Mercury(II) Complexes with Heterocyclic Thiones − Preparation and Characterization of the 1:1 and 1:2 Mercury(II) Complexes with Benzo-1,3-imidazole-2-thione

Zora Popović,*[a] Željka Soldin,[a] Dubravka Matković-Čalogović,[a] Gordana Pavlović,[b] Maša Rajić,[c] and Gerald Giester[d]

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A series of complexes $HgX_2(bzimtH_2)$ and $HgX_2(bzimtH_2)_2$ ($X = Cl^-, Br^-, I^-, SCN^-$; $bzimtH_2$ = benzo-1,3-imidazole-2-thione) was obtained by reaction of the mercury(II) salts with benzo-1,3-imidazole-2-thione in the appropriate molar ratio (1:1 or 1:2). $Hg(bzimtH)_2$ was obtained by the deprotonation of $bzimtH_2$ with mercury(II) acetate (irrespective of the molar ratio of the reactants). The complexes were characterised by chemical and thermal analysis, IR, ^1H, and ^{13}C NMR spectroscopy, and some [$HgX_2(bzimtH_2)$, $X = I^-$ and $HgX_2(bzimtH_2)_2$, $X = I^-$ and SCN^-] by X-ray single crystal diffractometry. ^1H and ^{13}C NMR spectroscopic measurements in dimethyl sulphoxide revealed that the sulphur atom is coordinated to the mercury centre. The greatest complexation effects on the chemical shifts were observed for the thione carbon atom and thioamide proton. The crystal structures of $HgI_2(bzimtH_2)_2$ and $Hg(SCN)_2(bzimtH_2)_2 \cdot C_2H_5OH$ consist of discrete monomeric molecules with halide or pseudohalide donor atoms and thione sulphur atoms tetrahedrally coordinated to the mercury atom. The structure of $HgI_2(bzimtH_2)$ is polymeric with a trigonal bipyramidal 3 + 2 coordination geometry around the mercury atom. Polymerisation occurs through Hg···I interactions with neighbouring molecules. The distribution of the π-electron density in $bzimtH_2$ corresponds to the thioketo tautomeric form in the solid state, and also in the DMSO solution of the complexes. Intermolecular hydrogen bonds of the type N–H···N, N–H···S and N–H···I are observed.

Introduction

The coordination chemistry of mercury(II) with sulphur-donor ligands is a topic of current research, largely because of the importance of such complexes as structural models in biological systems,[1] and also as solid-state materials.[2] The ability of mercury(II) halides and pseudohalides to form 1:1 and 1:2 complexes with neutral ligands has been known for years.[3,4] The most common neutral donors are phosphane and amine derivatives, and recently heterocyclic thiones.[5−7] Beside such complexes, heterocyclic thiones also give sulphide-like compounds of the type HgL_2 (L = deprotonated thione ligand), by deprotonation.[8,9]

The crystal structures of mercury(II) complexes with heterocyclic thiones revealed the monodentate thione sulphur-donating character of the ligand, although chelation was observed in a few cases.[8,10] The great structural variety of the aforementioned complexes reflects the flexibility of the coordination geometry of mercury. All structures can be regarded as being composed of an inner HgX_2 or HgX_3 unit. In these units the mercury behaves as a Lewis acid and becomes less strongly coordinated to an outer group. This leads to more highly coordinated species, HgX_2L_n or HgX_3L_m, where n is 2, 3 or 4, but m is most commonly 2. It is not fully clear what factors determine the coordination of mercury in such an environment. It is well known that mercury(II) halides form 1:1 or 1:2 complexes with neutral ligands, depending on the molar ratio of the reactants. The crystal structures of the 1:2 complexes usually consist of discrete monomeric molecules with a tetrahedrally coordinated mercury atom (more or less distorted). In contrast, the crystal structures of the 1:1 complexes often involve discrete dimeric molecules, with the mercury atom in a distorted tetrahedral environment.[8,12−16] We have examined a series of such complexes so as to gain an insight into the steric and electronic effects of halide or pseudohalide and heterocyclic thione ligands on the mercury coordination sphere, and into the donor potential towards the mercury atom.[8,11−16]

Continuing with our previous work, we now examine the structural characteristics of the 1:1 and 1:2 mercury(II) halide and mercury(II) thiocyanate complexes with benzo-1,3-

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[a] Laboratory of General and Inorganic Chemistry, Faculty of Science, Chemistry Department, University of Zagreb,
Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia
Fax: (internat.) + 385-1/4611191
E-mail: zpopovic@chem.pmf.hr
[b] Polytechnic of Karlovac,
I. Meštrovića 10, 47000 Karlovac, Croatia
[c] Laboratory for Thermal Analysis, Brodarski Institute, Marine Research and Special Technology,
Av. V. Holjevca 20, 10000 Zagreb, Croatia
[d] Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien,
Althanstrasse 14, 1090 Wien, Austria

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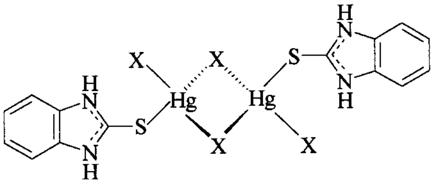
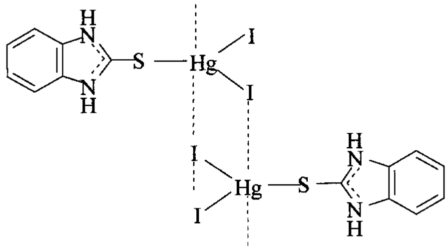
imidazole-2-thione in the solid state and in dimethyl sulphoxide.

Results and Discussion

Mercury(II) complexes $HgX_2(bzimtH_2)$ (**1−4**) and $HgX_2(bzimtH_2)_2$ (**5−8**) were prepared according to the following general procedure (Scheme 1). A methanol solution of $bzimtH_2$ was added dropwise to a methanol solution of the mercury(II) halide in the appropriate molar ratio. In the preparation of the thiocyanato complexes an ethanol solution was used instead of a methanol solution. Furthermore, due to the photosensitivity of the complexes, the reaction was performed in the dark. The reaction mixtures were left for a few days (with the exception of the thiocyanato complexes which were left for a few weeks), after which crystalline products formed and were filtered off, washed with cold methanol and dried. Complexes **1−8** are generally insoluble in common organic solvents, but fairly soluble in solvents with pronounced donor properties such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF), pyridine etc. $Hg(bzimtH)_2$ (**9**) was obtained by treating mercury(II) acetate with $bzimtH_2$ in a 1:2 molar ratio in ethanol. Complex **9** is insoluble in common organic solvents and also insoluble in DMSO, DMF, pyridine, or similar solvents.



