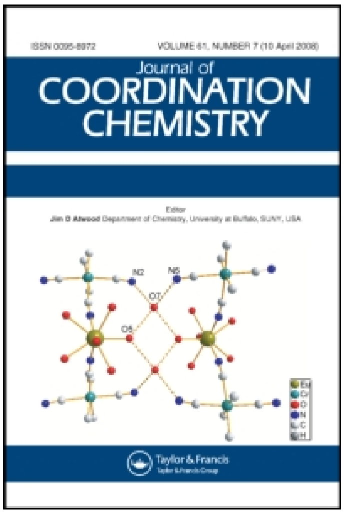

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Synthesis and crystal structures of bis(*N*-phenyl-3,5-dinitrothiobenzamidato)mercury(II) and bis(*N*-phenyl-4-nitrothiobenzamidato)mercury(II)

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Synthesis and crystal structures of bis(*N*-phenyl-3,5-dinitrothiobenzamidato)mercury(II) and bis(*N*-phenyl-4-nitrothiobenzamidato)mercury(II)

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The crystal structures of bis(*N*-phenyl-3,5-dinitrothiobenzamidato)mercury(II) (**1**) and bis(*N*-phenyl-4-nitrothiobenzamidato)mercury(II) (**2**) have been determined by single-crystal X-ray diffraction. Both the complexes crystallize in centrosymmetric monoclinic space groups with crystallographic inversion symmetry. The S–Hg–S linkage is thus precisely linear in each case. Significant secondary interactions include intramolecular π coordination by phenyl groups, aromatic ring stacking in the case of **1** only, and a number of intramolecular and intermolecular C–H $\cdots$ X contacts (X = O, N, S) influencing the molecular conformation and crystal packing.

Keywords: Thiobenzamide; Mercury(II); Crystal structure; Secondary interactions

1. Introduction

The coordination chemistry of mercury complexes with sulfur ligands is important for mercury–cysteine thionato interactions in the toxicological behavior of this metal [1] in the detoxification of mercury by metallothioneins [2], in DNA-binding proteins [3], and in the mercury reductase and related proteins [4]. The sustained interest in coordination chemistry of mercury and sulfur-containing ligands is related to environmental consequences of the high toxicity of mercury to living systems [5]. Mercury(II) interacts with many biological molecules through deprotonated thiol, imidazole, disulfide, thioether, amino, or carboxylate groups and its interactions in model molecules and proteins are well known [6]. We report here the crystal structures and other characterization data for mercury(II) complexes with *N*-phenyl-3,5-dinitrothiobenzamide and *N*-phenyl-4-nitrothiobenzamide, which are examples of simple model complexes for such biological systems.

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2. Experimental

2.1. *Synthesis of bis(N-phenyl-3,5-dinitrothiobenzamidato)mercury(II) (1)*

One mmol of mercury(II) oxide (0.216 g) was added to a solution of *N*-phenyl-3,5-dinitrothiobenzamide (0.303 g, 1 mmol) at an ambient temperature in acetonitrile (20 mL) and stirred for 80 min. The reaction was followed to completion by thin layer chromatography (TLC) with CCl_4/CH_3OH (15: 1) as eluent. The complex was found to be insoluble in acetonitrile; the white precipitate formed was filtered off, dissolved in chloroform, filtered under vacuum, crystallized from chloroform at room temperature as fine pale-yellow crystals, and dried *in vacuo*. Yield: 0.348 g, 87%. Anal. Calcd for $C_{26}H_{16}HgN_6O_8S_2$ (%): C, 38.78; H, 2.00; N, 10.44. Found (%): C, 38.96; H, 2.08; N, 10.39. m.p. 175–178°C.

2.2. *Synthesis of bis(N-(phenyl)-4-nitrothiobenzamidato)mercury(II) (2)*

The same method of preparation was followed, but using *N*-phenyl-4-nitrothiobenzamide (0.258 g, 1 mmol) in chloroform (20 mL, stirred for 80 min); the complex was recrystallized from chloroform as pale yellow crystals. Yield: 0.338 g, 95%. Anal. Calcd for $C_{26}H_{18}HgN_4O_4S_2$ (%): C, 43.67; H, 2.54; N, 7.83. Found (%): C, 43.73; H, 2.60; N, 7.44. m.p. 193–195°C.

