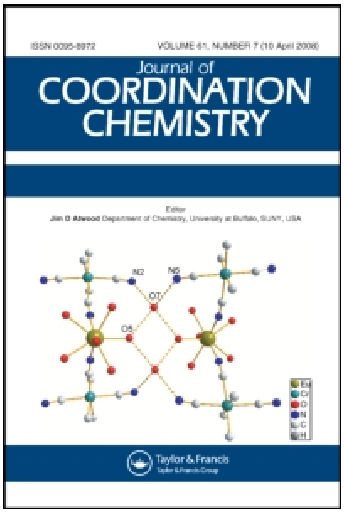

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Synthesis and crystal structure of diiodobis(thiourea)mercury (ii)-bis(diazafluoren-9-one)

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SYNTHESIS AND CRYSTAL STRUCTURE OF DIIODOBIS(THIOUREA)MERCURY (II)-BIS(DIAZAFLUOREN-9-ONE)

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The title compound, $[HgI_2(CH_4N_2S)_2] \cdot 2C_{11}H_6N_2O$, is comprised of the Hg(II)–thiourea complex and free 4,5-diazafluoren-9-one (DAFONE). The complex assumes a distorted tetrahedral geometry at mercury formed by two thiourea molecules and two I^- ions, the S–Hg–S angle [103.7°] being significantly smaller than S–Hg–I angles (115.2 and 114.3°). The complex and DAFONE molecules link to each other via hydrogen bonding to form a supramolecular structure. Significant π–π stacking is observed between neighboring DAFONE molecules.

Keywords: Hg(II) complex; Crystal structure; 4,5-Diazafluoren-9-one; π–π Stacking; Supramolecular structure

INTRODUCTION

The phenomenon of π–π stacking between aromatic rings is correlated with electron transfer processes in some biological systems [1]. Several kinds of aromatic compounds, such as phenanthroline, benzimidazole and so on, show π–π stacking interaction in their metal complexes [2]. As part of an investigation of π–π stacking, 4,5-diazafluoren-9-one (DAFONE) has recently been used for preparing metal complexes in our laboratory. The present X-ray structure reveals that DAFONE does not chelate to the metal ion in a mercury complex, but π–π stacking still occurs between DAFONE rings included in the crystal.

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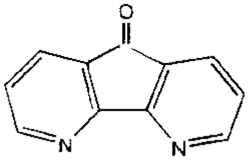
EXPERIMENTAL

Preparation

DAFONE was prepared in the manner reported by Henderson *et al.* [3]. An aqueous solution (15 cm^3) containing DAFONE (0.091 g, 0.5 mmol), HgI_2 (0.114 g, 0.25 mmol) and thiourea (0.038 g, 0.5 mmol) was refluxed for 2 h. The solution was filtered and the filtrate kept in a thermostat at 60°C. Yellow, single crystals were obtained after 2 d. C, N and H contents were analyzed on a Carlo-Erba 1160 instrument. *Anal.* Calc. for $Hg(CH_4N_2S)_2I_2 \cdot 2(C_{11}H_6N_2O)$ (%): C, 29.69; N, 11.54; H, 2.08. Found: C, 29.59; N, 11.48; H, 2.31.



Crystal Structure Determination

X-Ray diffraction data were collected on a Bruker SMART diffractometer with Mo Kα radiation up to 2θ equal to 50.2°. The crystal structure was solved by the heavy atom method followed by Fourier syntheses. Structure refinement was performed by full-matrix least-squares procedures using SHELXL-97 on F^2 [4]. H atoms were placed in calculated positions with N–H = 0.86 Å and C–H = 0.98 Å, and were included in the final cycles of refinement in riding mode, with $U_{iso}(H) = 1.2\,U_{eq}$ of the carrier atoms. Peaks with larger electron density in the final difference Fourier map (the highest peak 1.97 e Å^{-3} and the deepest hole -2.62 e Å^{-3}) are near the Hg atom (1.00 and 0.91 Å, respectively).

Crystal data and refinement conditions are summarized in Table I. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in Table II.

Full crystallographic data have been deposited at CCDC with deposition number 225889.

