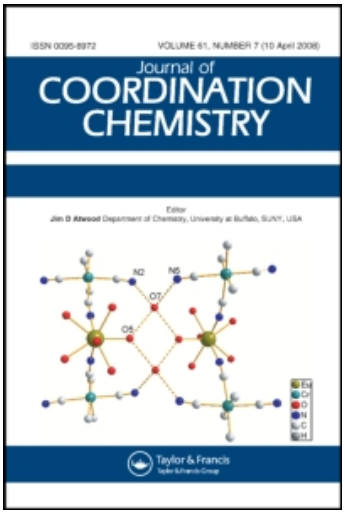

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Synthesis and crystal structure of *bis*[*N*-(phenyl)-3,5-dinitrothiobenzamidato]mercury(II) and *bis*[*N*-(phenyl)-4-nitrothiobenzamidato]mercury(II)

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Synthesis and crystal structure 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. Compound **1** is in the monoclinic space group $P2_1/n$ with $a = 11.770(2)$, $b = 7.0589(12)$, $c = 17.031(2)$ Å, $\beta = 100.216(2)°$, $V = 1327.8(4)$ Å^3 and $Z = 2$. Compound **2** is in the monoclinic space group $P2_1/c$ with $a = 9.5232(3)$, $b = 6.6685(6)$, $c = 19.3902(14)$ Å, $\beta = 99.412(5)°$, $V = 1214.81(15)$ Å^3 and $Z = 2$. The S–Hg–S is linear with angle of 180°. In the crystal packing the molecules are linked via weak intra- and intermolecular C–H···O, N, and S hydrogen bonds.

Keywords: Thiobenzamide; Mercury(II); Crystal structure

Introduction

Coordination chemistry of mercury complexes with sulfur ligands is important for mercury–cysteine thionato interactions in the toxicological behavior of this metal [1], in detoxification of mercury by metallothionenes [2], in a DNA-binding protein [3], and in mercury reductase and related proteins [4]. 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 of the Hg(II) complexes with *N*-(phenyl)-3,5-dinitrothiobenzamide and *N*-(phenyl)-4-nitrothiobenzamide.

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Table 1. Data collection and structure refinement parameters for **1** and **2**.

	1	**2**
Chemical formula	$C_{26}H_{16}HgN_6O_8S_2$	$C_{26}H_{18}HgN_4O_4S_2$
Formula weight	805.16	715.15
Crystal color	Yellow	Yellow
Temperature (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Crystal size (mm^3)	$0.17 \times 0.16 \times 0.12$	$0.58 \times 0.21 \times 0.10$
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)
α	90	90
β	110.216(10)	99.412(5)
γ	90	90
V ($Å^3$)	1327.8(4)	1214.81(15)
Z	2	2
D_{Calcd} ($g\,cm^{-3}$)	2.014	1.955
μ (mm^{-1})	6.017	6.3[illegible]
$F(000)$	780	692
Number of reflections collected	23668	8398
Number of independent reflections (R_{int})	3018 (0.0452)	2766 (0.0301)
Number of reflections used [$F^2 > 2\sigma$]	2307	2164
Final R indices [$F^2 > 2\sigma$]	$R_1 = 0.0218$, $wR_2 = 0.0327$	$R_1 = 0.0218$, $wR_2 = 0.0419$
Final R indices (all data)	$R_1 = 0.0362$, $wR_2 = 0.0367$	$R_1 = 0.0368$, $wR_2 = 0.0454$

Table 2. Hydrogen-bonding geometry (Å, °) for **1**.

