

COORDINATION COMPOUNDS

## Crystal Structure of Bis( $\alpha, \alpha'$ -Dithio-Bis(Formamidinium)) Bis( $\mu_2$ -Chloro)Hexachlorodimercurate(II)

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**Abstract**—The crystal and molecular structure of bis( $\alpha, \alpha'$ -dithio-bis(formamidinium)) bis( $\mu_2$ -chloro)hexachlorodimercurate(II)  $C_4H_{16}Hg_2Cl_8N_8S_4$  (**I**), where  $\alpha, \alpha'$ -dithio-bis(formamidine) is  $C_2H_6N_4S_2$ , was solved. Crystals are monoclinic,  $a = 8.6417(6)$  Å,  $b = 14.648(1)$  Å,  $c = 10.2111(8)$  Å,  $\beta = 104.949(1)^\circ$ ,  $V = 1248.8(2)$  Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 4$ . The crystal structure is built of  $HgCl_4^{2-}$  ions linked via inversion centers into  $[Hg_2Cl_8]^{4-}$  pairs and  $C_2H_8N_4S_2^{2+}$  cations.  $[Hg_2Cl_8]^{4-}$  anions and  $C_2H_8N_4S_2^{2+}$  cations form alternating layers linked by N–H...Cl hydrogen bonds into a framework structure.

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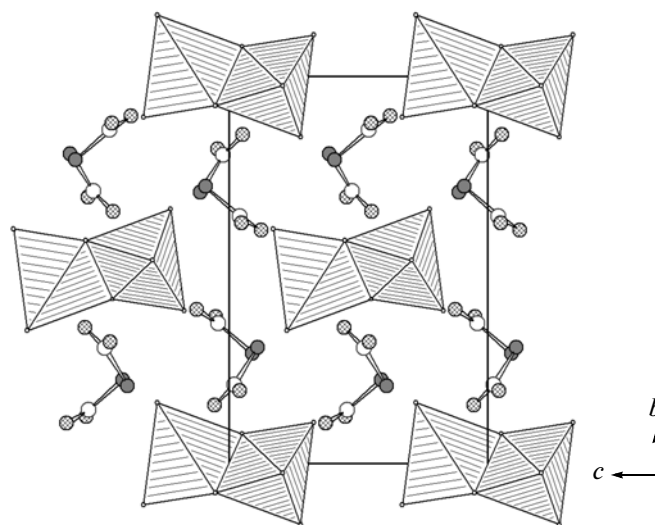
All mercury(II) species are toxic. Interactions of mercury with thiol and disulfide groups provokes oxidative stress and disturbs the metabolism of haem [1]. Organic mercury compounds promote the disruption of disulfide bonds. The behavior of disulfides in the presence of inorganic mercury(II) complexes is poorly studied [2]. Presumably, they can also favor the disruption of the –SS– bond or form Hg–S coordination bonds.

One of the known disulfides is  $\alpha, \alpha'$ -dithio-bis(formamidine), or simply formamidine disulfide (FDS,  $C_2H_6N_4S_2$ ). Its diprotonated form ( $FDSH_2^{2+}$ ) is formed in the oxidation of thiourea, one of the universal organic reagents. Acidic thiourea solutions are considered to be a real alternative to cyanide solutions in gold hydrometallurgy, and the  $FDSH_2^{2+}$  ion is suggested to have catalytic activity in the gold dissolution reaction [3]. New platinum(IV) preparations with potential medicinal properties were synthesized using  $FDSH_2^{2+}$  derivatives [4]. We have not discovered any literature data on the stability of the disulfide bond and the reactivity of  $FDSH_2^{2+}$  in the presence of mercury, nor on the structures of their compounds.

In this work, bis( $\alpha, \alpha'$ -dithio-bis(formamidinium)) bis( $\mu_2$ -chloro)hexachlorodimercurate(II) (**I**) single crystals were synthesized, and their structure was established by X-ray diffraction.

### EXPERIMENTAL

The reagents used in this study were chemically pure grade thiourea, HCl, HgO, and  $H_2O_2$ . The initial reagent used for the synthesis of the target product was formamidine disulfide dihydrochloride  $[(NH_2)_2CSSC(NH_2)_2]^{2+} \cdot 2Cl^-$  ( $FDSH_2Cl_2$ ) prepared by the oxidation of thiourea with hydrogen peroxide in hydrochloric acid [5].

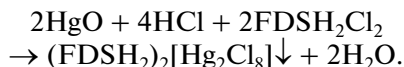


**Fig. 1.** Packing of structural units in compound **I** (projection onto the  $cb$  plane).  $[Hg_2Cl_8]^{4-}$  anions are shown in the form of polyhedra. Sulfur atoms are darkened, nitrogen atoms are shaded, and hydrogen atoms are omitted for simplicity.

