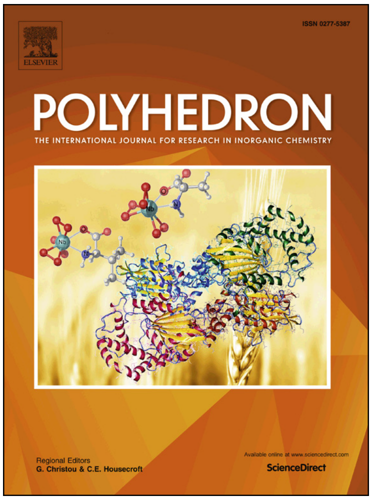
Accepted Manuscript



Novel complexes possessing Hg-(Cl, Br, I)···O=C halogen bonding and unusual $Hg_2S_2(Br/I)_4$ kernel. The usefulness of $_4$ structural parameter

Damian Rosiak, Andrzej Okuniewski, Jarosław Chojnacki

PII: S0277-5387(18)30083-4
DOI: https://doi.org/10.1016/j.poly.2018.02.016
Reference: POLY 13051

To appear in: *Polyhedron*

Received Date: 20 December 2017
Accepted Date: 16 February 2018

Please cite this article as: D. Rosiak, A. Okuniewski, J. Chojnacki, Novel complexes possessing Hg-(Cl, Br, I)···O=C halogen bonding and unusual $Hg_2S_2(Br/I)_4$ kernel. The usefulness of $_4$ structural parameter, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.02.016

Novel complexes possessing Hg–(Cl, Br, I)⋯O=C halogen bonding and unusual $Hg_2S_2(Br/I)_4$ kernel. The usefulness of τ_4' structural parameter

Damian Rosiak, Andrzej Okuniewski*, Jarosław Chojnacki

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

Keywords: halogen bond, binuclear complexes, benzoylthioureas, mercury complexes, bridging sulfur, metal cation-π interaction

Abstract

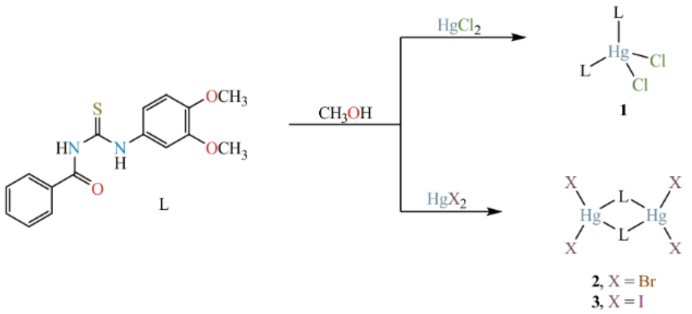
One mononuclear and two binuclear Hg^{II} complexes have been synthesized and characterized by X-ray diffraction, ATR IR and Hirshfeld surface analysis. Single-crystal X-ray diffraction showed that binuclear compounds are centrosymmetric and isostructural. All complexes form bifurcated intermolecular N−H⋯O hydrogen bonds that contribute to a formation of the centrosymmetric dimers. In binuclear complexes, sulfur atoms of thiourea ligands take the bridging role. These are the first examples of such compounds with mercury. In binuclear complexes of group 12 elements, halogens are usually the bridging atoms. The geometries of binuclear complexes are highly distorted with alarmingly low value of τ_4' parameter suggesting presence of additional donor that turned out to be phenyl ring (Hg⋯π interaction). The crystal structures are stabilized by additional noncovalent interactions, including halogen bonding which leads to the formation of chains. The differences and similarities of these complexes indicate that halogen ions have a great impact on the structures. Presented complexes comprise unique interactions between mercury-bonded halogen atoms and neighboring oxygen atoms of carbonyl groups (Hg–(Cl,Br,I)⋯O=C contacts).

1 Introduction

Acylthioureas possess both carbonyl and thiocarbonyl groups within one molecule. They readily form complexes with soft Lewis acids such as copper, gold, and mercury ions [1], where they serve as *S*-donor ligands. Because of the presence of thioamide functional group, thione-thiol tautomerism is possible for acylthioureas. However, the thione form is strongly preferred [2]. Moreover, a few years ago Okuniewski and coworkers analyzed 739 structures containing the CC(=O)NC(=S)N moiety found in the Cambridge Crystallographic Database [3]. From this study it can be clearly seen that 3-monosubsituted 1-acylthioureas adopt S-type conformation [4], with intramolecular N–H⋯O hydrogen bond forming **S**(6) motif [5].

Over the past few decades, benzoylthioureas and their complexes have received substantial attention not only due to their coordination ability, but also due to their antibacterial [6] and antimalarial activities [7]. These compounds play also an important role in flotation processes [8].