X = Cl⁻ (**1**), Br⁻ (**2**), SCN⁻ (**4**)



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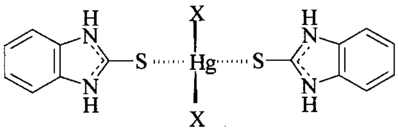
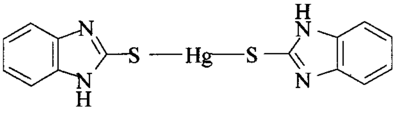


X = Cl⁻ (**5**), Br⁻ (**6**), I⁻ (**7**), SCN⁻ (**8**)

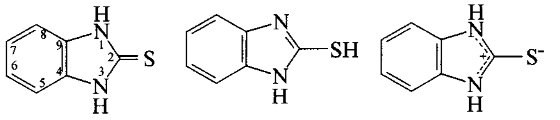


9

Scheme 1. Mercury(II) complexes of benzo-1,3-imidazole-2-thione

Infrared and NMR Spectra

The absence of the ν(S−H) absorption band at 2500 cm^{-1} in the spectrum of free $bzimtH_2$, as well as the presence of the ν(N−H) band confirm that the thione tautomer is the dominant form of the ligand in the solid state (Scheme 2, a). The spectra of **1−8** (Table 1) show strong absorption bands in the range 3180−3100 cm^{-1}, corresponding to the ν(N−H) stretching band. A small shift from the bands seen in the spectrum of free $bzimtH_2$ is observed, indicating that the nitrogen atom does not take part in the coordination to the mercury centre. This shift probably results from the variation in the hydrogen-bonding interactions and electronic changes within the ligand on coordination to the mercury ion. Absorption bands which are associated with the C−N vibration mode also show insignificant shifts, suggesting that $bzimtH_2$ is not bonded through the nitrogen atom. Coordination of the metal ion by the nitrogen atom in the thioamide ligands is accompanied by a negative shift of these bands. Such a shift, as well as the negative shift of the ν(N−H) absorption bands, is observed only in the spectrum of **9**, suggesting the existence of mercury and nitrogen interactions. Substitution of sulphur with selenium in $bzimtH_2$ was used to determine the vibrations related to the C−S modes.[17] In the IR spectrum of $bzimtH_2$, the region below 700 cm^{-1} undergoes substantial modification on selenation. Thus, the authors suggested the contribution of the C−S modes to these bands. In the spectra of **1−8**, a significant change in intensities and frequencies of these bands was observed, supporting the fact that $bzimtH_2$ is coordinated through the sulphur atom.



(a) (b) (c)

Scheme 2. (a) thione tautomer; (b) thiol tautomer; (c) zwitterionic resonance form of the thione tautomer

^{1}H and ^{13}C NMR spectroscopic data for **1−8** in their DMSO solutions are consistent with the finding that the sulphur atom is coordinated to the mercury atom, as previously found for similar mercury(II) complexes with imidazole-2-thione and some of its derivatives.[8,18−20] In the ^{1}H NMR spectra of $bzimtH_2$ and of complexes **1−8** (Table 2), the signals for the thioamide N−H protons (1-,3-H) are observed in the range $\delta = 12.50-13.90$ (numbering of the carbon atoms is displayed in Scheme 2). The absence of the signal for the thiol proton (−SH, $\delta \approx 3.5$) in the ^{1}H NMR

Table 1. Major infrared bands [cm^{-1}] of bzimtH$_2$ and complexes **1−9**

Compound	ν(N−H)	C−N modes	C−S modes
bzimtH$_2$	3154 vs	1514 s, 1468 vs, 1357 s	661 s, 602 s, 482 m
HgCl$_2$(bzimtH$_2$) (**1**)	3157 s, 3112 s	1508 vs, 1457 vs, 1347 m	663 m, 596 m, 478 w
HgBr$_2$(bzimtH$_2$) (**2**)	3176 s, 3120 m, 3006 m	1510 s, 1460 vs, 1365 s, 1348 m	652 m, 598 s, 480 m
HgI$_2$(bzimtH$_2$) (**3**)	3053 m	1498 vs, 1460 vs, 1360 m, 1344 m	642 m, 598 s, 478 m
Hg(SCN)$_2$(bzimtH$_2$) (**4**)	3155 s, 3103 s	1507 s, 1458 vs, 1364 m, 1348 m	647 m, 598 m, 468 m
HgCl$_2$(bzimtH$_2$)$_2$ (**5**)	3147 s	1503 vs, 1457 vs, 1365 s, 1348 s	656 m, 598 s, 478 m
HgBr$_2$(bzimtH$_2$)$_2$ (**6**)	3175 s, 3118 s	1500 s, 1458 vs, 1336 m, 1347 s	656 m, 598 s, 477 m
HgI$_2$(bzimtH$_2$)$_2$ (**7**)	3156 s, 3117 s	1514 m, 1460 vs, 1360 s, 1344 s	642 m, 598 s, 480 m
Hg(SCN)$_2$(bzimtH$_2$)$_2$ (**8**)	3147 vs, 3104 s	1509 s, 1457 s, 1361 s, 1347 m	658 m, 600 s, 472 m
Hg(bzimtH)$_2$ (**9**)	3138 s, 3087 s	1498 m, 1441 vs, 1458 m, 1375 vs, 1348 s	646 m, 601 m

spectrum of free bzimtH$_2$ confirms that the thione tautomer is the dominant form in the DMSO solution and also in the solid state.[17,21] The ^{1}H NMR spectra also show that the 1- and 3-H protons are more deshielded in the complexes by δ = 1.40−1.81, than in the free thione molecule. The deshielding occurs as a result of the positive charge in the imidazole ring and the stronger hydrogen bonding in the complexes than in the free bzimtH$_2$. Broadening of the N−H signal in the complexes also supports hydrogen bonding. For all other protons, small complexation effects are detected, due to their greater distance from the binding site. For the thiocyanato complexes, the N−H resonance is not discernible due to strong hydrogen bonding. Additional evidence with regard to the coordination site in complexes **1−8** is provided by the ^{13}C NMR spectra (Table 3). The greatest change in the chemical shift was found for the thione carbon (C-2) signal, which shifts from δ = 7.10 to δ = 12.70. These upfield shifts are consistent with the reduction of the π-electron density in the exocyclic carbon−sulphur bond, which occurs as a result of the *S*-bonded bzimtH$_2$.

Table 2. ^{1}H NMR chemical shifts (δ in ppm) and complexation shifts[a] (Δδ in ppm) of bzimtH$_2$ and complexes **1−8**

Compound	[a]	1-,3-H	5-,8-H	6-,7-H
bzimtH$_2$	δ	12.50	7.12	7.12
HgCl$_2$(bzimtH$_2$) (**1**)	δ	13.90	7.48	7.36
	Δδ	1.40	0.36	0.23
HgBr$_2$(bzimtH$_2$) (**2**)	δ	13.68	7.45	7.33
	Δδ	1.18	0.33	0.21
HgI$_2$(bzimtH$_2$) (**3**)	δ	13.61	7.45	7.33
	Δδ	1.11	0.33	0.21
Hg(SCN)$_2$(bzimtH$_2$) (**4**)	δ	−	7.48	7.32
	Δδ	−	0.36	0.20
HgCl$_2$(bzimtH$_2$)$_2$ (**5**)	δ	13.57	7.27	7.27
	Δδ	1.07	0.15	0.15
HgBr$_2$(bzimtH$_2$)$_2$ (**6**)	δ	13.50	7.35	7.26
	Δδ	1.00	0.23	0.14
HgI$_2$(bzimtH$_2$)$_2$ (**7**)	δ	13.31	7.36	7.27
	Δδ	0.81	0.24	0.15
Hg(SCN)$_2$(bzimtH$_2$)$_2$ (**8**)	δ	−	7.38	7.31
	Δδ	−	0.26	0.19

[a] Complexation shift is defined as the ^{1}H chemical shift difference of corresponding nuclei in the complex and in the free thione molecule.

