometer equipped with a graphite monocromator and Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions and intensity data were measured at 293 K with ω scans to 56° 2θ. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F^2 with anisotropic thermal parameters for non-hydrogen atoms using XCAD-49 (data reduction) and SHELXL (absorption correction, structure solution refinement and molecular graphics) [21]. H atoms were included in structure factor calculations in idealized positions.

A rod-like crystal of **2** was mounted on a Bruker SMART 1000 CCD diffractrometer employing graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at 150(2) K with ω scans to 56° 2θ. Data integration and reduction were undertaken with SAINT and XPREP [22a], and subsequent computations were carried out with the WinGX [22b] graphical user interface. The structure was solved by direct methods with SHELXS-86 [22c], and extended and refined with SHELXL-97 [22d]. A multi-scan absorption correction determined with SADABS [23] was applied to the data. Non-hydrogen atoms were modelled with anisotropic displacement parameters, and in general a riding atom model was used for the hydrogen atoms. The amine and C(7) hydrogen sites were located and modelled with isotropic displacement parameters.

3. Results and discussion

The formation of compounds **1** and **2** requires mild conditions to obtain crystalline material. Allowing the reaction mixture to stir for long periods or refluxing leads to decomposition of the products. The atom numbering schemes of complexes **1** and **2** are shown in figures 1 and 2, respectively. Crystal data are given in table 1 and bond lengths and angles are given in table 2.

In **1,** the ligand is deprotonated at N^2 and adopts the *Z*-configuration (Scheme 1). Phenylmercury(II) makes bonds to S and N^1 atoms of cyclohexanone thiosemicarbazonate ligand (chtsc$^-$). This N^1, S-chelate has a bite angle of 75.27(8)° with the result that N^1 atom does not lie at 90° to the C(1A)–Hg–S axis of PhHg(chtsc). Due to the small bite, the C(1A)–Hg–S angle is 161.91(10)°. Thus the Hg complex does not acquire a T-shaped structure and is rather severely distorted [24]. It can be seen from table 3 that C–Hg–S angles vary with the nature of the thiosemicarbazone and in **1** it is the smallest angle; the larger the C–Hg–S angle, the smaller is the corresponding C–Hg–N^1 angle. Variation in bite angle S–Hg–N^1 and the angles at S, viz. Hg–S–C, do not show significant changes.

The Hg–C bond distance of 2.084(4) Å is the largest among the compounds listed in table 3 [14, 16] and the Hg-S distance, 2.3803(10) Å, is similar to that in **3**, **5** and **6**. The Hg–N^1 bond distance, 2.525(3) Å, is smaller than that in **4** but larger than in **3**, **5** and **6**. All these Hg–N^1 bond distances are less than the sum of the van der Waals radii of Hg and N (3.28 Å) [25, 26]. In **1**, C(7)–S, 1.757(4) Å is shorter than a C–S single bond, 1.81 Å, but longer than a C-S double bond, 1.62 Å [27–29].

In **2**, Hbtsc is also deprotonated at N^2 and adopts the *Z*-configuration. The btsc anion chelates to Hg atom via its N^1 and S atoms. In addition, Hg is bonded to the

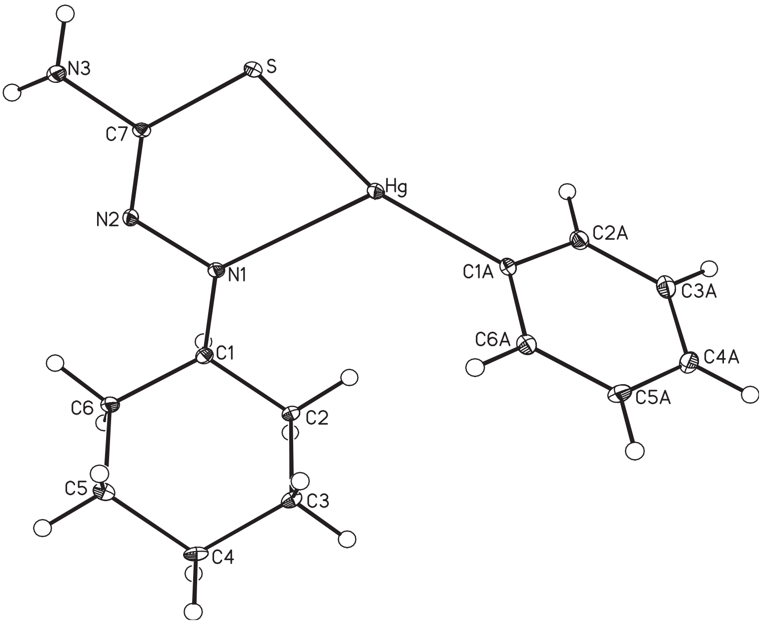


Figure 1. The structure of [Hg(C_6H_5)(chtsc)] **(1)** showing the atom numbering scheme.