**Table 1.** Experimental data and refinement details for the structure of compound I

Formula	(C <sub>2</sub> H <sub>8</sub> N <sub>4</sub> S <sub>2</sub> ) <sub>2</sub> [Hg <sub>2</sub> Cl <sub>8</sub> ]
FW	989.29
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	2
2θ <sub>max</sub> , deg	57
<i>a</i> ; <i>b</i> ; <i>c</i> , Å	8.6417(6); 14.648(1); 10.2111(8)
β, deg	104.949(1)
<i>V</i> , Å <sup>3</sup>	1248.8(2)
ρ <sub>calcd</sub> , g/cm <sup>3</sup>	2.631
μ, mm <sup>-1</sup>	13.48
Measured reflections	11614
Independent reflections	3148
Number of reflections with <i>F</i> > 4σ( <i>F</i> )	2794
Ranges of <i>h</i> , <i>k</i> , <i>l</i>	-11 ≤ <i>h</i> ≤ 11; -19 ≤ <i>k</i> ≤ 19; -13 ≤ <i>l</i> ≤ 13
Refinement results	
Weight refinement on <i>F</i> <sup>2</sup>	$w = [\sigma^2 + (0.0168P)^2 + 1.0000P]^{-1}$ , where $P = (F_o^2 + 2F_c^2)/3$
Number of refined parameters	120
<i>R</i> 1 [ <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )]	0.0217
<i>wR</i> 2	0.0491
GOOF	1.036
(Δρ) <sub>max</sub> , e/Å <sup>3</sup>	1.15
(Δρ) <sub>min</sub> , e/Å <sup>3</sup>	-0.79
(Δ/σ) <sub>max</sub>	0.001

**Synthesis of compound I.** HgO (0.38 g, 1.8 mmol) was dissolved in 12 M HCl (3 mL), thereupon the FDSH<sub>2</sub>Cl<sub>2</sub> crystalline salt (0.20 g, 0.9 mmol) was added to the resulting solution. Mercury(II) in hydrochloric acid solutions did not lead to any appreciable disruption of the disulfide bond in the C<sub>2</sub>H<sub>8</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup> cation. The reaction proceeded according to the equation



The formed precipitate was filtered out, washed with acetone, and dried in air.

For C<sub>2</sub>H<sub>8</sub>Cl<sub>4</sub>HgN<sub>4</sub>S<sub>2</sub>, anal. calcd. (%): C, 4.86; H, 1.63; N, 11.33; S, 12.97; Hg, 40.55.

Found (%): C, 4.57; H, 1.73; N, 11.06; S, 13.06; Hg, 39.89.

Single crystals for X-ray diffraction analysis were selected from the overall mass of the synthesized product. The crystallographic data for single crystals and powder samples are identical.

**Table 2.** Selected interatomic distances *d* (Å) and angles ω (deg) in the structure of compound I

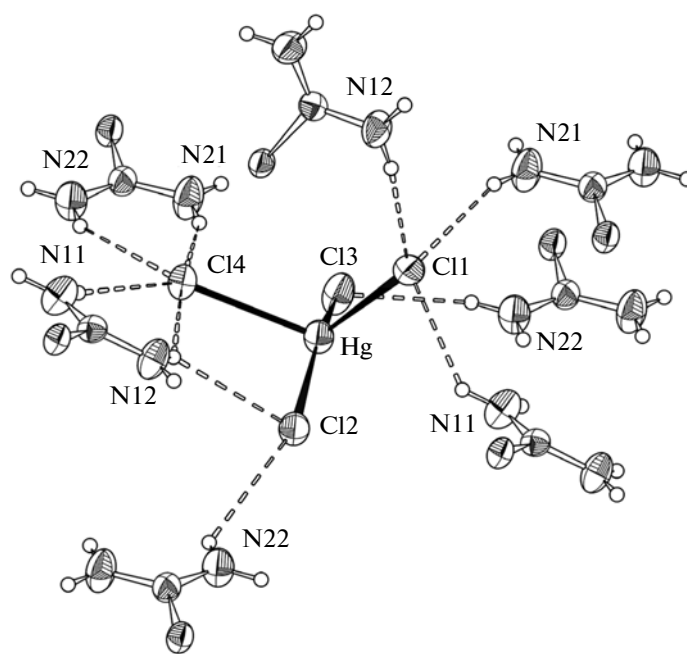
Bond	<i>d</i>	Bond	<i>d</i>
Hg–Cl1	2.654(1)	S1–C1	1.782(3)
Hg–Cl2	2.3858(8)	C1–N11	1.298(5)
Hg–Cl3	2.3624(9)	C1–N12	1.301(5)
Hg–Cl4	2.7782(9)	S2–C2	1.773(4)
Hg–Cl2 <sup>i</sup>	3.292(1)	C2–N21	1.303(5)
S1–S2	2.027(1)	C2–N22	1.302(5)
Angle	ω	Angle	ω
Cl1HgCl2	94.37(3)	Cl2HgCl4	93.79(3)
Cl1HgCl3	107.07(4)	Cl2HgCl2 <sup>i</sup>	80.67(3)
Cl1HgCl4	113.30(3)	Cl3HgCl4	92.93(3)
Cl1HgCl2 <sup>i</sup>	92.90(3)	Cl3HgCl2 <sup>i</sup>	81.64(3)
Cl2HgCl3	152.77(4)	Cl4HgCl2 <sup>i</sup>	153.62(3)
C1S1S2	102.6(1)	S1C1N12	114.3(3)
S1S2C2	103.9(1)	S2C2N12	114.1(3)
S1C1N11	123.5(3)	S2C2N22	123.4(3)
N11C1N12	122.2(3)	N21C2N22	122.5(4)