Table 3. ^{13}C NMR chemical shifts (δ in ppm) and complexation shifts[a] (Δδ in ppm) of bzimtH$_2$ and complexes **1−8**

Compound	[a]	C-2	C-4,-9	C-5,-8	C-6,-7
bzimtH$_2$	δ	168.5	132.5	109.8	122.6
HgCl$_2$(bzimtH$_2$) (**1**)	δ	156.71	131.70	112.1	124.70
	Δδ	−11.79	−0.80	2.30	2.10
HgBr$_2$(bzimtH$_2$) (**2**)	δ	156.72	131.72	112.0	124.68
	Δδ	−11.78	−0.78	2.20	2.08
HgI$_2$(bzimtH$_2$) (**3**)	δ	158.1	131.8	111.9	124.5
	Δδ	−10.4	−0.70	2.10	1.90
Hg(SCN)$_2$(bzimtH$_2$) (**4**)	δ	155.8	133.5	112.5	124.3
	Δδ	−12.7	1.00	2.70	1.70
HgCl$_2$(bzimtH$_2$)$_2$ (**5**)	δ	159.0	131.5	111.5	124.2
	Δδ	−9.50	−1.00	1.70	1.60
HgBr$_2$(bzimtH$_2$)$_2$ (**6**)	δ	160.2	131.8	111.3	124.0
	Δδ	−8.30	−0.70	1.50	1.40
HgI$_2$(bzimtH$_2$)$_2$ (**7**)	δ	161.4	132.21	111.4	124.1
	Δδ	−7.10	−0.29	1.60	1.50
Hg(SCN)$_2$(bzimtH$_2$)$_2$ (**8**)	δ	158.7	132.17	111.9	124.6
	Δδ	−9.80	−0.33	2.10	2.00

[a] Complexation shift is defined as the ^{13}C chemical shift difference of corresponding nuclei in the complex and in the free thione molecule.

Crystal Structures of 3, 7, and 8

Crystal Structure of HgI$_2$(bzimtH$_2$) (3)

In the structure of **3**, the mercury atom is coordinated by two iodine atoms [Hg−I1 2.676(1) and Hg−I2 2.816(1) Å] and one sulphur atom from bzimtH$_2$ [Hg−S1 2.467(2) Å]. It has a distorted trigonal geometry (Figure 1, Table 4). The Hg−I1 bond is shorter than the sum of the covalent radii for the trigonal mercury and iodine atoms (1.39 + 1.33 Å),[22,23] while Hg−I2 is longer, since I2 acts as the bridging atom. Further, in the structure of HgI$_2$(imtH$_2$)[8] (imtH$_2$ = 1,3-imidazole-2-thione), the Hg−I(terminal) distance is shorter [2.6518(7) Å] and closer to the value for linear mercury coordination (2.63 Å), while the Hg−I(bridging) distance is very similar [2.8187(7) Å] (Table 5). A similar trigonal coordination pattern is found in the structure of HgI$_2$(H$_4$pymtH)[16] (H$_4$pymtH = 3,4,5,6-tetrahydropyrimidine-2-thione), where the thione ligand contains a saturated heterocyclic ring. The analogous Hg−I bond lengths are 2.6872(7) and 2.7044(6) Å, respectively. The Hg−S bond in

3 is slightly longer than the sum of the covalent radii for trigonal Hg and S atoms (2.43 Å).[22,23] It is longer, but not significantly, than the corresponding bond in $HgI_2(imtH_2)$ [2.460(2) Å].

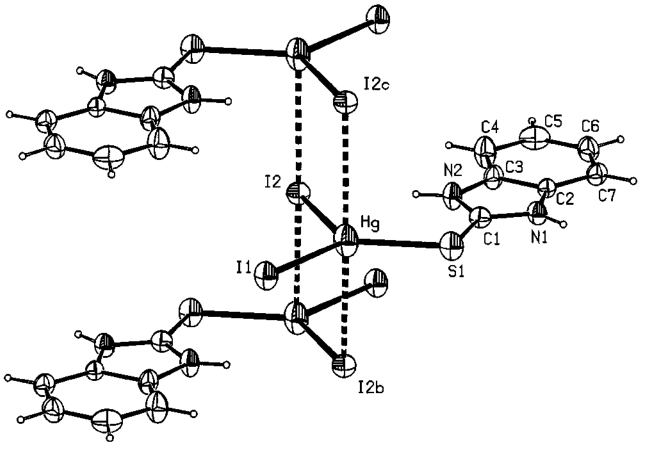


Figure 1. ORTEP drawing of di-μ-iodobis[iodo(benzo-1,3-imidazolium-2-thiolato-*S*)mercury(II)] (**3**), with the atom numbering scheme; the Hg···I contacts are drawn by dashed lines indicating trigonal pyramidal coordination around the mercury centre; symmetry transformation used to generate equivalent atoms: (b) = $1/2 - x$, $y - 1/2$, $1 - z$ and (c) = $1/2 - x$, $y + 1/2$, $1 - z$; the thermal ellipsoids are at the 50% probability level at 200 K

Distortion of the trigonal geometry is determined by the bond angles, which are in the range from 112.94(4) to 127.34(6)°. The largest angle is that of S1−Hg−I1, and is accompanied by the short Hg−I1 bond length. In $HgI_2(imtH_2)$, where the Hg−I bond is shorter than that in **3**, the S−Hg−I angle is greater [134.63(5)°].

The number of atoms coordinated to mercury increases to five through Hg···I interactions with two neighbouring molecules which are related by mirror plane symmetry, thus effectively forming a trigonal-bipyramidal coordination sphere around the mercury centre, elongated in the axial direction [Hg···I2^i 3.3774(6) Å; $i = 1/2 - x, -1/2 + y, 1 - z$]. By these interactions polymeric chains parallel to the *b* axis are formed. In $HgI_2(imtH_2)$ and $HgI_2(H_4pymtH)$, the mercury atom is disordered and is forced out of the mirror plane in order to form Hg···I contacts with distances of 3.486(1) and 3.517(3) Å, respectively. The distance to the other neighbouring I is very long (> 3.9 Å). While describing these two structures, we commented that if the mercury atom was in the mirror plane the distance to the neighbouring iodine atoms would be close to 3.7 Å which, in our opinion, would not be shorter than the sum of the van der Waals radii for Hg (1.55 to 1.65 Å)[24,25] and I (1.98 Å).[25] Therefore, only the 3 + 1 coordination was possible. The short Hg···I contacts and the 3 + 2 coordination in **3** are in support of our values.