2.3. *Crystal structure determination*

Crystals of **1** and **2** were examined on a Nonius Kappa CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) at 150 K. Crystal data, collection procedures, and refinement results are summarized in table 1. Selected bond distances and angles are shown in table 2. The unit cell parameters were determined using COLLECT [7] and refined based on the positions of all strong reflections using Eval CCD [8]. Absorption corrections were applied by SADABS [9] based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods using SIR97 [9] and refined by full-matrix least-squares on all unique F^2 values using SHELXTL [10]. Molecular graphics were produced using DIAMOND [11] and MERCURY [12]. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were first located in a difference map and then refined as riding atoms with idealized geometry.

3. Results and discussion

Complexes **1** and **2** were readily prepared in good yield by addition of an equimolar quantity of HgO to each ligand in acetonitrile (scheme 1). Although the complexes contain 1: 2 stoichiometry of mercury to ligand, use of reagents in this ratio led to lower yields. The molecular structures with atom numbering schemes are depicted in figures 1 and 2. The mercury of both complexes lies on an inversion center and the S–Hg–S unit is thus precisely linear with an angle of exactly 180°. The Hg–S, S–C7, and C7–N1 bond lengths are 2.3382(7), 1.770(3), and 1.274(3) Å, respectively, in **1**, and 2.3432(8),

Table 1. Crystal data and structure refinement information for **1** and **2**.

	1	**2**
Empirical formula	$C_{26}H_{16}HgN_6O_8S_2$	$C_{26}H_{18}HgN_4O_4S_2$
Formula weight	805.2	715.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	11.770(2)	9.5232(3)
b	7.0589(12)	6.6685(6)
c	17.031(2)	19.3902(14)
β	110.216(10)	99.412(5)
Volume (Å^3), Z	1327.8(4), 2	1214.81(15), 2
Absorption coefficient (mm^{-1})	6.02	6.55
Crystal size (mm^3)	$0.17 \times 0.16 \times 0.12$	$0.58 \times 0.21 \times 0.10$
Transmission factors	0.521–0.722	0.145–0.522
Reflections collected	23668	8398
Independent reflections	3018 [R(int) = 0.045]	2766 [R(int) = 0.030]
Refined parameters	196	169
$R(F)$ (reflections with $F^2 > 2\sigma$)	0.018	0.022
$R_w(F^2)$ on all data	0.037	0.045
Goodness-of-fit on all F^2	1.01	1.03
Difference map extremes (e Å^{-3})	+0.59, −0.41	+0.62, −0.67

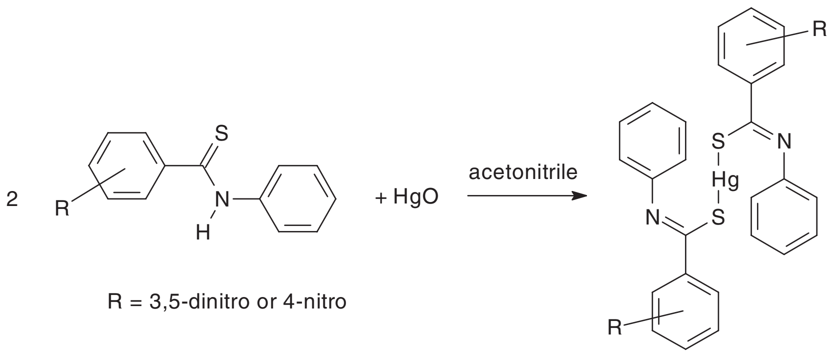
Table 2. Selected bond lengths (Å), bond angles (°), and torsion angles (°).