**X-ray diffraction analysis.** The experimental data set was collected from a prismatic 0.431 × 0.334 × 0.297-mm sample at 298 K using a Bruker AXS SMART APEX II single crystal diffractometer (CCD detector, MoK<sub>α</sub> radiation). A sample represented a twin of two domains turned at 3.6° relative to each other. For this reason, the data set was processed using the Cell\_now software from the SADABS software suit [6]. Absorption corrections applied were calculated by the multi-scan method. The structural model found by direct methods using the data from one domain was further refined with consideration for the contributions from both domains (the contribution of the second domain to the diffraction picture was 16.5(3)%). All non-hydrogen atoms were refined in the anisotropic approximation, hydrogen atoms were specified geometrically, and their positions were refined as “riding” (SHELXTL [7]). Crystallographic and experimental data and refinement details are given in Table 1.

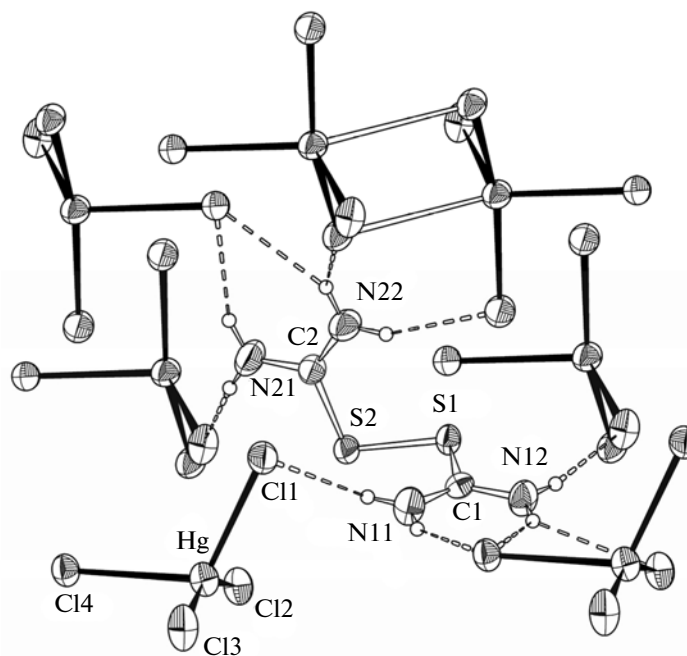
The structure was deposited with the Cambridge Structure Database (no. 919829). The data can be accessed at the site [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

The crystal structure units of compound I are HgCl<sub>4</sub><sup>2-</sup> anions and C<sub>2</sub>H<sub>8</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup> cations. HgCl<sub>4</sub><sup>2-</sup> ions linked via the inversion center into [Hg<sub>2</sub>Cl<sub>8</sub>]<sup>4-</sup> pairs are far from tetrahedral geometry: the ClHgCl angles range from 92.9° to 152.8° (Table 2). Moreover, the geometric structure of the HgCl<sub>4</sub><sup>2-</sup> ion does not correspond to either typical coordination polyhedra of mer-



**Fig. 2.** Geometry of hydrogen bonds with the participation of  $\text{HgCl}_4^{2-}$  ions. For clarity,  $\text{C}_2\text{H}_8\text{N}_4\text{S}_2^{2+}$  ion fragments are shown instead of ions themselves.