Complexes of aroylthioureas with heavy metals are isolated mainly as mono- or binuclear [2]. Some members of this class are insoluble in most of the common solvents and precipitate as polycrystalline powders. However, some powder X-ray structures were successfully refined [9]. Because of the different kinds of binding features, the crystal structures of these compounds are also important for application in coordination and bioorganic chemistry [10-15]. Despite many years of research, interest in the discussed group of compounds is not decreasing [16-21]. In our previous work [22] we have characterized four 1D coordination polymers and two mononuclear complexes of HgX_2 (X = Cl, Br, I) with 1-benzoyl-3-phenylthiourea and 1-benzoyl-3-(2-methylphenyl)thiourea. In this work, we wanted to check if and how the exchange of the substituent would influence the topology of the complexes and the crystal packing. We have used ligand with methoxy groups: 1-benzoyl-3-(3,4-dimethoxyphenyl)thiourea (L), that we described earlier [21]. Herein, we report the synthesis and crystal structures of the three complexes (Scheme 1) as well as a discussion of the influence of halogenide ions on the product formation.



Scheme 1. Synthesis outline.

2 Experimental

2.1 Syntheses

1-Benzoyl-3-(3,4-dimethoxyphenyl)thiourea (L) was prepared as described in literature [21]. Complexes were synthesized according to the same procedure as in our previous work [22]: 0.5 mmol of commercially available HgX$_2$ (X = Cl, Br, I) was dissolved in 15 ml of methanol and 0.5 mmol of 1-benzoyl-3-(3,4-dimethoxyphenyl)thiourea was dissolved in 45 ml of methanol. These solutions were combined and stirred for 15 min and then filtered. The filtrate was left to slowly evaporate at room temperature. Synthesis in acetone resulted an amorphous product.

Each product was collected from the reaction liquor in form of several monocrystals so the reaction yield was not determined. Obtained crystals were highly soluble in tetrahydrofuran, well soluble in acetone and chloroform, quite soluble in methanol and ethanol, but insoluble in diethyl ether, toluene, 2-propanol and water.

For **1**, 0.136 g of HgCl$_2$ and 0.158 g of L were used. After few hours, colorless plate crystals were isolated. Mp.: 147(1)°C. IR (ATR, cm^{-1}) $\nu_{C=O}$ 1693, ν_{N-H} 3173.

For **2**, 0.180 g of HgBr$_2$ and 0.158 g of L were used. After a week, colorless diamond-shaped crystals were isolated. Mp.: 162(1)°C. IR (ATR, cm^{-1}) $\nu_{C=O}$ 1691, ν_{N-H} 3331 and 3144.

For **3**, 0.227 g of HgI$_2$ and 0.158 g of L were used. After few hours, yellowish, block-shaped crystals were isolated. Mp.: 169(7)°C. IR (ATR, cm^{-1}) $\nu_{C=O}$ 1689, ν_{N-H} 3335 and 3138.

Table 1. Crystal and final structure refinement data for **1**, **2** and **3**.

Compound reference	**1** (CCDC 1579759)	**2** (CCDC 1579758)	**3** (CCDC 1579760)
Chemical formula	$C_{32}H_{32}Cl_2HgN_4O_6S_2$	$C_{32}H_{32}Br_4Hg_2N_4O_6S_2$	$C_{32}H_{32}Hg_2I_4N_4O_6S_2$
M, g/mol	904.25	1353.55	1541.51
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	29.5396(19)	9.9088(9)	10.1781(5)
b, Å	6.9354(9)	26.060(3)	26.4742(19)
c, Å	16.963(3)	7.6223(8)	7.7759(6)
β, °	103.905(9)	90.378(9)	91.682(5)
V, Å^3	3373.3(7)	1968.2(3)	2094.4(2)
Z; $F(000)$	4; 1784	2; 1264	2; 1408
d_{calc}, g/cm^3	1.780	2.284	2.444
μ, 1/mm	4.91	12.00	10.40
N_{ref}	34002	13468	15170
N_{ref} [independent]	9130	3882	4116
N_{ref} [$I > 2\sigma(I)$]	3403	2441	2989
R_{int}	0.087	0.069	0.074
R [$F^2 > 2\sigma(F^2)$]	0.058	0.052	0.065
wR (F^2)	0.169	0.115	0.195
Diffractometer	STOE	KUMA	KUMA

2.2 Measurements

X-ray analyses were carried out using KUMA KM4CCD or STOE IPDS instruments.

KUMA: Diffraction data were recorded at 293(2) K on a KUMA KM4 diffractometer with graphite-monochromated Mo$K\alpha$ radiation (0.71073 Å), equipped with a Sapphire 2 CCD camera (Oxford Diffraction). Data collection was performed using CrysAlis PRO (Oxford Diffraction) in the ω-scan mode. Analytical absorption correction was applied for all crystals.

STOE: Diffraction intensity data were collected on an IPDS 2T dual-beam diffractometer (STOE & Cie GmbH) at 120.0(2) K with Mo$K\alpha$ radiation of a microfocus x-ray source (GeniX 3D Mo High Flux, Xenocs, 50 kV, 1.0 mA, λ = 0.71069 Å). The crystal was thermostated in nitrogen stream at 120 K using CryoStream-800 device (Oxford CryoSystem) during the entire experiment. Data collection and data reduction were controlled by X-Area 1.75 program (STOE). An absorption correction was performed on the integrated reflections by a combination of frame scaling, reflection scaling and a spherical absorption correction. Outliers have been rejected according to Blessing's method.