	1	**2**
Hg–S	2.3382(7)	2.3432(8)
S–C7	1.770(3)	1.768(3)
N1–C7	1.274(3)	1.267(4)
C7–C8	1.507(3)	1.500(4)
N1–C1	1.418(3)	1.404(4)
S–Hg–S′	180	180
Hg–S–C7	104.47(8)	107.09(10)
S–C7–N1	130.3(2)	130.5(2)
S–C7–C8	113.20(18)	112.97(19)
N1–C7–C8	116.5(2)	116.5(3)
C7–N1–C1	123.0(2)	125.9(3)
Hg–S–C7–N1	23.4(3)	2.0(3)
Hg–S–C7–C8	−156.75(15)	−177.58(18)

The prime denotes an atom generated by inversion symmetry.

1.768(3), and 1.267(4) Å, respectively, in **2** (table 3). In these and other respects there are no major differences between the two molecular structures, and the bond lengths and angles are similar to those of related complexes found in the Cambridge Structural Database [13].

In both structures the mercury is sandwiched between two strictly parallel benzene rings, one attached to nitrogen in each ligand; this feature is highlighted in the view direction chosen for figure 2. The shortest Hg $\cdots$ C distances are 2.953 and 3.066 Å in **1**, and 2.951, 3.194, and 3.209 Å in **2**, with the other Hg $\cdots$ C distances in the range 3.33–3.88 Å, indicating weak π coordination of these rings to Hg as a significant secondary interaction in each case. The distances of Hg from the ring centroids and



Scheme 1. Synthesis of **1** and **2**.

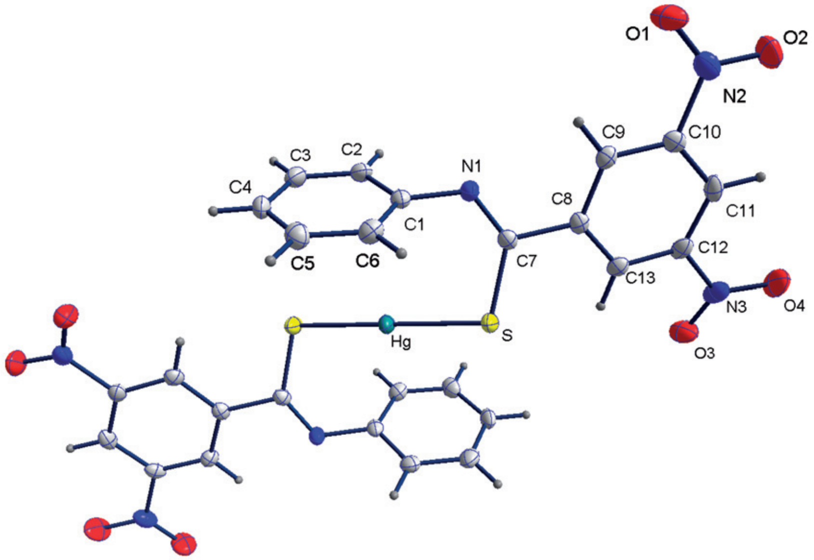


Figure 1. Molecular structure of **1** with 50% probability displacement ellipsoids and with non-H atoms of the asymmetric unit labeled.

perpendicular distances from the ring planes are, respectively, 2.922 and 3.122 Å in **1**, and 2.934 and 3.144 Å in **2**. The hapticity is best described as η^2 in **1** and η^3 in **2**. A similar bis-η^3 arrangement has been observed in the closely related [Hg(nptb)$_2$] (nptb = *N*-(4-nitrophenyl)thiobenzamidato) [14], although here the molecule has approximate C_2 rather than exact inversion symmetry. Hence, the two benzene rings are not exactly parallel and have slightly different distances to Hg (closest $\mathrm{Hg}\cdots\mathrm{C} = 2.979$–3.319 Å and 3.008–3.279 Å), and the S–Hg–S linkage is not strictly linear (174.37°). By contrast, [Hg(thioacetanilide)$_2$] in the solid state is quite unsymmetrical, having a π coordination interaction (also η^3) for only one of the two ligands (shortest $\mathrm{Hg}\cdots\mathrm{C} = 2.963$–3.275 Å), while the other is oriented well away from mercury [15], and [HgL$_2$] in which L is a ligand with methoxy attached to the