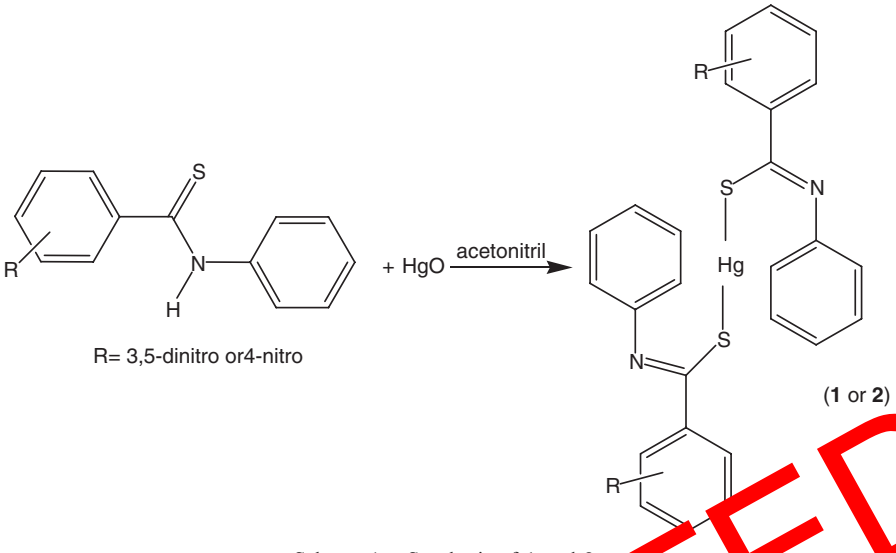
D–H···A	D–H	H···A	D···A	D–H···A
C9–[illegible]···O1	0.95	2.426	2.716	97.37
C11–H11···O2	0.95	2.404	2.688	96.83
C13–H13···O3	0.95	2.436	2.721	96.99
C11–H11···O4	0.95	2.453	2.721	95.97
C9–H9···N1	0.95	2.459	2.761	98.24
C13–H13···S1	0.95	2.587	3.001	106.70
C3–H3···O1^{i}	0.95	2.643	3.443	142.31
C6–H6···O2^{ii}	0.95	2.556	3.313	136.85
C11–H11···O3^{iii}	0.95	2.640	3.425	140.30
C2–H2···O4^{iv}	0.95	2.651	3.459	143.08

Symmetry codes: (i) $-1/2+x$, $1.5-y$, $1/2+z$; (ii) $-1+x$, $-1+y$, z; (iii) $-1.5+y$, $1/2-y$, $-1/2+z$; (iv) $-1+x$, y, z.

2. Experimental

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

One millimolar of mercury(II) oxide (0.216 g) (excess) was added to a solution of *N*-(phenyl)-3,5-dinitrothiobenzamide (0.303 g, 1 mmol) at ambient temperature in acetonitrile (20 mL) for 80 min with stirring. The reaction was followed to completion



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

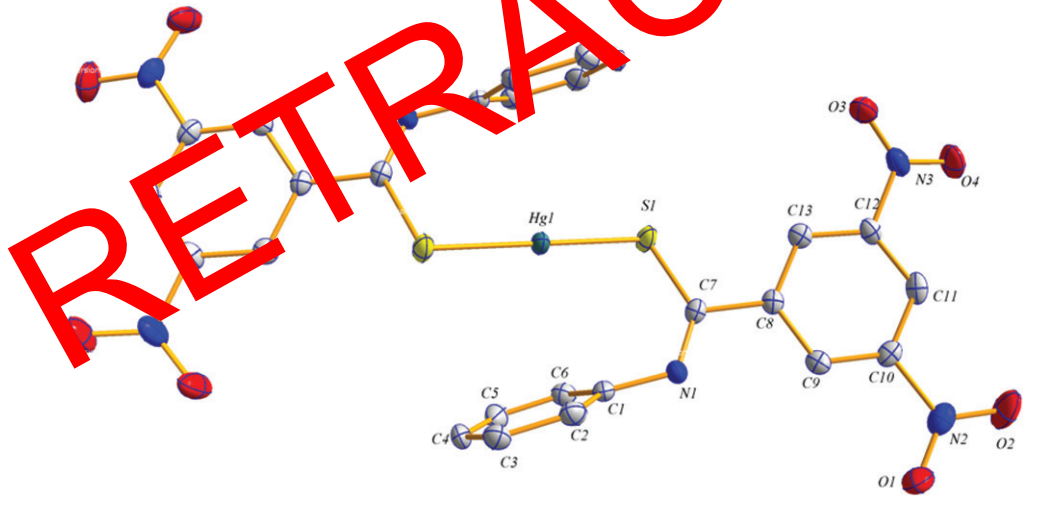


Figure 1. Molecular structure of **1** showing displacement ellipsoids at 50% probability. All H atoms have been omitted for clarity.

by thin layer chromatography (TLC) with CCl_4/CH_3OH 15 : 1 as eluent. The complex is insoluble in acetonitrile and 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: 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.