The structures were solved by direct methods and refined anisotropically using the program packages OLEX^2 [23] and SHELX-2015 [24]. Positions of the hydrogen atoms were calculated geometrically and taken into account with isotropic temperature factors. Further information on crystal structure refinement can be found in Table 1.

The solid state IR spectra were measured using Nicolet iS50 FT-IR spectrometer equipped with the Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory controlled by Omnic computer software in range 4000-400 cm^{-1}.

Melting points were measured on SMP30 (Stuart) and were uncorrected.

2.3 Auxiliary parameters

In the description of the coordination polyhedra we have used Okuniewski's τ_4' [22] and Addison's τ_5 [25] structural parameters described as:

$$\tau_4' = \frac{\beta - \alpha}{360° - \theta} + \frac{180° - \beta}{180° - \theta}$$

$$\tau_5 = \frac{\beta - \alpha}{60°}$$

where $\beta > \alpha$ are two greatest valence angles and $\theta = \cos^{-1}\left(-\frac{1}{3}\right) \approx 109.5°$ is the tetrahedral angle. For square planar geometry $\tau_4' = 0$ and for tetrahedral geometry $\tau_4' = 1$, while for square pyramidal geometry $\tau_5 = 0$ and for trigonal bipyramidal geometry $\tau_5 = 1$.

Isostructurality of **2** and **3** was analyzed using two parameters: unit cell identity parameter Π [26] (for two identical unit cells $\Pi = 0$) and isostructurality index I' [27] (for two identical structures $I' = 1$).

Hydrogen bonds motifs are described using Etter's graph-set notation [5].

2.4 Hirshfeld surface

Hirshfeld surfaces and 2D fingerprints were calculated using the CrystalExplorer package ver. 3.1. [28]. Crystal structures were imported from CIF files. Hirshfeld surfaces were generated using a high surface resolution and mapped with the d_{norm} function.

3 Results and discussion

3.1 Crystal structure of **1**

Compound **1** is an example of a mononuclear seemingly symmetrical complex, which in fact does not have a 2-fold axis passing through the central atom. The whole molecule is present in the asymmetric unit (Fig. 1). The central atom has a coordination number of 4 and the $HgCl_2S_2$ coordination center adopts distorted tetrahedral geometry ($\tau_4' = 0.79$). Ligand molecules have retained the native S conformation with intramolecular N–H⋯O hydrogen bond [21].

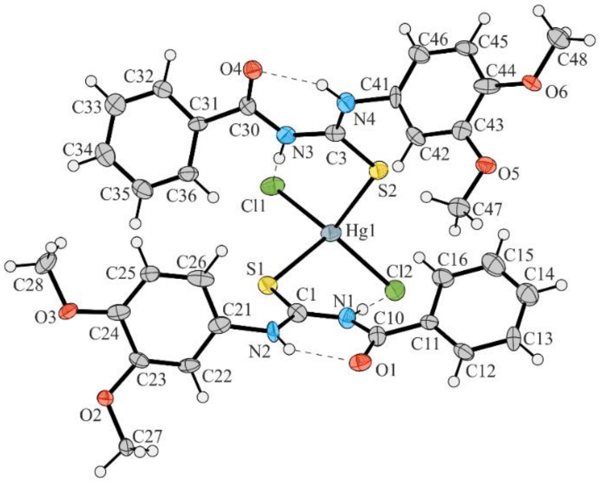


Fig. 1. Molecular structure and atom numbering scheme for **1**. Ellipsoids are drawn at 50% probability level. Selected hydrogen bonds are denoted with dashed lines.

Ligands are arranged in such a way that both of them take part in bifurcated hydrogen bonds (inter- and intramolecular) resulting in the formation of chains propagating in [001] direction. Besides intermolecular hydrogen bonds, both ligands are involved in intramolecular N−H⋯Cl hydrogen bonding. The parameters of all hydrogen bonds are summarized in Table 2.

Table 2. Hydrogen bond parameters in **1**. Symmetry codes: (i) $x, -y+3/2, z+1/2$; (ii) $x, -y+3/2, z-1/2$.

D−H⋯A	D−H, Å	H⋯A, Å	D⋯A, Å	D−H⋯A, °
N3−H⋯Cl1	0.88	2.63	3.435(8)	153
N2−H⋯O1	0.88	2.00	2.683(10)	133
N2−H⋯O4^{i}	0.88	2.33	2.983(10)	131
N1−H⋯Cl2	0.88	2.74	3.603(7)	168
N4−H⋯O1^{ii}	0.88	2.32	3.045(10)	139
N4−H⋯O4	0.88	2.05	2.712(10)	131

In the structure of **1**, a number of halogen interactions can be also found. We can distinguish significant interactions between the atoms of chlorine (having anisotropic electron density) and neighboring oxygen atoms of carbonyl groups (Fig. 2.).

No classical stacking interactions are present in this structure, however CgS1⋯CgS3^{ii} stacking of parallel ($\alpha = 0°$) quasi-aromatic pseudo-rings with centroid-centroid distance of 3.947(4) Å can be found. CgS1 and CgS3 are the centroids of O1/C10/N1/C1/N2/H1 and O4/C30/N3/C3/N4/H4 pseudo-rings respectively. In the crystal structure of sole ligand quasi-aromatic pseudo-rings were interacting with phenyl rings, not with each other. Symmetry operations are defined in Fig. 2.

