

# Coordination polymers and molecular structures among complexes of mercury(II) halides with selected 1-benzoylthioureas



Andrzej Okuniewski\*, Damian Rosiak, Jarosław Chojnacki, Barbara Becker

Department of Inorganic Chemistry, Chemical Faculty, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

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## ABSTRACT

Six new 1-benzoyl-3-phenylthiourea and 1-benzoyl-3-(2-methylphenyl)thiourea complexes of mercury(II) were obtained in the reactions of the ligands with  $\text{HgX}_2$  in methanol ( $X = \text{Cl}, \text{Br}, \text{I}$ ). Their structures, determined by single-crystal X-ray diffraction analysis, exhibit different stoichiometries and molecular organization. Coordination centers adopt more or less distorted tetrahedral geometry (five structures) or distorted trigonal bipyramidal geometry (one structure). In four cases 1D coordination polymers were formed and in the other two molecular compounds were found. In three cases solvent molecules ( $\text{H}_2\text{O}$  or  $\text{MeOH}$ ) were found in crystal structure. Although all compounds share common intramolecular  $\text{N}-\text{H} \cdots \text{O}=\text{C}$  structural motif they exhibit unique hydrogen bonding pattern. Common  $\mathcal{P}c11$  rod group symmetry of polymer chains (where applicable) allows simplified classification of the 3D packing as parallel stacking of trapezoidal prisms.

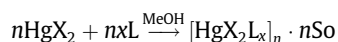
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## 1. Introduction

Thiourea and its derivatives found many applications in analytical chemistry [1], heterocyclic synthesis [2], metal flotation, leaching and extraction [3,4], rubber processing [5,6] and many others [7]. Especially interesting group of thiourea derivatives are acylthioureas [8] due to the simple synthesis [9], their stability and biological activity [10,11].

According to Pearson's HSAB theory [12], the mercury(II) ions are soft Lewis acids and thiourea derivatives are soft Lewis bases, so they are likely to form strong coordination bonds. Therefore, extensive studies are conducted to examine chemistry of these species. It is very important, because mercury compounds exhibit high toxicity to living organisms and their chelation can help in human detoxification [13]. Other S-donor ligands commonly used for mercury(II) complexation are: dithiocarbamates [14,15], thiosemicarbazones [16] and thiocyanates [17].

During our research we have synthesized new complexes of 1-benzoyl-3-phenylthiourea (bptu) and 1-benzoyl-3-(2-methylphenyl)thiourea (bmtu) with mercury(II) halides:



	L	X	N	x	So
1	bptu	Cl	1	2	MeOH
2	bptu	Br	$\infty$	1	$\text{H}_2\text{O}$
3	bptu	I	$\infty$	1	—
4	bmtu	Cl	$\infty$	1	$\text{H}_2\text{O}$
5	bmtu	Br	$\infty$	1	—
6	bmtu	I	1	2	—

We have obtained and structurally characterized six new compounds: bis(1-benzoyl-3-phenylthiourea- $\kappa\text{S}$ )dichloromercury(II) methanol monosolvate (1), catena-poly[[1-benzoyl-3-phenylthiourea- $\kappa\text{S}$ ]mercury(II)]-di- $\mu$ -bromo monohydrate (2), catena-poly[[1-benzoyl-3-phenylthiourea- $\kappa\text{S}$ ]iodomercury(II)]- $\mu$ -iodo (3), catena-poly[[1-benzoyl-3-(2-methylphenyl)thiourea- $\kappa\text{S}$ ]chloromercury(II)]- $\mu$ -chloro monohydrate (4), catena-poly[[1-benzoyl-3-(2-methylphenyl)thiourea- $\kappa\text{S}$ ]bromomercury(II)]- $\mu$ -bromo (5) and bis(1-benzoyl-3-(2-methylphenyl)thiourea- $\kappa\text{S}$ )diiodomercury(II) (6). Four of them are coordination polymers [18–20] – for nomenclature, see: [21].

## 2. Experimental

### 2.1. Synthesis of ligands

Thiourea derivatives were prepared according to procedure proposed by Douglas and Dains [9]: 92 mmol of ammonium

\* Corresponding author. Tel.: +48 58 347 2522.

E-mail address: [andrzej.okuniewski@gmail.com](mailto:andrzej.okuniewski@gmail.com) (A. Okuniewski).

thiocyanate and 60 ml of acetone were placed in a two-necked flask. Through the dropping funnel 80 mmol of benzoyl chloride in 20 ml of acetone was added with stirring. After addition was complete the mixture was refluxed for additional 15 min and then 80 mmol of amine in 30 ml of acetone was added through the dropping funnel. Reaction mixture was poured into 500 ml of water with stirring. The resulting precipitate was filtered on a Büchner funnel. Crude product was recrystallized from acetone.