**Fig. 3.** Geometry of hydrogen bonds around the  $\text{C}_2\text{H}_8\text{N}_4\text{S}_2^{2+}$  ion.

cury(II). Their centrosymmetric “antipodes” are in such an orientation that the  $\text{Hg}-\text{Hg}^i$  distance is  $4.3673(4)$  Å, and the distance between the mercury atom of the initial group and the  $\text{Cl}2^i$  atom of the neighboring group transformed via the symmetry center is  $3.292(1)$  Å. The analysis of the distances in  $\text{Hg}-\text{Cl}-\text{Hg}$

groups from the Cambridge Structure Database [8] shows that a close value of the  $\text{Hg}-\text{Cl}$  distance ( $3.298$  Å) was taken into account in selecting the shape of the coordination polyhedron of  $(\text{Hg}_4(\text{DMPY})_2\text{Cl}_8)_n$ , where DMPY stands for 3,5-dimethylpyridine [9]. If the  $\text{Cl}2^i$  atom is incorporated into the surrounding of mercury,

**Table 3.** Geometric characteristics of hydrogen contacts and shortest molecular contacts in the structure of compound **I**

D–H...A	Distance, Å			DHA angle, deg	Symmetry codes for the A atom
	D–H	H...A	D...A		
N11–H11a...Cl4	0.86	2.49	3.274(3)	152.1	1 + x, y, z
N11–H11b...Cl1	0.86	2.57	3.217(3)	132.3	x, y, z
N12–H12a...Cl4	0.86	2.71	3.440(4)	144.0	1 + x, y, z
N12–H12a...Cl2	0.86	2.77	3.368(3)	127.7	1 + x, y, z
N12–H12b...Cl1	0.86	2.32	3.166(4)	167.4	1/2 + x, 1/2 – y, z – 1/2
N21–H21a...Cl4	0.86	2.41	3.226(4)	157.6	1/2 – x, y – 1/2, 3/2 – z
N21–H21b...Cl1	0.86	2.45	3.245(4)	154.2	x – 1/2, 1/2 – y, z – 1/2
N22–H22a...Cl4	0.86	2.69	3.435(3)	145.5	1/2 – x, y – 1/2, 3/2 – z
N22–H22a...Cl2	0.86	2.78	3.319(4)	122.1	1/2 + x, 1/2 – y, 1/2 + z
N22–H22b...Cl3	0.86	2.55	3.353(4)	156.0	3/2 – x, y – 1/2, 3/2 – z

the resulting  $\text{HgCl}_5$  polyhedron will be a tetragonal pyramid with the axial (ax) Cl11 atom. The shared Cl2–Cl2<sup>i</sup> edge links the polyhedra together (Fig. 1). The ClHgCl angles of the pyramidal base (eq) are from 80.7° to 93.8°, and the Cl1<sub>ax</sub>HgCl<sub>eq</sub> angles are from 92.9° to 107.1° (Table 2). The deviation of the mercury atom from the average equatorial plane is 0.5888(4) Å. The deviations of the basal Cl3, Cl4, Cl2, and Cl2<sup>i</sup> atoms from their plane are ±0.0987(6) Å. With allowance for the weak Hg–Cl2<sup>i</sup> contact (3.292 Å), the structure of compound **I** contains discrete bis(μ<sub>2</sub>-chloro)hexachlorodimercurate(II) anion. We know the structure of only one compound that contains a discrete dimer anion [10]. In  $(\text{H}_2\text{PyBIm})_2[\text{Hg}_2\text{Cl}_8]$  (**II**) where PyBIm is 2-(3-pyridyl)benzimidazol, mercury(II) atoms form two trigonal bipyramids linked together by a shared edge. The longest Hg–Cl distance in the  $[\text{Hg}_2\text{Cl}_8]^{4-}$  anion of the structure of compound **II** is 2.946 Å, which is 0.35 Å shorter than the Hg–Cl distance found in compound **I**.

The S–S bond in the α,α'-dithio-bis(formamidinium)  $\text{C}_2\text{H}_8\text{N}_4\text{S}_2^{2+}$  cation in compound **I** is ordinary, and its length (2.027 Å) approaches the S–S bond length found in the other salts of this cation [11]. The two  $\text{SCN}_2\text{H}_4$  structural fragments are planar. The dihedral angle between their planes is 88.59(9)°, and the torsion C1S1S2C2 angle is 101.4(2)°.

The crystal structure of compound **I** is stabilized by the network of N–H...Cl hydrogen bonds (Table 3; Figs. 2, 3) with the participation of all hydrogen atoms. Hydrogen bonds close six-membered C–N–H–Cl–H–N rings (supramolecular  $R_1^2(6)$  motif [11]) and a four-membered Hg–Cl–H–Cl ring ( $R_1^2(4)$ ).

$[\text{Hg}_2\text{Cl}_8]^{4-}$  ions form layers that are perpendicular to the *b* axis, and  $\text{C}_2\text{H}_8\text{N}_4\text{S}_2^{2+}$  cations are also arranged in layers between the layers of anions (Fig. 1). These layers are linked by N–H...Cl hydrogen bonds with the formation of a three-dimensional framework structure.

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