In complex **3**, the larger $bzimtH_2$ allows shorter Hg···I contacts as a result of the hydrogen-bonding pattern. In the structure of $HgI_2(imtH_2)$,[8] only N−H···S intermolecular hydrogen bonds are formed (Table 5), while in **3** hydrogen bonds of the type N−H···I are observed, with values of 3.586(7) Å for the intramolecular, and 3.807(9) Å for the intermolecular hydrogen bonds (Table 6). We believe that the strength of Hg···I contacts in **3** is also influenced by the

Table 4. Selected interatomic distances [Å] and angles [°] for the compounds **3**, **7**, and **8**

	$HgI_2(bzimtH_2)$ (**3**)	$HgI_2(bzimtH_2)_2$ (**7**)	$Hg(SCN)_2(bzimtH_2)_2 \cdot EtOH$ (**8**)
Interatomic distances			
Hg−X1[a]	2.676(1)	2.7204(8)	2.500(6)
Hg−X2[a]	2.816(1)	2.6970(9)	2.679(6)
Hg−X2[i]	3.3774(6)	−	−
Hg−S1	2.467(2)	2.612(2)	2.500(6)
Hg−S2	−	2.640(3)	2.508(6)
S1−C11 (S1−C1in **3**)	1.714(9)	1.709(9)	1.75(2)
S2−C21	−	1.715(9)	1.68(2)
C11−N11(C1−N1 in **3**)	1.35(1)	1.36(1)	1.32(3)
C11−N12 (C1−N2 in **3**)	1.33(1)	1.34 (1)	1.30(2)
C21−N21	−	1.33(1)	1.34(2)
C21−N22	−	1.35(1)	1.37(3)
C12−N11 (N1−C2 in **3**)	1.39(1)	1.39(1)	1.39(2)
C22−N21		1.39(1)	1.38(3)
C13−N12 (N2−C3 in **3**)	1.42(1)	1.37(1)	1.41(2)
C23−N22	−	1.39(1)	1.42(2)
Bond angles			
S1−Hg−X1	127.34(6)	109.41(6)	119.3(2)
S1−Hg−X2	119.72(6)	110.80(6)	99.8(2)
X1−Hg−X2	112.94(4)	124.43(3)	97.1(2)
S1−Hg−S2	−	88.36(8)	115.61(18)
S2−Hg−X1	−	102.94(6)	113.2(2)
S2−Hg−X2	−	114.86(6)	108.1(2)
I1−Hg−I2[i]	94.14(3)	−	−
S1−Hg−I2[i]	91.24(3)	−	−
I2−Hg−I2[i]	84.02(3)	−	−

[a] X1 = S3 in **8**; X2 = S4 in **8**; $i = 1/2 - x, -1/2 + y, 1 - z$.

Table 5. Selected structural parameters [Å] of mercury(II) iodide complexes with thione ligands

Compound HgI_2L_2	Coordination sphere	Hg−S	Hg−I and Hg···I	Hydrogen bonds	Ref.
$HgI_2(meimtH_2)_2$[a]	def. tetrahedron	2.526(3) 2.571(3)	2.7866(11) 2.8047(9)	3.586 (N−H···I) inter 3.601 (N−H···I) intra	[20]
$HgI_2(meimtH_2)_2$[b]	def. tetrahedron	2.520(3) 2.576(3)	2.7809(9) 2.7999(8)	3.596(8) (N−H···I) intra 3.611(9) (N−H···I) inter	[14]
$HgI_2(H_4pymtH)_2$	def. tetrahedron	2.612(2)	2.7123(5)	3.599(6) (N−H···S) inter 3.725(5) (N−H···I) inter	[13]
$HgI_2(bzimtH_2)_2$[c]	def. tetrahedron	2.612(2)	2.7204(8)	3.339(8) (N−H···S) inter 3.553(8) (N−H···S) intra	present work
		2.640(3)	2.6970(9)	3.657(7) (N−H···I) intra	
3.733(8) (N−H···I) inter					
HgI_2L					
$HgI_2(imtH_2)$	3+1 dimer	2.460(2)	2.8187(7) 2.6518(7) 3.486(1) for Hg···I	2.692(2) (N−H···S) inter	[8]
$HgI_2(H_4pymtH)$[c]	3+1 dimer	2.456(2)	2.6872(7) 2.7044(6) 3.517(3) for Hg···I	3.696(4) (N−H···I) inter	[16]
$HgI_2(bzimtH_2)$	3+2 polymer	2.467(2)	2.676(1) 2.816(1) 3.3774(6) for Hg···I	3.586(7) (N−H···I) intra 3.807(9) (N−H···I) inter	present work

[a] 160 K data. [b] 293 K data. [c] 200 K data.

extended π-delocalized ring system in $bzimtH_2$, which in comparison with the five-membered aromatic ring in $imtH_2$ and also with the saturated ring in H_4pymtH, enables a better π-stacking assembly of the ligand molecules. The stacking occurs along the *b* axis. Centrosymmetrical dimers parallel to the *ac* plane are formed through intermolecular hydrogen bonds. The intermolecular hydrogen bonds and Hg···I contacts interconnect molecules of **3** into a 2D network parallel to the *ab* plane (Figure 2).

Crystal Structure of $HgI_2(bzimtH_2)_2$ (7)

The molecular structure of **7** reveals a tetrahedrally coordinated mercury atom, with two thione sulphur atoms [Hg−S1 2.612(2) and Hg−S2 2.640(3) Å] and two covalently linked iodine atoms [Hg−I1 2.7204(8) and Hg−I2 2.6970(9) Å] (Figure 3). The Hg−S bond lengths are longer than the sum of covalent radii for tetrahedral Hg and S atoms (2.52 Å), but the Hg−I bond lengths are significantly shorter than 2.81 Å (1.48 + 1.33 Å).[22,24]

The tetrahedral environment is distorted since the bond angles are in the range from 88.36(8) to 124.43(3)° for S1−Hg−S2 and I1−Hg−I2, respectively. The largest bond angle is seen for the strong bonds formed with the iodine atoms.[14,16,20] In the structure of an analogous iodo derivative, $HgI_2(meimtH_2)_2$, the Hg−S distances are shorter and the Hg−I distances are longer than in **7** (Table 5).[14,20] This

Table 6. Hydrogen-bond geometry [Å, °] in **3**, **7**, and **8**

D−H···A	*d*(D−H)	*d*(H···A)	∠ (DHA)	*d*(D···A)	Symmetry code
$HgI_2(bzimtH_2)$ (**3**)					
N1−H1···I1^{i}	0.86	2.99	159	3.807(9)	*i* =1 − *x*, *y*, 1 − *z*
N1−H1···I1^{ii}	0.86	2.99	159	3.807(9)	*ii* =1 − *x*, −*y*, 1 − *z*
N2−H2···I2	0.86	2.73	174	3.586(7)	
$HgI_2(bzimtH_2)_2$ (**7**)					
N11−H11···I1^{iii}	0.86	2.98	147	3.733(8)	*iii* =1 − *x*, 1 − *y*, 2 − *z*
N12−H12···I2	0.86	2.83	163	3.657(7)	
N21−H21···S2^{iv}	0.86	2.49	169	3.339(8)	*iv* = 1 − *x*, 1 − *y*, 1 − *z*
N22−H22···S1	0.86	2.81	146	3.553(8)	
$Hg(SCN)_2(bzimtH_2)_2 \cdot EtOH$ (**8**)					
N11−H11...O1^{v}	0.86	1.95	172	2.81(3)	*v* = *x*, *y*, −1 + *z*
N12−H12...N4^{vi}	0.86	2.06	165	2.90(3)	*vi* = 1 − *x*, 1 − *y*, 1 − *z*
N21−H21...N3^{vii}	0.86	1.97	175	2.82(4)	*vii* = 1 − *x*, 1 − *y*, −*z*
N22−H22...N4	0.86	2.17	169	3.02(2)	