RESULTS AND DISCUSSION

The molecular structure of the title compound is illustrated in Fig. 1. The asymmetric unit contains one complex Hg(II) molecule and two free DAFONE molecules. The complex assumes a distorted tetrahedral coordinate geometry at mercury formed by two thiourea ligands and two I^- ions, with the S1–Hg–S2 bond angle [103.70(8)°] being significantly smaller than S1–Hg–I2 [115.17(6)°] and S2–Hg–I2 [114.34(6)°] angles (see Table III). The coordination plane defined by I1, I2 and Hg atoms is perpendicular to the plane defined by S1, S2 and Hg atoms; the dihedral angle of 89.65(6)° differs considerably from 76.76(2)° found in a reported Hg(II)–thiourea

TABLE I Crystal data and details of the structure determination

Formula	$2(C_{11}H_6N_2O)$, $C_2H_8HgI_2N_4S_2$
Formula weight	971.01
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c (Å)	7.3473(19), 13.191(3), 16.248(4)
α, β, γ (°)	88.984(5), 77.062(5), 80.452(5)
V (Å^3)	1513.2(6)
Z	2
D(calc) (g cm^{-3})	2.131
μ (MoKa) (mm^{-1})	7.300
F(000)	908
Crystal size (mm)	0.20 × 0.15 × 0.12
Tot., uniq. data, R(int)	8143, 5345, 0.036
Observed data [$I > 2\sigma(I)$]	4246
Nref, Npar	5345, 353
R, wR_2	0.0483, 0.1231
S	0.97
Max., av. shift/error	0.00, 0.00
Min., max. resd. dens. (e Å^{-3})	−2.62, 1.97

$w = 1/[\sigma^2(Fo^2) + (0.0807\,P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Final coordinates and equivalent isotropic displacement parameters of the nonhydrogen atoms

Atom	*x/a*	*y/b*	*z/c*	*U(eq)* (Å^2)
Hg	0.47889(5)	0.24052(2)	0.36179(2)	0.0494(1)
I1	0.79127(8)	0.23720(4)	0.43102(4)	0.0585(2)
I2	0.60267(12)	0.24765(5)	0.18798(4)	0.0780(3)
S1	0.2317(4)	0.39009(17)	0.42820(15)	0.0661(8)
S2	0.3291(3)	0.08511(16)	0.41263(15)	0.0596(7)
O1	0.2812(12)	1.0116(5)	0.0946(5)	0.087(3)
O2	1.0979(10)	−0.5126(5)	0.0861(5)	0.081(3)
N1	0.1569(10)	0.5831(5)	0.3953(5)	0.060(2)
N2	0.3155(10)	0.4869(5)	0.2825(4)	0.059(3)
N3	0.4652(11)	−0.1092(5)	0.3828(5)	0.059(3)
N4	0.5550(10)	−0.0082(5)	0.2742(5)	0.057(3)
N5	0.1065(9)	0.7768(5)	0.3121(4)	0.049(2)
N6	0.3716(10)	0.6569(5)	0.1622(4)	0.050(2)
N7	0.6731(9)	−0.3042(5)	0.3035(4)	0.049(2)
N8	0.7867(9)	−0.1697(5)	0.1529(4)	0.047(2)
C1	0.2378(11)	0.4937(6)	0.3630(5)	0.042(2)
C2	0.4622(10)	−0.0173(6)	0.3521(5)	0.043(2)
C3	−0.0097(12)	0.8478(6)	0.3691(5)	0.055(3)
C4	−0.0414(13)	0.9515(6)	0.3549(6)	0.060(3)
C5	0.0412(13)	0.9896(7)	0.2799(6)	0.059(3)
C6	0.1583(11)	0.9204(6)	0.2202(5)	0.045(3)
C7	0.2703(13)	0.9332(6)	0.1341(6)	0.053(3)
C8	0.3650(11)	0.8272(6)	0.1042(5)	0.048(3)
C9	0.4840(12)	0.7909(7)	0.0289(5)	0.054(3)
C10	0.5446(13)	0.6864(8)	0.0221(6)	0.062(3)
C11	0.4897(12)	0.6231(7)	0.0874(6)	0.058(3)
C12	0.3136(10)	0.7594(5)	0.1678(5)	0.040(2)
C13	0.1850(10)	0.8164(5)	0.2401(5)	0.039(2)
C14	0.6447(13)	−0.3788(6)	0.3600(6)	0.055(3)
C15	0.7285(14)	−0.4805(7)	0.3465(7)	0.064(3)
C16	0.8457(13)	−0.5109(7)	0.2711(6)	0.060(3)
C17	0.8782(11)	−0.4358(6)	0.2113(6)	0.049(3)
C18	0.9982(12)	−0.4394(6)	0.1231(6)	0.053(3)
C19	0.9662(11)	−0.3320(6)	0.0924(6)	0.050(3)
C20	1.0306(12)	−0.2884(7)	0.0161(6)	0.060(3)
C21	0.9725(13)	−0.1852(8)	0.0098(6)	0.065(3)
C22	0.8555(12)	−0.1292(7)	0.0780(6)	0.058(3)
C23	0.8450(10)	−0.2703(6)	0.1581(5)	0.042(2)
C24	0.7908(10)	−0.3348(6)	0.2305(5)	0.041(2)