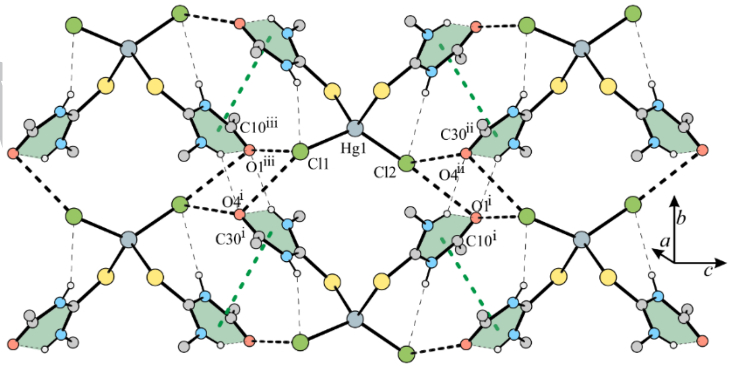


Fig. 2. The intra- and intermolecular interactions (hydrogen bonds – thin dashed lines, halogen interactions – thick dashed lines and quasi-aromatic pseudo-ring stacking interactions – green dashed lines) in **1.** The parameters of halogen contacts are (Å, °): Cl1⋯O1^{iii} 3.768(8), Cl1⋯O4^{i} 3.436(7), Cl2⋯O1^{i} 3.308(7), Cl2⋯O4^{ii} 3.598(8), Hg1−Cl1⋯O1^{iii} 88.7(1), Hg1−Cl1⋯O4^{i} 124.6(1), C10^{iii}−O1^{iii}⋯Cl1 132.9(6), C30^{i}−O4^{i}⋯Cl1 83.0(5), Hg1−Cl2⋯O1^{i}

142.8(1), Hg1–Cl2···O4^{ii} 96.4(1), C10^{i}–O1^{i}···Cl2 83.3(5), C30^{ii}–O4^{ii}···Cl2 144.0(6). Symmetry operations: (i) $x, -1+y, z$; (ii) $x, -y+1/2, z+1/2$; (iii) $x, -y+1/2, z-1/2$. Aromatic rings are omitted for clarity.

3.2 Crystal structure of **2** and **3**

The complexes **2** and **3** exhibit great similarity, both are binuclear and centrosymmetric (Fig. 3). At first glance, mercury atoms have a coordination number of 4 with the $HgBr_2S_2$/HgI_2S_2 coordination centers adopting highly distorted tetrahedral geometry (for **2** $\tau_4' = 0.67$ and for **3** $\tau_4' = 0.65$). Thiourea's sulfur is the bridging atom.

For highly distorted tetrahedral geometries, when $\tau_4' < 0.75$, one should check if the coordination number of metallic center isn't greater. Additional $Cg2$···Hg1 contact with 3.686(3) Å and 3.731(5) Å distance for **2** and **3** can be found respectively ($Cg2$ is a centroid of C21-C26 ring). Distorted geometry between square pyramidal and trigonal bipyramidal with $\tau_5 = 0.43$ (**2**) and $\tau_5 = 0.45$ (**3**) can be assigned to mercury.

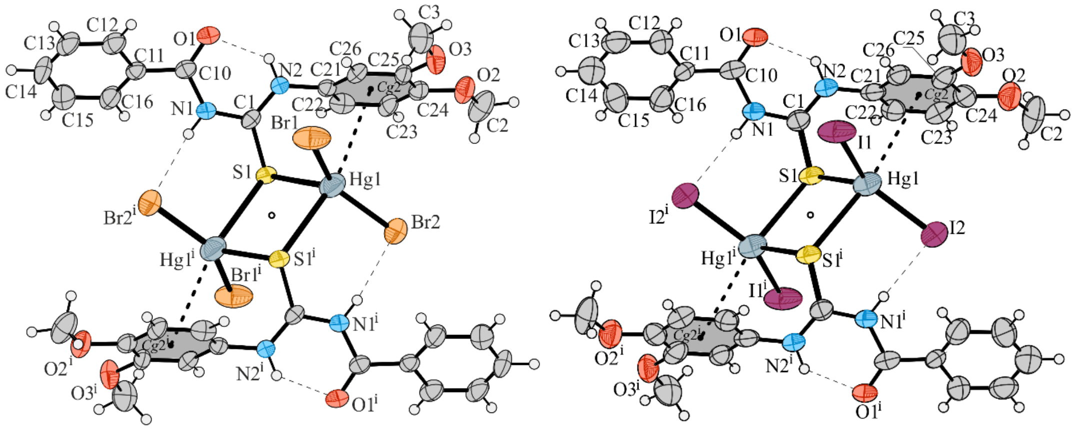


Fig. 3. Molecular structure and numbering scheme for **2** and **3**. Ellipsoids are drawn at 50% probability level. Selected hydrogen bonds are denoted with thin dashed lines, $Cg2$···Hg1 interactions are marked with thick dashed lines. The parameters of selected distances and angles in the coordination centers (first value is for **2** and second value is for **3**; Å, °): S1–Hg1 2.647(2)/2.685(3), S1–Hg1^{i} 2.998(2)/3.157(3), Hg1–X1 2.464(1)/2.635(1), Hg1–X2 2.462(1)/2.627(1), $Cg2$···Hg1 3.686(3)/3.731(5), Hg1–S1–Hg1^{i} 89.67(7)/85.54(7), S1–Hg1–S1^{i} 90.33(7)/94.46(7), X1–Hg1–X2 141.00(4)/143.55(4). Symmetry operation: (i) $-x+1, -y+1, -z+1$. ∘ denotes the center of the inversion.