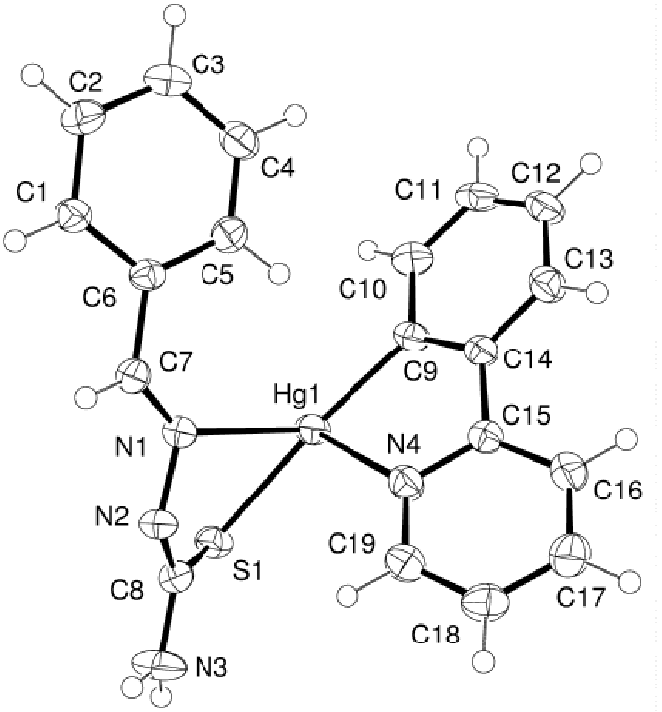


Figure 2. Structure of **2** with the atom numbering scheme.

Table 1. Crystallographic data for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{13}H_{18}HgN_3S$	$C_{19}H_{16}HgN_4S$
M	448.95	533.02
T (K)	93(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	28.642(3)	37.21(2)
b (Å)	11.0291(13)	12.545(6)
c (Å)	8.9847(10)	7.666(4)
β (°)	102.778(2)	96.384(14)
V, Å^3	2767.9(6)	3557(3)
Z	8	8
D_{calcd} (g cm^{-3})	2.155	1.991
μ (mm^{-1})	11.258	8.781
Reflections collected	10406	17178
Unique reflections	3369 ($R_{int} = 0.0463$)	4203 ($R_{int} = 0.0359$)
Reflections with $[I > 2\sigma(I)]$	3163	3605
R indices	$R = 0.0247$, $wR = 0.0616$	$R = 0.0235$, $wR = 0.0536$

Table 2. Bond lengths (Å) and angles (°) for **1** and **2**.

[Hg(C_6H_5)(chtsc)] **1**			
Hg–C(1A)	2.084(4)	Hg–N(1)	2.525(3)
Hg–S	2.3830(10)	S–C(7)	1.757(4)
C(1A)–Hg–S	161.91(10)	S–Hg–N(1)	75.27(8)
C(1A)–Hg–N(1)	121.69(13)	C(7)–S–Hg	103.36(12)
[Hg($C_6H_5C_6H_4N$)(btsc)] **2**			
Hg(1)–C(9)	2.081(3)	Hg(1)–N(1)	2.715(3)
Hg(1)–S(1)	2.3637(12)	S(1)–C(8)	1.772(4)
Hg(1)–N(4)	2.596(3)		
C(9)–Hg(1)–N(1)	116.60(10)	S(1)–Hg(1)–N(1)	72.12(7)
C(9)–Hg(1)–N(4)	74.60(12)	N(1)–Hg(1)–N(4)	79.07(9)
C(9)–Hg(1)–S(1)	171.21(9)	Hg(1)–S(1)–C(8)	99.09(12)
S(1)–Hg(1)–N(4)	107.29(7)		