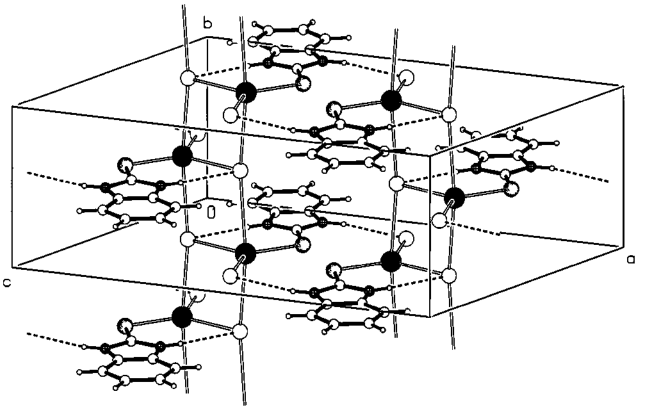


Figure 2. The crystal packing of **3** showing endless polymeric chains along the *b* axis and the centrosymmetrical dimer formed by hydrogen bonding in the *ac* plane; the N−H···I intra- and intermolecular hydrogen bonds are indicated by dashed lines

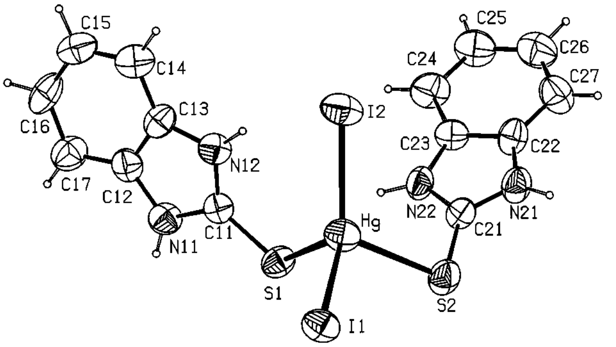


Figure 3. ORTEP drawing of bis[iodo(benzo-1,3-imidazolium-2-thiolato-*S*)]mercury(II) (**7**), with the atom numbering scheme; the thermal ellipsoids are at the 50% probability level at 293 K

is caused by different intermolecular interactions. In both structures (obtained at 293[14] and at 160 K[20]), the NH groups of the imidazole ring take part in the intra- and intermolecular hydrogen bonds of the type N−H···I, and are in the range 3.586−3.611(9) Å. In **7**, the N−H···I hydrogen bonds are slightly longer (Table 6). Furthermore, in **7** there is an intermolecular bond of the type N−H···S with a length of 3.339(8) Å, and a longer intramolecular bond with a length of 3.553(8) Å (Table 6, Figure 4), while in $HgI_2(meimtH_2)_2$ such hydrogen bonds do not exist at all.

Crystal Structure of $Hg(SCN)_2(bzimtH_2)_2\cdot EtOH$ (8)

The less accurate geometrical parameters of **8** are associated with the significant intensity decay due to crystal decomposition under X-rays (see Exp. Sect.). The mercury atom is coordinated by two sulphur atoms of $bzimtH_2$ [Hg−S1 2.499(6) and Hg−S2 2.508(6) Å] and two sulphur atoms of SCN^- [Hg−S3 2.500(5) and Hg−S4 2.680(6) Å], thereby having a deformed tetrahedral geometry (Figure 5). The bond angles around the mercury centre range from 97.1(2)° for S3−Hg−S4, to 119.3(2)° for S1−Hg−S3. The Hg−S(thione) bond lengths are comparable with those observed in the structures of $Hg(SCN)_2(H_4pymtH)_2$[13] and the two polymorphs of $Hg(SCN)_2(pySH)_2$ (pySH = pyridine-2-thione)[11] [the bond ranges are 2.458(1)−2.526(2) Å for Hg−S(thione) bonds, and 2.556(2)−2.685(2) Å for Hg−S(SCN) bonds in these three structures].

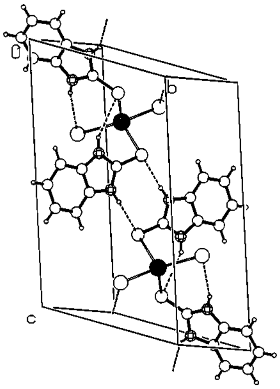


Figure 4. The crystal packing of **7**; dashed lines indicate N−H···S and N−H···I hydrogen-bonds

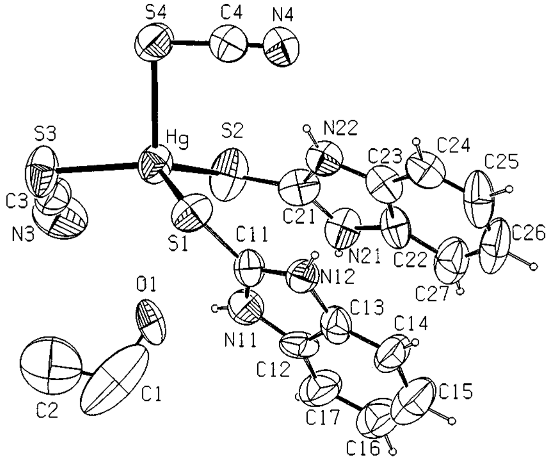


Figure 5. ORTEP drawing of the 1:1 ethanol solvate of bis[thiocyanato(benzo-1,3-imidazolium-2-thiolato-*S*)]mercury(II) (**8**), with the atom numbering scheme; the thermal ellipsoids are at the 50% probability level at 293 K

The Hg−S1, Hg−S2, as well as the Hg−S3 bond in **8** are shorter than the sum of covalent radii for tetrahedral Hg and S atoms. This is an unexpected result for the Hg−S3 bond. In contrast, the Hg−S4 bond is among the longest ones found so far, but still in the range of the Hg−S(SCN) bonds. This could be due to the involvement of the N4 atom as a proton acceptor in both intra- and intermolecular N−H···N hydrogen bonds with the NH groups from $bzimtH_2$, while N3 participates only in one intermolecular hydrogen bond (Table 6).

Besides intra- and intermolecular N−H···N hydrogen bonds, an intermolecular N−H···O hydrogen bond, with a length of 2.82(3) Å (Table 6), forms between the complex and the ethanol molecules (Figure 6).

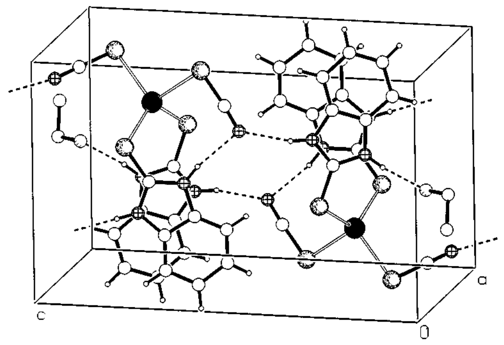


Figure 6. The crystal packing of **8**; dashed lines indicate intermolecular N−H···N and N−H···O hydrogen bonds between complex molecules and complex molecule and ethanol, respectively

Geometry of bzimtH$_2$ in 3, 7, and 8

The crystal structure of bzimtH$_2$ reveals a thioketo C=S bond length of 1.684(3) Å.[21] Such a bond possesses approx. 58% of the π-bond character. On complexation, the C=S bond exhibits a decrease in the π-bond character, to approx. 40%.[26]

The C−N bond lengths in all three complexes are similar to those in the free ligand,[21] with shorter C−N bonds involving the thioketo C atom and longer C−N bonds involving the C atoms common to the five- and six-membered ring. All C−N bonds are shorter than the theoretical C−N single bond length of 1.47 Å, and longer than the C=N double bond length of 1.27 Å (Table 4).[27]

The internal bond lengths, as well as the planarity of the bzimtH$_2$ molecule, strongly confirm that the aromatic character of the imidazole ring is preserved in the mercury(II) complexes, and suggest that the zwitterionic resonance form participates in the structure of the ligand (Scheme 2, c).