In structure **2** and **3** there are no significant stacking interactions. However, interesting halogen bonds formed by Br1/I1 and surrounding oxygen atoms of carbonyl groups can be found (Fig. 4).

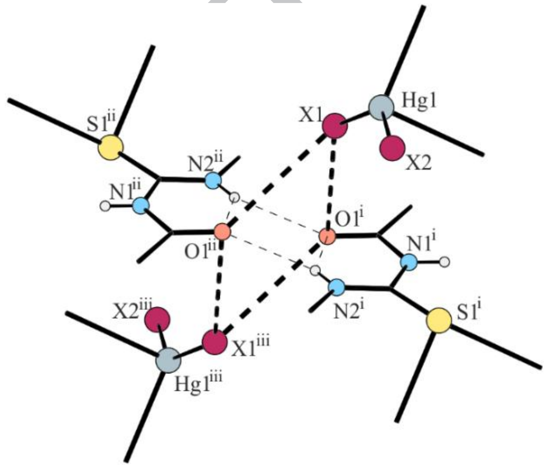


Fig. 4. The system of hydrogen bonds (thin dashed lines) and halogen interactions (thick dashed lines) on the example of **2**. Only selected atoms of ligands are shown for clarity. The parameters of halogen contacts are (first value is for **2** and second value is for **3**; Å, °): X1···O1^{i} 3.493(5)/3.652(8), X1···O1^{ii} 3.714(5)/3.839(8), Hg1–X1···O1^{i} 136.8(1)/137.6(1), Hg1–X1···O1^{ii} 122.09(9)/124.2(1), C10^{i}–O1^{i}···X1 86.8(4)/85.2(6), C10^{ii}–O1^{ii}···X1 137.5(5)/137.7(7). Symmetry operations: (i) $x, y, z+1$; (ii) $-x, -y+1, -z+1$; (iii) $-x, -y+1, -z+2$.

Isostructurality parameters for **2** and **3** (described in chapter Auxiliary parameters) are equal to: $\Pi = 0.019$, $I' = 0.94$. Additionally we have calculated powder XRD diffractograms from CIF files using Mercury 3.10 software [29] (Fig. 5). It can be clearly seen that both diffractograms overlay well. Diffraction peaks for **3** are distributed tighter as the unit cell parameters are slightly greater (Table 1). In diffractogram of **2** some diffraction peaks overlap – eg. $(11\bar{1})$ and (111).

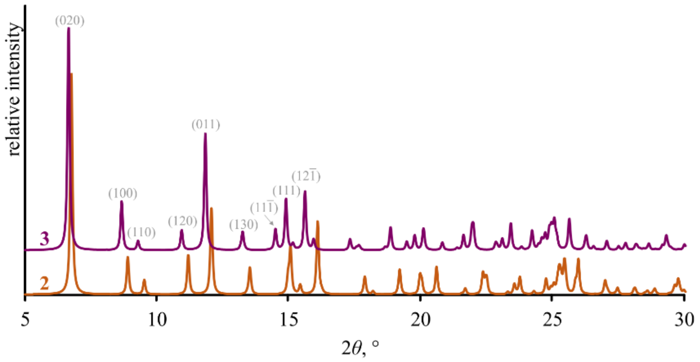


Fig. 5. Overlay of powder XRD diffractograms calculated form CIF files of 2 and 3. Gray numbers in parentheses indicate Miller indices of lattice planes.

We have analyzed structures of mercury complexes with acylthioureas among entries deposited into the CSD v. 5.39 (November 2017 update) [30] and these are the first examples of mercury complexes with bridging acylthiourea. In binuclear complexes of group 12 elements, halogens are usually the bridging atoms. There are only two examples of such complexes of 12 group with zinc [31, 32]. Binuclear complexes in which sulfur atoms take the bridging role are typical for transition elements [33-36]. Moreover, in our previous work [22] we have shown that acylthioureas in the reaction with HgX_2 readily form coordination polymers and mononuclear complexes.

The crystal cohesion of the complexes is ensured by intermolecular N–H···O hydrogen bonds, X···O=C halogen bonds, quasi-aromatic pseudo-ring stacking, van der Waals and electrostatic interactions that create a three-dimensional network.

In all structures ligand molecules adopt most abundant S-type conformation [3, 4], with intramolecular N–H···O hydrogen bond forming **S**(6) motif [5]. These hydrogen bonds are bifurcated at hydrogen atom and form $\mathbf{R}_2^2(12)$ motifs. In all structures of **2** and **3**, two of such hydrogen bonds combine each pair of dimers to form chains propagating in $[10\bar{1}]$ direction (Fig. 6). The second N–H group serves as a donor for halogen atom and forms intramolecular N–H···X hydrogen bond. The parameters of all the hydrogen bonds found in **2** and **3** are summarized in Table 3.