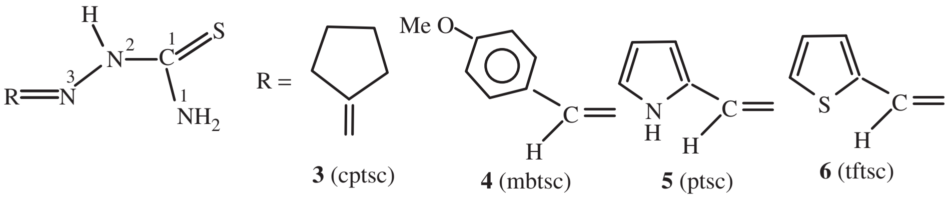
phenyl ring and N^4 of the pyridyl ring. The Hg–N^1 bond length is 2.715(3) Å, which is longer than that found in **1** and **3**–**6**, but shorter than that {3.126(6) Å, cf. sum of van der Waals radii [30]} in the related complex [Hg($C_6H_5C_5H_4N$)(Hstsc)], **8** (Hstsc$^-$ = anion of salicyladehyde thiosemicarbazone) [15]. The weak Hg···N^1 interaction in **8** is due to strong intramolecular hydrogen bonding between the OH group and the N^1 hydrogen {O–H···N(1), 2.647(7) Å; sum of van der Waals radii 3.05 Å [30]}, which prohibits N^1 from forming a strong bond with Hg. Further, the Hg–N(4) bond, 2.596(3) Å, in **2** is longer than that {2.576(6) Å} in **8**, but shorter than that {2.73(1) Å} in [Hg($C_6H_5C_6H_4N$)(OAc)], **9** [31]. The Hg–S bond distance of 2.3637(12) Å in **2** is similar to those in complexes **1** and **3**–**6** (table 3). Finally, the Hg–C bond distance is similar to that in **1**, but longer than that {1.99(1) Å} in [Hg($C_6H_5C_6H_4N$)(OAc)], **9** [31]. The C–S bond distance, 1.772(4) Å, indicates a partial double character similar to that in **1** and **3**–**6** (table 3).

The C(9)–Hg(1)–S(1) bond angle of 171.2(9)° is smaller than in **8** [15], but larger than in most of the compounds listed in table 3. The bite angle N(1)–Hg(1)–S(1) is 72.12(7)° and pyridyl nitrogen forms a C(9)–Hg(1)–N(4) angle of 74.60(12)°. The geometry around Hg is neither square planar nor tetrahedral. A distorted seesaw geometry

Table 3. A comparison of bond lengths (Å) and angles (°) for related complexes.*

	$Hg–C_{Ph}$	Hg–S	$Hg–N^1$	$S–C^1$
[PhHg(cptsc)] **3**[a]	2.063(7)	2.382(2)	2.489(6)	1.751(7)
[PhHg(mbtsc)] **4**[a]	2.069(10)	2.357(3)	2.611(7)	1.781(9)
[PhHg(ptsc)] **5**[a]	2.049(11)	2.377(3)	2.492(9)	1.742(11)
[PhHg(tftsc)] **6**[b]	2.067(15)	2.380(4)	2.475(13)	1.729(17)
[PhHg(chtsc)] **1**	2.084(4)	2.383(1)	2.525(3)	1.757(4)
	$C_{Ph}–Hg–S$	$C_{Ph}–Hg–N^1$	$S–Hg–N^1$	$Hg–S–C^1$
3	162.9(2)	120.3(2)	75.69(13)	101.4(2)
4	174.2(3)	109.9(3)	75.4(2)	100.6(3)
5	165.8(3)	118.4(4)	75.8(2)	102.4(4)
6	168.1(4)	115.9(5)	76.0(3)	101.4(5)
1	161.91(10)	121.69(13)	75.27(8)	103.36(12)

[a]From [14]. [b]From [16]. *For numbering scheme and ligand abbreviations refer to Scheme 2, below.



Scheme 2.

may be assigned to this complex with C(9)–Hg(1)–S as the central bar with $Hg–N^1$ and $Hg–N^4$ making the two resting supports.

Supplementary material

Full details have been deposited with the Cambridge Crystallographic Data Centre, CCDC 267366 for **1** and 268702 for **2**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336-033; email: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

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