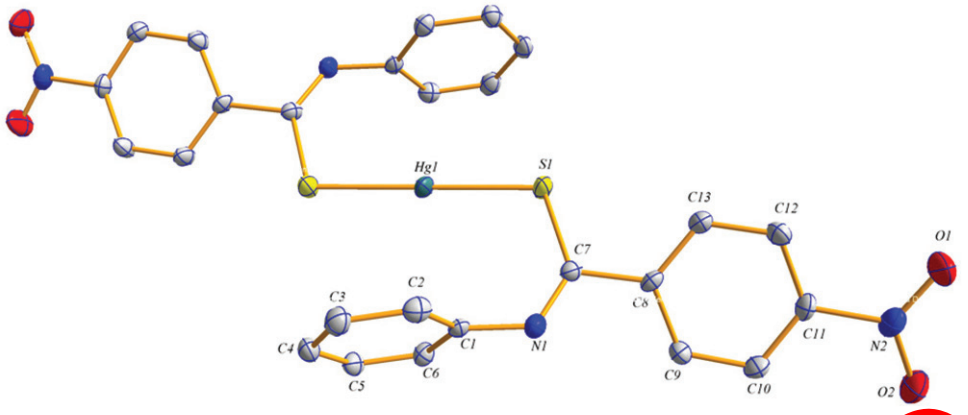


Figure 2. Molecular structure of **2** showing displacement ellipsoids at 50% probability. All H atoms have been omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°).

1		**2**	
Hg1–S1	2.3382(7)	Hg1–S1	2.3432(8)
S1–C7	1.770(3)	N1–C1	1.404(4)
C7–N1	1.274(3)	S1–C7	1.768(3)
C10–N2	1.476(3)	C7–C8	1.500(4)
N1–C1	1.418(3)	C7–N1	1.267(4)
C7–C8	1.50[illegible]	C10–N2	1.231(3)
S1–Hg1–S1A	180.0[illegible](3)	S1–Hg1–S1A	180.0
C8–C7–N1	[illegible]	C8–C7–N1	116.5(3)
C1–N1–C7	123.0(2)	Hg1–S1–C7	107.09(10)
O1–N2–O2	124.4(2)	C1–N1–C7	125.9(3)
Hg1–S1–C7	104.47(8)	S1–C7–N1	130.5(2)
S1–C7–N1	130.3(2)	O1–N2–O2	123.4(3)
S1–C7–C8	113.20(18)	S1–C7–C8	112.97(19)
O1–N2–C10	117.8(2)	O1–N2–C11	118.4(3)
Hg1–S1–C7–C8	−156.75(15)	Hg1–S1–C7–C8	−177.58(18)
Hg1–S1–C7–N1	23.4(3)	Hg1–S1–C7–N1	2.0(3)

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

The same method of preparation but using *N*-(phenyl)-4-nitrothiobenzamide (0.258 g, 1 mmol) in chloroform (20 mL for 80 min) was followed; the complex was recrystallized from chloroform as pale yellow crystals. Yield: 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 mounted on a Nonius Kappa CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å). Crystal data, collection procedures and refinement results are summarized in table 1. Bond distances and angles are shown in table 2. The unit cell

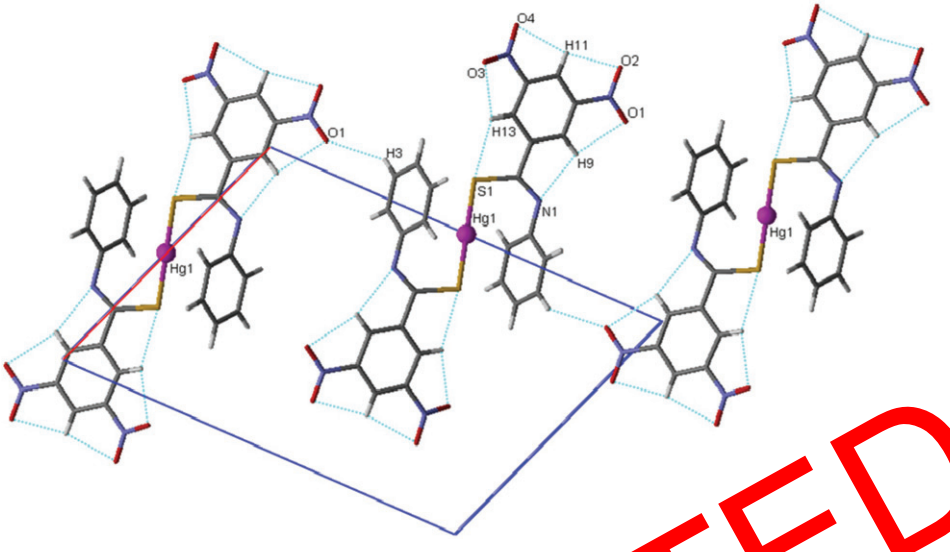


Figure 3. Packing diagram of **1** viewed down the *b*-axis via weak C–H···O, S, and N hydrogen bonds.