Thermal Analysis (TGA-DTA)

The samples of bzimtH$_2$ and **1−9** were heated from room temperature to 700 °C. Thermal data are summarised in Table 7. The DTA curve of free bzimtH$_2$ shows a single and broad endothermic peak at 300 °C that corresponds to its degradation.

The DTA and TGA curves for **1−8** essentially show two degradation processes. The TGA profile for these compounds suggests that bzimtH$_2$ is lost first (two endothermic overlapping peaks), and degradation of the mercury(II) halide or pseudohalide follows (determined by the third endothermic peak). Some of the complexes undergo melting as presented in Table 7. The relatively high melting points of these compounds suggest the presence of strong intermolecular bonding. The observed mass losses for the aforementioned processes are in good agreement with the calculated ones. The DTA curve for **9** shows three processes. Both endothermic minima at 240 °C and 290 °C, with a corresponding mass loss of 46.58%, represent degradation of the ligand due to the breaking of the C−S bond. Decomposition of the residue starts at 390 °C.

Experimental Section

Materials and Physical Measurements: Mercury(II) halides and benzo-1,3-imidazole-2-thione were used as received from Aldrich

Table 7. Thermoanalytical data for benzo-1,3-imidazole-2-thione and its mercury(II) complexes

Compound	Process	Temperature [°C]	Accumulated weight loss (%)	
			Found	Calculated
bzimtH$_2$	degradation (*endo*)	292.87	100	100
HgCl$_2$(bzimtH$_2$) (**1**)	bzimtH$_2$ degradation (*endo*)	247.94, 303.98	70.05	71.14
	elimination of HgCl$_2$ (*endo*)	408.63	29.95	28.86
HgBr$_2$(bzimtH$_2$) (**2**)	melting (*endo*)	234.71	−	−
	bzimtH$_2$ degradation (*endo*)	overlap with melting	57.89	58.75
	elimination of HgBr$_2$ (*endo*)	322.33	42.11	41.25
HgI$_2$(bzimtH$_2$) (**3**)	melting (*endo*)	215.92	−	−
	bzimtH$_2$ degradation (*endo*)	226.50, 239.04	48.58	49.62
	elimination of HgI$_2$ (*endo*)	276.92	51.24	50.38
Hg(SCN)$_2$(bzimtH$_2$) (**4**)	melting (*endo*)	174.28	−	−
	bzimtH$_2$ degradation (*endo*)	209.63, 252.38	61.86	62.25
	elimination of Hg(SCN)$_2$ (*endo*)	363.20	38.14	38.14
HgCl$_2$(bzimtH$_2$)$_2$ (**5**)	bzimtH$_2$ degradation (*endo*)	255.11, 291.43	50.25	52.46
	elimination of HgCl$_2$ (*endo*)	381.74	49.75	47.54
HgBr$_2$(bzimtH$_2$)$_2$ (**6**)	melting (*endo*)	226.35	−	−
	bzimtH$_2$ degradation (*endo*)	overlap with melting	50.65	51.68
	elimination of HgBr$_2$ (*endo*)	335.33	49.35	48.32
HgI$_2$(bzimtH$_2$)$_2$ (**7**)	melting (*endo*)	213.82	−	−
	bzimtH$_2$ degradation (*endo*)	231.63, 240.21	40.12	39.75
	elimination of HgI$_2$ (*endo*)	275.31	59.88	60.25
Hg(SCN)$_2$(bzimtH$_2$)$_2$ (**8a**)	melting (*endo*)	174.26	−	−
	bzimtH$_2$ degradation (*endo*)	214.34, 268.33	47.59	48.61
	elimination of Hg(SCN)$_2$ (*endo*)	415.36	52.41	51.39
Hg(bzimtH)$_2$ (**9**)	bzimtH$^-$ degradation (*endo*)	243.14, 296.58	46.58	47.30
	elimination of HgS	350−400	53.42	52.70

without further purification. Mercury(II) thiocyanate was prepared by the reaction of mercury(II) nitrate monohydrate and ammonium thiocyanate. The mercury content in the complexes was determined by complexometric titration, with sodium diethyl dithiocarbamate, of the solution obtained after decomposition of the specimen in aqua regia.[28] CHNS analyses were performed in the Analytical Services Laboratories of the Institute Ruder Boškovic. The IR spectra were obtained from KBr pellets in the range 4000−450 cm^{-1} with a Perkin−Elmer FTIR 1600 spectrometer. The ^1H and ^{13}C NMR spectra were measured with a Varian Gemini 300 spectrometer, operating at 75.46 MHz for the ^{13}C nucleus. The samples were dissolved in [D_6]DMSO in 5-mm NMR tubes. The concentration was 0.05 M for ^1H NMR measurements and 0.25 M for the ^{13}C NMR measurements. Spectra were recorded at 20 °C. Chemical shifts (ppm) were referred to TMS. Digital resolution was 0.32 Hz per point in ^1H and 0.70 Hz per point in the ^{13}C one-dimensional spectra. The thermal measurements were performed using a simultaneous TGA-DTA analyser (TA Instruments, SDT Model 2960 coupled with MS). The samples were placed in small alumina sample pans. The TGA and DTA curves were obtained by placing the samples (approximately 2 mg in mass) in open sample pans, with a heating rate of 10 °C/min and nitrogen (purity $> 99.996\%$) flowing at a rate of 50 mL/min. The SDT was calibrated with indium.

$HgCl_2(bzimtH_2)$ (1): A solution of benzo-1,3-imidazole-2-thione (0.25 g, 1.66 mmol) in 20 mL of methanol was added dropwise to a solution of mercuric chloride (0.4 g, 1.47 mmol) in 10 mL of methanol. A pale pink crystalline product was obtained the following day, which was filtered off, washed with cold methanol and dried in air. Yield: 0.50 g (81%). $C_7H_6Cl_2HgN_2S$ (421.7): calcd. C 19.92, H 1.42, Hg 47.57, N 6.64, S 7.59; found C 20.25, H 1.61, Hg 47.82, N 6.64, S 7.50.

$HgBr_2(bzimtH_2)$ (2): A solution of benzo-1,3-imidazole-2-thione (0.19 g, 1.26 mmol) in 20 mL of methanol was added dropwise to a solution of mercuric bromide (0.4 g, 1.11 mmol) in 10 mL of methanol. A pale yellow crystalline product was obtained the following day, which was filtered off, washed with cold methanol and dried in air. Yield: 0.45 g (79%). $C_7H_6Br_2HgN_2S$ (510.6): calcd. C 16.45, H 1.18, Hg 39.29, N 5.48, S 6.27; found C 17.07, H 1.06, Hg 39.58, N 5.41, S 6.35.

$HgI_2(bzimtH_2)$ (3): A solution of benzo-1,3-imidazole-2-thione (0.15 g, 0.99 mmol) in 10 mL of methanol was added dropwise to a solution of mercuric iodide (0.4 g, 0.88 mmol) in 20 mL of methanol. After a few days, the yellow crystals were filtered off, washed with cold methanol and dried in air. Yield: 0.50 (94%). $C_7H_6I_2HgN_2S$ (604.6): calcd. C 13.89, H 0.99, Hg 33.18, N 4.63; found C 14.38, H 1.54, Hg 33.32, N 5.22.