1-Benzoyl-3-phenylthiourea (bptu) [22] was obtained with 87% yield. Mp.: 160(1) °C. <sup>1</sup>H NMR: δ (500 MHz, CDCl<sub>3</sub>, ppm) = 7.26–7.91 (m, 10H), 9.12 (s, 1H), 12.60 (s, 1H).

1-Benzoyl-3-(2-methylphenyl)thiourea (bmtu) [23] was obtained with 89% yield. Mp.: 117(1) °C. <sup>1</sup>H NMR: δ (500 MHz, CDCl<sub>3</sub>, ppm) = 2.38 (s, 3H), 7.24–7.93 (m, 9H), 9.21 (s, 1H), 12.27 (s, 1H).

Full <sup>1</sup>H NMR spectra for bptu and bmtu are provided in Supplementary materials (Figs. s1 and s2).

## 2.2. Synthesis of complexes

All complexes were synthesized by the general procedure as follows: 1 mmol of commercially available HgX<sub>2</sub> (X = Cl, Br, I) and 1 mmol of thiourea derivative (see above) were added to 35 ml of methanol, the mixture was stirred for 15 min and then filtrated. The filtrate was left to slowly evaporate at room temperature.

For **1**, 0.27 g of HgCl<sub>2</sub> and 0.26 g of bptu were used. After several days colorless plates were isolated with 42% yield. Mp.: 118(1) °C. Elem. Anal. Calc. for C<sub>29</sub>H<sub>28</sub>Cl<sub>2</sub>HgN<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 42.68; H, 3.46; N, 6.86; S, 7.86. Found: C, 42.70; H, 3.45; N, 7.03; S, 7.85%.

For **2**, 0.36 of HgBr<sub>2</sub> and 0.26 g of bptu were used. After several days colorless plates were isolated with 15% yield. Mp.: 152(1) °C – dehydration, 168(1) °C – melting point. Elem. Anal. Calc. for C<sub>14</sub>H<sub>14</sub>Br<sub>2</sub>HgN<sub>2</sub>O<sub>2</sub>S: C, 26.49; H, 2.22; N, 4.41; S, 5.05. Found: C, 26.04; H, 2.17; N, 4.36; S, 5.22%.

For **3**, 0.45 g of HgI<sub>2</sub> and 0.26 g of bptu were used. After several days pale yellow plates were isolated with 33% yield. Mp.: 147(1) °C. Elem. Anal. Calc. for C<sub>14</sub>H<sub>12</sub>HgI<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S: C, 23.66; H, 1.70; N, 3.94; S, 4.51. Found: C, 23.58; H, 1.72; N, 3.98; S, 4.57%.

For **4**, 0.27 g of HgCl<sub>2</sub> and 0.27 g of bmtu were used. After several days colorless plates were isolated with 70% yield. Mp.: 168(1) °C. Elem. Anal. Calc. for C<sub>15</sub>H<sub>16</sub>Cl<sub>2</sub>HgN<sub>2</sub>O<sub>2</sub>S: C, 32.18; H, 2.88; N, 5.00; S, 5.73. Found: C, 32.19; H, 2.87; N, 5.02; S, 5.88%.

For **5**, 0.36 g of HgBr<sub>2</sub> and 0.27 g of bmtu were used. After one day colorless blocks were isolated with 59% yield. Mp.: 184(1) °C. Elem. Anal. Calc. for C<sub>15</sub>H<sub>14</sub>Br<sub>2</sub>HgN<sub>2</sub>O<sub>2</sub>S: C, 28.56; H, 2.24; N, 4.44; S, 5.08. Found: C, 28.31; H, 2.21; N, 4.40; S, 5.13%.

For **6**, 0.45 g of HgI<sub>2</sub> and 0.27 g of bmtu were used. After several minutes colorless plates were isolated with 35% yield. Mp.: 188(1) °C. Elem. Anal. Calc. for C<sub>30</sub>H<sub>28</sub>HgI<sub>2</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 36.21; H, 2.84; N, 5.63; S, 6.44. Found: C, 35.92; H, 2.86; N, 5.69; S, 6.54%.

Far Infra-Red spectra (600–50 cm<sup>-1</sup>) for **1–6** are provided in supplementary materials (Fig. s3).