Table 3. Hydrogen bond parameters in structure of **2** and **3**. Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z$.

		D–H, Å	H···A, Å	D···A, Å	D–H···A, °
2	N1–H···Br2^{i}	0.86	2.90	3.591(7)	139
	N2–H···O1	0.86	2.00	2.672(9)	134
	N2–H···O1^{ii}	0.86	2.42	3.077(8)	134
3	N1–H···I2^{i}	0.86	3.16	3.805(9)	134
	N2–H···O1	0.86	2.01	2.678(12)	134
	N2–H···O1^{ii}	0.86	2.40	3.083(11)	137

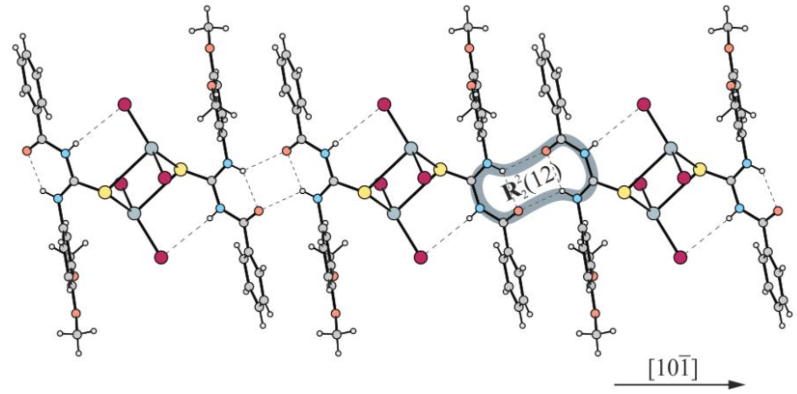


Fig. 6. Centrosymmetric dimers found in the structure of **2** and **3**, linked by intermolecular hydrogen bonds (dashed lines) into chains spreading in $[10\bar{1}]$ direction.

In **2** and **3** the methoxy groups are almost coplanar with parent aromatic ring (maximum distance is between C3 and mean plane of phenyl ring – 0.201 Å for **2** and 0.121 Å for **3**), but in **1** those substituents are slightly twisted (maximum distance between mean plane of phenyl ring and C27 is 0.442 Å, and 0.290 Å for C28).

3.3 Hirshfeld surface analysis

The Hirshfeld surface (HS) of compound **1** mapped with d_{norm} function has four big red areas corresponding to the strong, bifurcated hydrogen bonds (N2–H···O4^{i}, N4–H···O1^{ii}, symmetry operations are defined in Table 2) and four smaller ones on the sides corresponding to the weaker hydrogen bonds with oxygen atoms of methoxy groups C48–H···O5[$-x+1$, $y-1/2$, $-z+1/2$] and C34–H···O2[$-x$, $y-1/2$, $-z+1/2$] (see Fig. 7). Moreover, two small spots related to the Cl···O halogen bond should be noticed. On the HS, we can also notice twenty two very small red areas corresponding to weak C···C and C···H interactions. A study of the decomposed fingerprint plots shows that the most important interactions between molecules in **1** are van der Waals forces. Around 2% of HS is associated with relatively close Cl···O contacts.

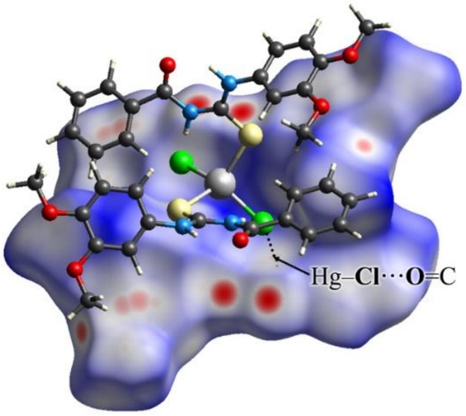


Fig. 7. Hirshfeld surface of complex **1** mapped with d_{norm} function.

Due to their similarity, HS of **2** and **3** will be described together. On the surfaces mapped with d_{norm} function we can notice four big red areas which correspond to weak C2–H···O2[x, $-y+3/2$, $z-1/2$] hydrogen bond and strong bifurcated N2–H···O1[$-x$, $-y+1$, $-z$] hydrogen bonds (Fig. 8). The latter are responsible for the formation of a supramolecular chains. Furthermore, on the HS of **2** there are two more small red spots corresponding to weak C13–H···O3[$-x$, $y-1/2$, $-z+1/2$] hydrogen bonds with 2.578(5) Å distance (in **3** distance 2.701(8) Å is too large to see red spots on HS).

The differences of interaction in these two structures are shown in the diagrams based on 2D Hirshfeld surface fingerprint decomposition (Fig. 9). The main difference is the lack of sulfur-halogen and sulfur-mercury interactions on the HS of **3**. In both structures around 1% of HS is associated with relatively close X···O contacts (X = Br, I).