$Hg(SCN)_2(bzimtH_2)$ (4): A solution of benzo-1,3-imidazole-2-thione (0.21 g, 1.40 mmol) in 20 mL of 96% ethanol was added dropwise to a solution of mercuric thiocyanate (0.4 g, 1.26 mmol) in 120 mL of 96% ethanol. The reaction mixture was left in the dark due to the photosensitivity of the complex. After a few weeks, the yellow crystalline product was filtered off, washed with cold ethanol and dried in air. Yield: 0.36 g (61%). $C_9H_6HgN_4S_3$ (466.9): calcd. C 23.13, H 1.28, Hg 42.96, N 11.99, S 20.56; found C 23.08, H 1.49, Hg 43.27, N 11.88, S 20.58.

$HgCl_2(bzimtH_2)_2$ (5): A solution of benzo-1,3-imidazole-2-thione (0.49 g, 3.26 mmol) in 40 mL of methanol was added dropwise to a solution of mercuric chloride (0.4 g, 1.47 mmol) in 10 mL of methanol. A pale pink crystalline product was obtained the following day, which was filtered off, washed with cold methanol and dried in air. Yield: 0.62 g (74%). $C_{14}H_{12}Cl_2HgN_4S_2$ (571.9): calcd. C 29.38, H 2.10, Hg 35.08, N 9.79, S 11.19; found C 29.72, H 2.48, Hg 35.27, N 9.65, S 11.24.

$HgBr_2(bzimtH_2)_2$ (6): A solution of benzo-1,3-imidazole-2-thione (0.37 g, 2.46 mmol) in 30 mL of methanol was added dropwise to a solution of mercuric bromide (0.4 g, 1.11 mmol) in 10 mL of methanol. After a few days, the pale pink crystalline product was filtered off, washed with cold methanol and dried in air. Yield: 0.61 g (84%). $C_{14}H_{12}Br_2HgN_4S_2$ (660.8): calcd. C 25.42, H 1.82, Hg 30.36, N 8.47, S 9.69; found C 25.57, H 2.23, Hg 30.81, N 8.25, S 9.56.

$HgI_2(bzimtH_2)_2$ (7): A solution of benzo-1,3-imidazole-2-thione (0.29 g, 1.93 mmol) in 20 mL of methanol was added dropwise to a solution of mercuric iodide (0.4 g, 0.88 mmol) in 20 mL of methanol. After a few days, the yellow crystals were filtered off, washed with cold methanol and dried in air. Yield: 0.28 g (42%). $C_{14}H_{12}I_2HgN_4S_2$ (754.8): calcd. C 22.26, H 1.59, Hg 33.20, N 7.45; found C 22.00, H 1.79, N 8.60, Hg 33.70.

$Hg(SCN)_2(bzimtH_2)_2\cdot EtOH$ (8): A solution of benzo-1,3-imidazole-2-thione (0.42 g, 2.80 mmol) in 20 mL of 96% ethanol was added dropwise to a solution of mercuric thiocyanate (0.4 g, 1.26 mmol) in 120 mL of 96% ethanol. The reaction mixture was left in the dark due to the photosensitivity of the complex. After a few weeks, the pale yellow crystals were filtered off, washed with cold ethanol and dried in air. Yield: 0.55 g (71%). Since the crystals lose ethanol on standing, especially on grinding, analysis of the non-solvated sample has been carried out. $C_{16}H_{12}HgN_6S_4$ (617.1): calcd. C 31.11, H 1.94, Hg 32.50, N 13.61, S 20.74; found C 31.25, H 2.57, Hg 32.75, N 13.51, S 20.80.

$Hg(bzimtH)_2$ (9): A solution of benzo-1,3-imidazole-2-thione (0.41 g, 2.73 mmol) in 30 mL of methanol was added dropwise to a solution of mercuric acetate (0.4 g, 1.26 mmol) in 30 mL of methanol. The colourless crystalline product was filtered off, washed with cold methanol and dried in air. Yield: 0.51 g (81%). $C_{14}H_{10}HgN_4S_2$ (499.0): calcd. C 33.67, H 2.00, Hg 40.20, N 11.27, S 12.88; found C 33.02, H 2.52, Hg 40.25, N 11.00, S 12.80.

X-ray Crystallographic Structure Determination of 3, 7, and 8: Single-crystal X-ray diffraction data were collected for **3**, **7**, and **8** using Mo-K_α radiation (graphite monochromator). Data for the small crystals of **3** were collected with a Nonius Kappa CCD diffractometer (capillary optics) at 200 K, while those of **7** and **8** were collected at room temperature with the Philips PW1100 diffractometer. Crystal data and details of the data collection and refinement procedure are given in Table 8. The unit-cell parameters were obtained by the least-squares refinement procedure of the setting angles of well-centred reflections: 35 in the range $10.0° \le \theta \le 15.1°$ for **7**, 42 reflections in the range $10.0° \le \theta \le 16.5°$ for **8**, and of all reliable data in the structure of **3**. Data reduction was done by the Denzo-SMN program[29] for **3** and by the STADI4 program[30] for **7** and **8**. Due to the significant crystal decay of **8** under X-ray exposure (approx. 30% in 2 d), a reliable data set for the structure refinement was obtained from 3 crystals. Data were corrected for the Lorentz polarisation and absorption effects and then scaled. The numerical Gaussian method for absorption correction based on crystal dimensions was applied for **7** and **8** by the X-RED program,[31] while for **3**, a semi-empirical method was applied by XEMP.[32] The non-H atoms of the ethanol molecule in **8** exhibit large thermal displacement parameters due to crystal decay. The freshly prepared crystals could be described as a 1:1 ethanol solvate, but after the data collection procedure only half of the ethanol molecule is found within the asymmetric unit. The geometry of the

Table 8. General and crystal data and summary of intensity data collection and structure refinement for compounds **3**, **7**, and **8**; data in common: diffractometers used for data collection: PW1100 (Stoe upgraded) with λ(Mo-K_α) = 0.71073 Å at 293 K for **7** and **8** and Kappa CCD for **3** at 200 K