## 2.3. Measurements

X-ray diffraction measurements were carried out with a KM4 diffractometer (Kuma Diffraction, Wrocław, Poland) with CCD detector (Oxford Diffraction, Yarnton, United Kingdom) using graphite monochromated Mo Kα radiation at 298 K. The structures were solved by direct methods and refined anisotropically using the program packages WinGX 2013.3 [24] and SHELX-2013 [25]. Positions of the hydrogen atoms were calculated geometrically (except of those in OH groups) and taken into account with isotropic temperature factors. Further information on crystal structure refinement can be found in Table 1.

Elemental analyses were carried on Vario El Cube (Elementar Analysensysteme GmbH, Hanau, Germany).

<sup>1</sup>H NMR spectra were collected on Unity 500 plus (Varian, California, United States) spectrometer in chloroform-d at room temperature.

Far Infra-Red spectra were collected on Nicolet 8700 (Thermo Electron, Massachusetts, United States) spectrometer with polyethylene windows in Nujol at room temperature.

Melting points were measured on SMP30 (Stuart, Stone, United Kingdom) and were uncorrected.

## 2.4. Auxiliary structural parameters

In analysis of coordination polyhedra in presented structures we have used three structural index parameters. For five-coordinate complexes the τ<sub>5</sub> is in common use [26]. If β > α are the two greatest valence angles, then its value indicates whether the structure is square pyramidal (τ<sub>5</sub> = 0), trigonal bipyramidal (τ<sub>5</sub> = 1), or somewhere in between:

**Table 1**  
Crystal and final structure refinement data for [HgCl<sub>2</sub>(bptu)<sub>2</sub>·MeOH (**1**), [HgBr<sub>2</sub>(bptu)]<sub>n</sub>·nH<sub>2</sub>O (**2**), [HgI<sub>2</sub>(bptu)]<sub>n</sub> (**3**), [HgCl<sub>2</sub>(bmtu)]<sub>n</sub>·nH<sub>2</sub>O (**4**), [HgBr<sub>2</sub>(bmtu)]<sub>n</sub> (**5**) and [HgI<sub>2</sub>(bmtu)<sub>2</sub>] (**6**).

Compound reference	<b>1</b> (CCDC 971976)	<b>2</b> (CCDC 971977)	<b>3</b> (CCDC 971978)	<b>4</b> (CCDC 971979)	<b>5</b> (CCDC 971980)	<b>6</b> (CCDC 971981)
Chemical formula	C <sub>29</sub> H <sub>28</sub> Cl <sub>2</sub> HgN <sub>4</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>14</sub> Br <sub>2</sub> HgN <sub>2</sub> O <sub>2</sub> S	C <sub>14</sub> H <sub>12</sub> HgI <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S	C <sub>15</sub> H <sub>16</sub> Cl <sub>2</sub> HgN <sub>2</sub> O <sub>2</sub> S	C <sub>15</sub> H <sub>14</sub> Br <sub>2</sub> HgN <sub>2</sub> O <sub>2</sub> S	C <sub>30</sub> H <sub>28</sub> HgI <sub>2</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>
<i>M</i> (g/mol)	816.16	634.74	710.71	559.85	630.75	995.07
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>C2/c</i>
<i>a</i> (Å)	17.9343(11)	18.5937(14)	10.8279(5)	19.4695(12)	11.8229(7)	20.921(2)
<i>b</i> (Å)	11.9226(6)	7.5632(4)	8.7422(5)	7.5529(5)	20.5663(9)	8.7913(6)
<i>c</i> (Å)	29.1985(12)	24.6859(18)	37.5981(19)	23.982(4)	7.8419(4)	20.216(3)
β (°)	90	90	90	90	103.466(6)	118.344(14)
<i>V</i> (Å <sup>3</sup> )	6243.3(6)	3471.5(4)	3559.0(3)	3526.5(6)	1854.36(17)	3272.3(7)
<i>Z</i>	8	8	8	8	4	4
<i>F</i> (000)	3200	2352	2560	2128	1168	1880
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.737	2.429	2.653	2.109	2.259	2.020
μ, (1/mm)	5.27	13.60	12.24	9.16	12.72	6.75
<i>N</i> <sub>ref</sub>	14388	21104	21074	22149	6849	5714
<i>N</i> <sub>ref</sub> [independent]	6130	3410	3495	3464	3651	3194
<i>N</i> <sub>ref</sub> [ <i>I</i> > 2σ( <i>I</i> )]	4174	2152	2873	2374	2403	2394
<i>R</i> <sub>int</sub>	0.052	0.114	0.066	0.113	0.035	0.042
<i>R</i>	0.059	0.077	0.059	0.071	0.046	0.051
w <i>R</i>	0.147	0.234	0.153	0.194	0.121	0.135

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