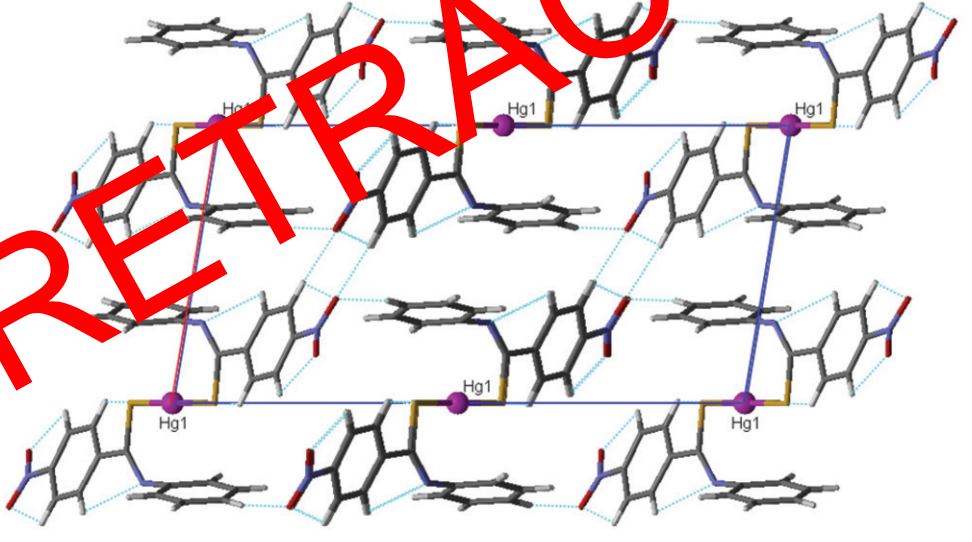


Figure 4. Packing diagram of **2** viewed down the *b*-axis with weak C–H···O, S, and N hydrogen bonds.

parameters were determined using SMART [7] and refined based on the positions of all strong reflections using SAINT [7]. Absorption correction was done by SADABS [8] 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 F^2 using SHELXTL [10]. Molecular graphics were produced using DIAMOND-3 [11] and Mercury 1.4 [12]. Nonhydrogen atoms were refined anisotropically; hydrogen atoms were first located in a difference map and then refined.

Table 4. Hydrogen-bonding geometry (Å, °) for **2**.

D–H···A	D–H	H···A	D···A	D–H···A
C12–H12···O1	0.95	2.441	2.724	96.95
C10–H10···O2	0.99	2.436	2.720	96.97
C9–H9···N1	0.95	2.523	2.791	96.31
C13–H13···S1	0.95	2.672	3.057	104.89
C4–H4···O2^{i}	0.95	2.542	3.483	170.47
C10–H10···O2^{ii}	0.95	2.480	3.290	143.21

Symmetry codes: (i) $1+x$, $1.5-y$, $1/2+z$; (ii) $1-x$, $1/2+y$, $1/2-z$.

3. Results and discussion

Complexes **1** and **2** were readily prepared in good yield by addition of equimolar quantities of HgO to the ligands in acetonitrile (scheme 1). The molecular structures with the atom numbering scheme are depicted in figures 1 and 2. The mercury of both complexes lies on an inversion center and the S–Hg–S is linear with angle of 180°. The Hg1–S1, S1–C7, and C7–N1 bond lengths are 2.3382(7), 1.770(3), and 1.274(3) Å, respectively (table 3). Hg–S bond distances are similar in the [Hg(bztzS)$_2$] complex [2.348(3) and 2.344(3) Å] [13]. The Hg–S(1)–C(7) and C(7)–N(1)–C(1) angles are 104.47(2) and 123.02(3) in **1**, slightly smaller than reported for [Hg(Nnptb)$_2$] [14]. The dihedral angle between C1–C6 and C8–C13 rings is 77.82°. The torsion angles Hg1–S1–C7–C8 and Hg1–S1–C7–N1 are −156.5(15) and 23.4(3)°, respectively. The N(1)–C(7)–S(1), N(1)–C(7)–C(8), and S(1)–C(7)–C(8) angles in **1** are 130.30(6), 116.50(4), and 113.20(2)°, respectively. The crystal packing of **1** and **2** are viewed along the *b*-axis in figures 3 and 4. Dashed lines indicate intra- and intermolecular C–H···O, S, and N hydrogen bonds with H(13)···S(1) 2.587, H(9)···N(1) 2.459, H(12)···O(2) 2.404, and H(3)···O(1)^{i} 2.672 Å [Symmetry code: (i) $-1/2+x$, $1.5-y$, $1/2+z$] (tables 2 and 4).

Supplementary material

Crystallographic data, tables of atomic coordinates and thermal parameters, and full lists of bond lengths and angles 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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