Compound	$HgI_2(bzimtH_2)$ (**3**)	$HgI_2(bzimtH_2)_2$ (**7**)	$Hg(SCN)_2(bzimtH_2)_2 \cdot EtOH$ (**8**)
Empirical formula	$C_7H_6HgI_2N_2S$	$C_{14}H_{12}HgI_2N_4S_2$	$C_{18}H_{18}HgN_6OS_4$
M_r	604.59	754.79	663.21
Crystal system and habit	monoclinic, prism	triclinic, plate	triclinic, plates
Space group	$C2/m$	$P\bar{1}$	$P\bar{1}$
Crystal dimensions [mm]	0.065 × 0.049 × 0.048	0.285 × 0.142 × 0.045	0.547 × 0.490 × 0.042 0.731 × 0.419 × 0.042 0.600 × 0.400 × 0.051
Unit cell parameters:			
a [Å]	17.417(3)	8.1711(7)	7.8037(14)
b [Å]	6.7140(10)	8.6217(10)	10.285(3)
c [Å]	11.080(2)	14.7494(10)	15.202(3)
α [°]		76.246(9)	90.02(2)
β [°]	114.60(3)	81.199(9)	98.18(2)
γ [°]		86.001(11)	96.96(2)
V [Å^3]	1178.1(3)	996.80(16)	1198.6(5)
Z	4	2	2
D_c [gcm^{-3}]	3.409	2.515	1.838
μ [mm^{-1}]	18.442	11.030	6.786
F(000)	1056	684	614
2θ range for data collection [°]	3−29	3−27	3−27
h,k,l range	−22 to 20, −7 to 8, 13 to 14	−10 to 10, −10 to 10, 0 to 18	−9 to 9, −13 to 13, 0 to 19
Scan type	ω	ω	ω
No. measured reflections	7086	4430	5460
No. independent reflections (R_{int})	1488 (0.11)	4261 (0.032)	4850 (0.060)
No. refined parameters	80	208	271 (3 restraints)
No. observed reflections, $I \geq 2\sigma(I)$	1376	2654	3192
Transmission factors, min, max.[a]	0.352, 0.413	0.166, 0.609	0.034−0.752 for 1st crystal 0.167−0.3511 for 2nd crystal 0.0872 −0.7264 for 3rd crystal
Face indices, distances from centroid [mm]	−	(1 0 1, −1 0 −1) 0.0710 (−1 0 1; 1 0 −1) 0.0225 (0 1 1, 0 −1 −1) 0.1425	(1 0 0, −1 0 0) 0.2734; 0.3657; 0.300 (0 1 0, 0 −1 0) 0.1633; 0.2095;0.2000 (0 0 1; 0 0 −1) 0.0210; 0.0210; 0.0256
g_1, g_2 in w[b]	0.0821, 0	0.0632, 0	0.2000, 0
R[c], wR[d] [$I \geq 2\sigma(I)$]	0.0489, 0.1224	0.0461, 0.0964	0.1235, 0.3006
R, wR [all data]	0.0516, 0.1252	0.0961, 0.1137	0.1717, 0.3431
Goodness of fit on F^2, S[e]	1.041	0.986	1.323
Max., min. electron density [e·Å^{-3}][f]	2.18, −3.39	1.68, −1.79	−5.23, 4.24
Extinction coefficients, x[g]	0.0011(3)	−	−
Maximum Δ/σ	0.001	0.001	0.001

[a] Absorption correction type: semiempirical for **3** and numerical Gaussian for **7** and **8**. [b] $w = 1/[\sigma^2(F_o^2) + [g_1P + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [e] $S = \Sigma[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$. [f] In all structures the max. electron density in the last difference Fourier map is near Hg. [g] $F_c^2 = kF_c[1 + 0.001 \times F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, $k = 0.10926$.

EtOH molecule (C−C and C−O bonds and C−C−O angle) has been modelled with restraints. All structures were solved by direct methods in SHELXS,[33] and refined by the least-squares procedure with anisotropic thermal parameters for non-H atoms by the SHELXL97 program.[34] The hydrogen atoms were placed at calculated positions and refined by the riding model [Csp^2−H 0.93 Å; Nsp^2−H 0.86 Å; with $U_{iso}(H) = 1.2\ U_{eq}$]. The molecular geometry calculations and drawings were performed by PLATON.[35] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162383−162385 for complexes **3**, **7**, and **8**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] J. G. Wright, M. J. Natan, F. M. MacDonnell, D. M. Ralston, T. V. O’Halloran, *Prog. Inorg. Chem.* **1990**, *38*, 323−412 (and refs. therein).

[2] M. Bochmann, K. J. Webb, *J. Chem. Soc., Dalton Trans.* **1991**, 2325−2329.

[3] P. A. Dean, *Prog. Inorg. Chem.* **1978**, *24*, 109−178.

[4] D. P. Graddon, *Rev. Inorg. Chem.* **1982**, *4*, 211−282.

[5] E. S. Raper, *Coord. Chem. Rev.* **1985**, *61*, 115−184.

[6] E. S. Raper, *Coord. Chem. Rev.* **1996**, *153*, 199−255.

[7] E. S. Raper, *Coord. Chem. Rev.* **1997**, *165*, 475−567.

[8] Z. Popović, D. Matković-Čalogović, Ž. Soldin, G. Pavlović, N. Davidović, D. Vikić-Topić, *Inorg. Chim. Acta* **1999**, *294*, 35−46.

[9] Ž. Žugaj, Z. Popović, D. Mrvoš-Sermek, *Bull. Czech and Slovak Crystallogr. Association* **1998**, *5 (special* issue B, Abstracts) p. 322.

[10] A. K. Das, S. Seth, *J. Inorg. Biochem.* **1997**, *65*, 207−218.

[11] Z. Popović, D. Matković-Calogović, J. Hasić, D. Vikić-Topić, *Inorg. Chim. Acta* **1999**, *285*, 208−216.

[12] G. Pavlović, Z. Popović, Ž. Soldin, D. Matković-Čalogović, *Acta Crystallogr., Sect. C* **2000**, *56*, 61−63.

[13] Z. Popović, G. Pavlović, D. Matković-Čalogović, Ž. Soldin, M. Rajić, D. Vikić-Topić, D. Kovaček, *Inorg. Chim. Acta* **2000**, *306*, 142−152.

[14] G. Pavlović, Z. Popović, Ž. Soldin, D. Matković-Čalogović, *Acta Crystallogr., Sect. C* **2000**, *56*, 801−803.

[15] Z. Popović, D. Matković-Čalogović, G. Pavlović, Ž. Soldin, G. Giester, M. Rajić, D. Vikić-Topić, *Croat. Chem. Acta* **2001**, *74*, 359−380.

[16] D. Matković-Čalogović, Z. Popović, G. Pavlović, Ž. Soldin, G. Giester, *Acta Crystallogr., Sect. C* **2001**, *57*, 409−411.

[17] F. A. Devillanova, G. Verani, *Aust. J. Chem.* **1980**, *33*, 279−286.

[18] R. Shunmugam, D. N. Sathyanarayana, *J. Coord. Chem.* **1983**, *12*, 151−156.

[19] E. S. Raper, J. R. Creighton, N. A. Bell, W. Clegg, L. Cucurull-Sánchez, *Inorg. Chim. Acta* **1998**, *277*, 14−20.

[20] N. A. Bell, T. N. Branston, W. Clegg, J. R. Creighton, L. Cucurull-Sánchez, M. R. J. Elsegood, E. S. Raper, *Inorg. Chim. Acta* **2000**, *303*, 220−227.

[21] K. Ravikumar, K. Ch. Mohan, M. Bidyasagar, G. Y. S. K. Swamy, *J. Chem. Crystallogr.* **1995**, *25*, 325−329.

[22] D. Grdenić, *Quat. Rev.* **1965**, *19*, 303−328.

[23] D. Matković-Čalogović, PhD Thesis (in Croatian; Abstract in English), University of Zagreb, **1994.**

[24] L. Pauling, The Nature of the Chemical Bond, Ithaca, New York, Cornell University Press, **1960.**

[25] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[26] N. Trinajstić, *Tetrahedron Lett.* **1968**, 1529−1532.

[27] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[28] P. Gouverneur, W. Hoedeman, *Anal. Chim. Acta* **1964**, *30*, 519−523.

[29] Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, in: *Methods in Enzymology*, vol. 276 (Eds.: C. W. Carter, Jr., R. M. Sweet), Macromolecular Crystallography, part A, Academic Press, London, **1997**, p.307.

[30] Stoe & Cie, *STADI4, Diffractometer Control Program for Windows*, Darmstadt, Germany, **1995**.

[31] Stoe & Cie, *X-RED, Data Reduction Program for Windows*, Darmstadt, Germany, **1995**.

[32] G. M. Sheldrick, *XEMP, Program for Semimpirical Absorption Correction*, University of Göttingen, Germany, **1988**.

[33] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[34] G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[35] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

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