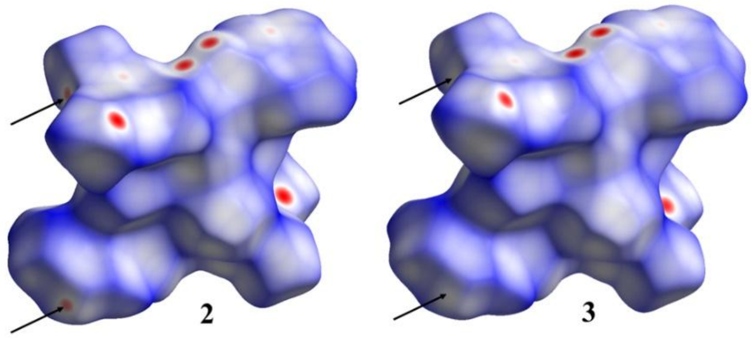


Fig. 8. Hirshfeld surface of **2** and **3** mapped with d_{norm} function (arrows show main differences).

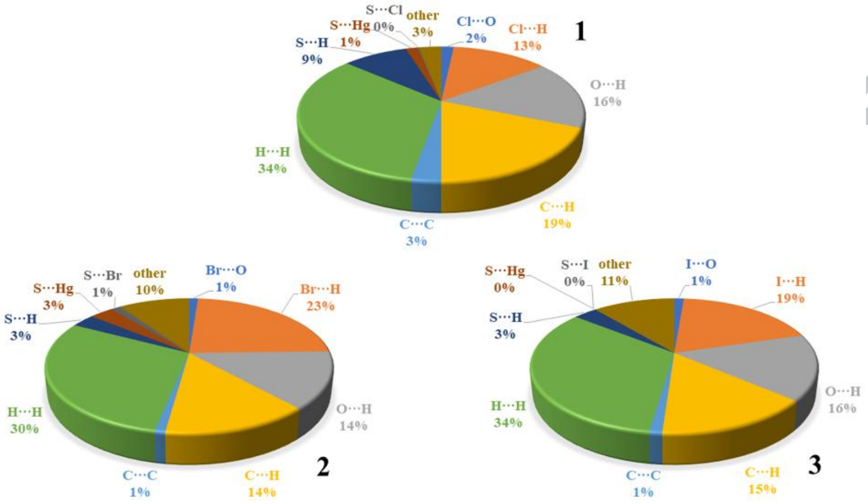


Fig. 9. Hirshfeld surface fingerprint decompositions showing main types of interactions for **1**, **2** and **3**.

4 Conclusion

Within presented work, we have synthesized and characterized three new HgX_2 (X = Cl, Br, I) complexes with 1-benzoyl-3-(3,4-dimethoxyphenyl)thiourea.

The study shows that halogen type have a significant influence on the final structure of complex. At the first glance, complexes **1-3** have coordination number 4 and their geometries can be described as highly distorted tetrahedral. However, τ_4' parameter for **1** (0.79) is significantly greater than for **2** (0.67) and **3** (0.65). This is caused by additional $Cg2\cdots$Hg1 short contact present in latter ones (Fig. 10). In fact, low values of τ_4' parameter should alarm authors to check if there are additional interactions with metallic center. Such Hg⋯π interactions can be found in many structures deposited to CSD, including phenyl rings substituted with methoxy groups [37]. The lower polarizability of the chlorine may cause the mercury ion adopts less distorted tetrahedral geometry ($\tau_4' = 0.79$) than in the case of bromide and iodide complexes.

Appendix A. Supplementary data

CCDC 1579759, 1579758, 1579760 contains the supplementary crystallographic data for **1-3.** These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] M. Mirzaei, H. Eshtiagh-Hosseini, M. Mohammadi Abadeh, M. Chahkandi, A. Frontera, A. Hassanpoor, *CrystEngComm*, **15** (2013) 1404-1413.

[2] A. Saeed, U. Florke, M. F. Erben, *J. Sulf. Chem.* **35** (2014) 318-355.

[3] A. Okuniewski, J. Chojnacki, B. Becker, *Acta Crystallogr. E* **68** (2012) o619–o620.

[4] M. G. Woldu, J. Dillen, *Theor. Chem. Acc*. **121** (2008) 71-82.

[5] M. C. Etter, *Acc. Chem. Res*. **23** (1990) 120-126.

[6] S. S. Cunha, F. C. Macedo, G. A. N. Costa, M. T. Rodrigues, R. B. V. Verde, L. C. de Souza Neta, I. Vencato, C. Lariucci, F. P. Sá, *Monats. Chem.* **138** (2007) 511-516.

[7] T. J. Egan, K. R. Koch, P. L. Swan, C. Clarkson, D. A. Van Schalkwyk, P. J. Smith, *J. Med. Chem.* **47** (2004) 2926-2934.

[8] G. A. Hope, R. Woods, S. E. Boyd, K. Watling: *Colloid Surf. A – Physicochem. Eng. Asp.* **232** (2004) 129-137.

[9] O. Estévez-Hernández, J. Duque, J. Rodríguez-Hernández, E. Reguera, *Polyhedron* **97** (2015) 148-156.