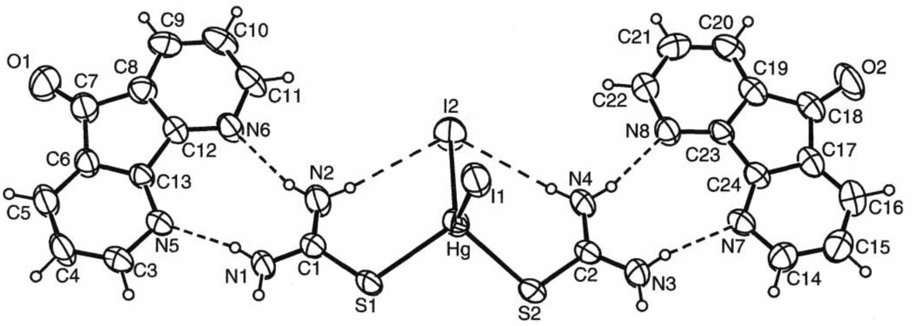


FIGURE 1 The molecular structure of the title compound with 50% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding.

TABLE III Selected bond distances and angles (Å, °) for the complex

Hg–S1	2.523(3)	Hg–S2	2.525(2)
Hg–I1	2.7669(10)	Hg–I2	2.7713(10)
S1–C1	1.715(8)	S2–C2	1.711(8)
O1–C7	1.212(11)	O2–C18	1.191(11)
N1–C1	1.292(10)	N2–C1	1.303(10)
N3–C2	1.301(10)	N4–C2	1.310(11)
I1–Hg–I2	107.32(3)	I1–Hg–S1	107.86(7)
I1–Hg–S2	108.12(5)	I2–Hg–S1	115.17(6)
I2–Hg–S2	114.34(6)	S1–Hg–S2	103.70(8)
Hg–S1–C1	110.4(3)	Hg–S2–C2	106.6(3)
S1–C1–N1	118.0(6)	N1–C1–N2	118.3(7)
S1–C1–N2	123.7(6)	S2–C2–N4	122.9(6)
N3–C2–N4	118.0(7)	S2–C2–N3	119.0(6)

complex [5]. Intramolecular hydrogen bonding occurs between amino groups of thiourea and coordinated I2 atom (Fig. 1); it stabilizes the molecular structure.

Two planar thiourea molecules coordinating to a Hg(II) atom are nearly parallel to each other, with a small dihedral angle of 8.8(3)°. This agrees with the situation in a tricoordinated Cu(I)–thiourea complex, bis(thiourea)chlorocopper(I)di(4,5-diazafluoren-9-one) [6], but differs from that found in the Hg(II)–thiourea complex cited above [5]; in the latter, the two planar thiourea ligands are almost perpendicular to each other with a dihedral angle of 89.81(2)°. In the present crystal two thiourea molecules are also roughly parallel to the SI–S2–I2 plane of the complex, dihedral angles being 14.3(2) and 8.1(2)°, respectively.