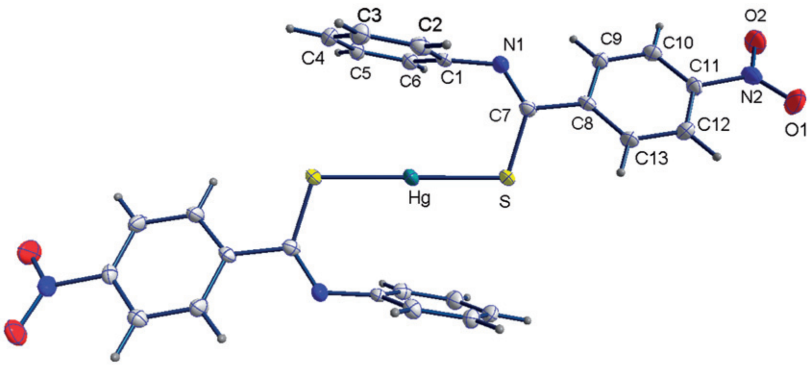


Figure 2. Molecular structure of **2** with 50% probability displacement ellipsoids and with non-H atoms of the asymmetric unit labeled.

Table 3. C–H $\cdots$ X interactions in **1** and **2**.

C–H $\cdots$ X	C–H (Å)	H $\cdots$ X (Å)	C $\cdots$ X (Å)	C–H $\cdots$ X (°)
1				
C13–H13 $\cdots$ S1	0.95	2.59	3.001(3)	107
C6–H6 $\cdots$ O2^{i}	0.95	2.56	3.314(3)	137
2				
C13–H13 $\cdots$ S1	0.95	2.67	3.057(3)	105
C4–H4 $\cdots$ O2^{i}	0.95	2.54	3.483(4)	170
C10–H10 $\cdots$ O2^{ii}	0.95	2.48	3.290(4)	143

Symmetry code for **1**: (^{i}) $2-x, 2-y, -z$. Symmetry codes for **2**: (^{i}) $x, 3/2-y, ½+z$; (^{ii}) $1-x, ½+y, ½-z$.

thiocyanate carbon of phenyl isothiocyanate having both phenyl rings distant from mercury, the shortest and preferred contacts here being Hg $\cdots$ O = 2.859 and 2.967 Å for the methoxy groups [16].

A search of the Cambridge Structural Database (version 5.30 plus 4 updates to September 2009) [13] finds about 20 examples of structures in which a mercury lies in an approximately perpendicular line above a benzene ring with at least one Hg $\cdots$ C distance $<$ 3.1 Å (about 60 if the search is extended to 3.2 Å), in many of which this arrangement is not imposed by intramolecular bonding constraints. In crystallographic studies, secondary π interactions of mercury with aromatic rings have been investigated by NMR spectroscopy, magnetic measurements, and luminescence properties [17–22], and they appear to be weak but significant.

In both structures, the relative positions of Hg and the phenyl rings also bring each sulfur into close proximity of the phenyl ring of the other ligand, with three short S $\cdots$ C distances of 3.498–3.887 Å in **1** and 3.360–3.619 Å in **2**, because the phenyl rings diverge from the S–Hg–S line rather than being parallel; however, these distances are somewhat larger than the Hg $\cdots$ C distances and probably do not indicate any significant interaction.

With regard to intermolecular interactions, the dinitrophenyl rings in **1** are arranged parallel in pairs across inversion centers, with a centroid $\cdots$ centroid distance of 3.524 Å and a perpendicular distance of 3.293 Å between the ring planes, representing a π–π stacking interaction. There is no such interaction in **2**, the shortest distance between the centroids of benzene rings being more than 4.6 Å. Both structures contain a number of C–H $\cdots$ X contacts with H $\cdots$ X significantly shorter than the sum of van der Waals radii (those with a C–H $\cdots$ X angle under 100° are listed in table 3). Of these, the intramolecular contacts in which X is nitro O, imine N, or S, stabilize the near-coplanarity of benzene rings and their substituents, for which repulsive steric interactions would otherwise lead to twists out of plane. The intermolecular contacts may be regarded as weak non-classical C–H $\cdots$ O hydrogen bonds, but their contribution to the overall lattice energy must be very small.

Supplementary material

Crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 663092 for **1** and 663091 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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