[10] T. S. Lobana, R. Sharma, R. Sharma, R. Sultana, R. J. Butcher, *Z. Anorg. Allg. Chem*. **634** (2008) 718-723.

[11] A. A. Isab, M. Fettouhi, M. R. Malik, S. Ali, A. Fazal, S. Ahmad, *Russ. J. Coord. Chem.* **37** (2010) 180-185.

[12] M. R. Malik, S. Ali, S. Ahmad, M. Altaf, H. Stoeckli-Evans, *Acta Crystallogr. E* **66** (2010) m1060-m1061.

[13] S. Ahmad, H. Sadaf, M. Akkurt, S. Sharif, I. U. Khan, *Acta Crystallogr*. *E* **65** (2009) m1191-m1192.

[14] M. Altaf, H. Stoeckli-Evans, S. Ahmad, A. A. Isab, A. R. Al-Arfaj, M. R. Malik, S. Ali, *J. Chem. Crystallogr*. **40** (2010) 1175-1179.

[15] H. Sadaf, S. Ahmad, S. Sharif, I. U. Khan, M. Akkurt, S. W. Ng, M. I. Khan, S. A. Bashir, M. Mufakkar, *J. Struct. Chem*. **53** (2012) 151-155.

[16] M. K. Rauf, S. Zaib, A. Talib, M. Ebihara, A. Badshah, M. Bolte, J. Iqbal, *Bioorg. Med. Chem.* **24** (2016) 4452-4463.

[17] J.-H. Hu, J.-B. Li, J. Qi, Y. Sun, *Phosphorus Sulfur Silicon Relat. Elem.* **191** (2015) 984-987.

[18] L. Qiao, J. Huang, W. Hu, Y. Zhang, J. Guo, W. Cao, K. Miao, B. Qin, J. Song, *J. Mol. Struct.* **1139** (2017) 149-159.

[19] L. Qiao, Y. Zhang, W. Hu, J. Guo, W. Cao, Z. Ding, Z. Guo, A. Fan, J. Song, J. Huang, *J. Mol. Struct.* **1141** (2017) 309-321.

[20] D. Wang, S.-Y. Wu, H.-P. Li, Y. Yang, H. W. Roesky, *Eur. J. Inorg. Chem.* (2017) 1406-1413.

[21] A. Okuniewski, D. Rosiak, J. Chojnacki, B. Becker, *Acta Crystallogr. C* **73** (2017) 52-56.

[22] A. Okuniewski, D. Rosiak, J. Chojnacki, B. Becker, *Polyhedron* **90** (2015) 47-57.

[23] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **42** (2009) 339-341.

[24] G. M. Sheldrick, *Acta Crystallogr. C* **71** (2015) 3-8.

[25] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* (1984) 1349-1356.

[26] L. Fábián, A. Kálmán, *Acta Crystallogr. B* **55** (1999) 1099-1108.

[27] M. Kubicki and M. Szafrański, *J. Mol. Struct*. **446** (1998) 1-9.

[28] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, Crystal Explorer ver. 3.1, University of Western Australia, Perth, Australia, 2012.

[29] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.* **41** (2008) 466-470.

[30] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr. B* **72** (2016) 171-179.

[31] K. S. Anjali, J. J. Vittal, *Main Group Met. Chem.* **24** (2001) 129-130.

[32] M. C. Brianso, J. L. Brianso, W. Gaete, J. Ros, C. Suner, *J. Chem. Soc., Dalton Trans.* (1981) 852-854.

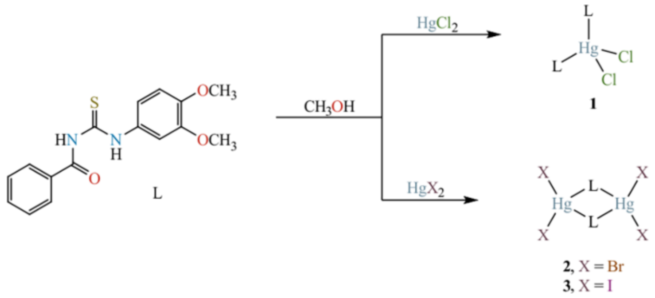
[33] U. Rychlewska, B. Warzajtis, B. Jasiewicz, T. Tolinski, *Polyhedron* **30** (2011) 458-464.

[34] P. Amo-Ochoa, O. Castillo, A. Guijarro, P. J. S. Miguel, F. Zamora, *Inorg. Chim. Acta* **417** (2014) 142-147.

[35] G. Li, D.-J. Che, Z.-F. Li, Y. Zhu, D.-P. Zou, *New J. Chem.* **26** (2002) 1629-1633.

[36] Ch. Wang, W. Lu, Y. Tong, Y. Zheng, Y. Yang, *RSC Adv.* **4** (2014) 57009-57015.

[37] B. Tirloni, E. Schulz Lang, G. Manzoni de Oliveira, P. Piquini, M. Hörner, *New J. Chem.* **38** (2014) 2394-2399.


S
HN
N
H
O
OCH$_3$
OCH$_3$
L
CH$_3$OH
HgCl$_2$
HgX$_2$
L
L
Hg
Cl
Cl
1
X
X
Hg
L
L
Hg
X
X
2, X = Br
3, X = I