Two crystallographically independent DAFONE molecules display a similar planar structure. Although DAFONE is structurally similar to phenanthroline (phen), most reported crystal structures containing the DAFONE molecule, as well as the present structure, show that DAFONE does not chelate to the metal ion [7]. The carbonyl bridge in DAFONE distorts the bipyridine portion and results in a longer N···N separation. The N5···N6 separation of 3.036(9) Å and N7···N8 separation of 3.042(9) Å are much longer than 2.724 Å, as found in the solid state for phen [8]. The longer N···N separation may reduce overlap of nitrogen–metal orbitals [3] and result in weak chelating ability for DAFONE.

An extensive intermolecular hydrogen bond network exists in the crystal. Two independent DAFONE molecules link with the Hg(II) complex via N–H···N hydrogen

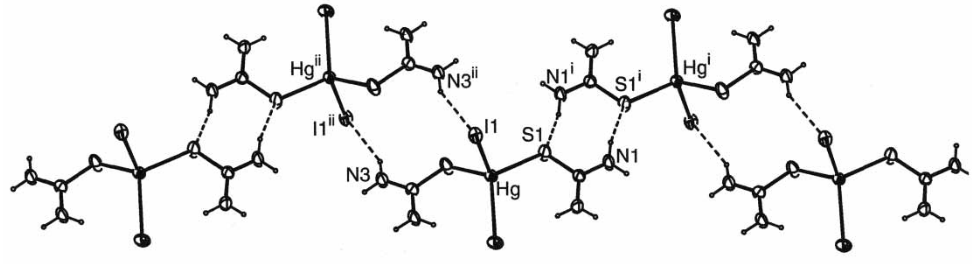


FIGURE 2 The hydrogen bonding network between complex Hg(II) molecules [symmetry codes: (i) $-x$, $1-y$, $1-z$; (ii) $1-x$, $-y$, $1-z$].

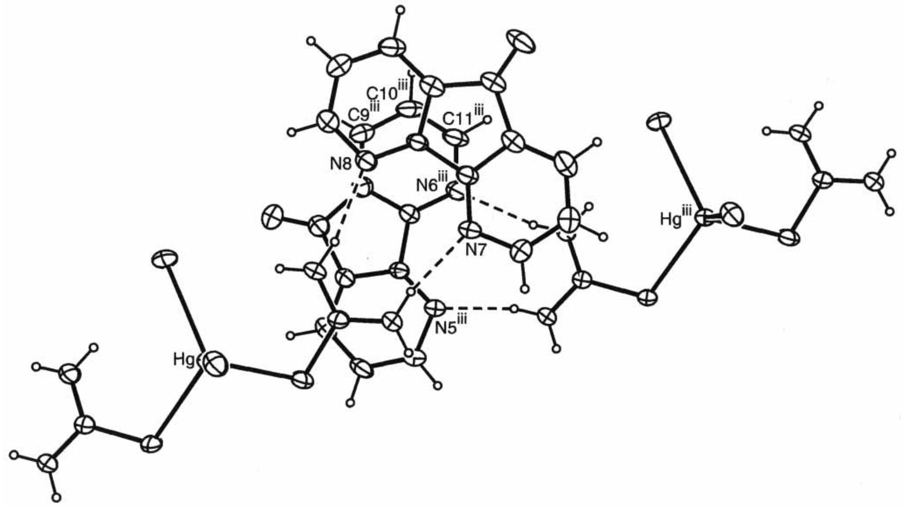


FIGURE 3 Aromatic π–π stacking between neighboring DAFONE molecules [symmetry code: (iii) x, $-1+y$, z].

bonding as shown in Fig. 1. N−H···S and N−H···I hydrogen bonds link complex molecules to form a supramolecular structure (Fig. 2).

The N5^{iii}/N6^{iii}-DAFONE mean plane [symmetric code (iii), x, $-1+y$, z] is approximately parallel to the neighboring N7/N8-DAFONE plane, the dihedral angle being 4.47(19)°. The two planes partially overlap as shown in Fig. 3. Atoms C9^{iii}, C10^{iii} and C11^{iii} lie out of the N7/N8-DAFONE plane by 3.273(10), 3.378(10) and 3.451(9) Å, respectively, and thus suggest the existence of π–π stacking between DAFONE molecules.

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