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# Two-dimensional polymeric $[Hg_4(\mu_2\text{-}I)_6I_2(\mu_2\text{-}C_4S_6)]_n$

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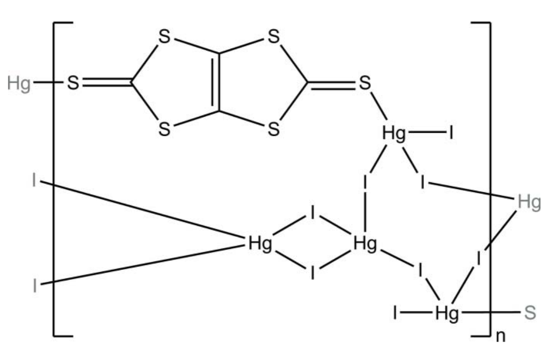
Key indicators: single-crystal X-ray study; $T$ = 173 K; mean $\sigma$(C–C) = 0.014 Å; $R$ factor = 0.039; $wR$ factor = 0.114; data-to-parameter ratio = 25.4.

The title compound, poly[($\mu_2$-2$H$,5$H$-1,3-dithiolo[4,5-$d$][1,3]dithiole-2,5-dithione)hexa-$\mu_2$-iodido-diiodidotetramercury(II)], $[Hg_4I_8(C_4S_6)]_n$, represents the first example of a coordination polymer assembled by the $\alpha,\alpha$-$C_4S_6$ dithione ligand. The $Hg^{II}$ ions are four-coordinated in a distorted tetrahedral geometry, the coordination demand being satisfied either by four bridging iodide ligands or by three iodide ligands (one terminal and two bridging) and a thiocarbonyl S atom. Due to the bridging nature of the dithione ligand, the coordination polymer has a two-dimensional structure, built up of undulated layers parallel to (001). There is an inversion center at the mid-point of the central C=C double bond.

## Related literature

For the synthesis and structure of the $\alpha,\alpha$-$C_4S_6$ ligand, see: Krug *et al.* (1977); Beck *et al.* (2006). For related studies on polymeric binary carbon sulfides, see: Galloway *et al.* (1994). For the synthesis and structures of coordination polymers with sulfur-rich ligands, see: Peindy *et al.* (2005); Hameau *et al.* (2006); Ndiaye *et al.* (2007); Guyon *et al.* (2008).




## Experimental

*Crystal data*

$[Hg_4I_8(C_4S_6)]$
$M_r$ = 1028.98
Monoclinic, $P2_1/c$
$a$ = 8.5502 (6) Å
$b$ = 11.2156 (8) Å
$c$ = 13.4634 (9) Å
$\beta$ = 91.343 (1)°
$V$ = 1290.73 (16) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 33.76 mm$^{-1}$
$T$ = 173 K
0.30 × 0.10 × 0.10 mm

*Data collection*

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min}$ = 0.035, $T_{max}$ = 0.133
24415 measured reflections
2543 independent reflections
2337 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.086

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.114
$S$ = 1.03
2543 reflections
100 parameters
$\Delta\rho_{max}$ = 3.56 e Å$^{-3}$
$\Delta\rho_{min}$ = −3.29 e Å$^{-3}$

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2103).

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# supporting information

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## Two-dimensional polymeric $[Hg_4(\mu_2\text{-}I)_6I_2(\mu_2\text{-}C_4S_6)]_n$

**Aurélien Hameau, Fabrice Guyon, Michael Knorr, Victoria P. Colquhoun and Carsten Strohmann**

### S1. Comment

Molecular and polymeric binary carbon sulfides have been the subject of numerous studies (see for example Galloway *et al.*, 1994). In the context of our interest in using sulfur-rich ligands to synthesize coordination polymers (Peindy *et al.*, 2005; Hameau *et al.*, 2006; Ndiaye *et al.* 2007; Guyon *et al.* 2008), carbon sulfides and especially 1,3-dithiol*o*-(4,5-d)-1,3-dithiol-2,5-dithione ($\alpha,\alpha$-$C_4S_6$) appears attractive due to the presence of two potentially coordinating thiocarbonyl sulfur atoms. The $\alpha,\alpha$-$C_4S_6$ carbon sulfide compound, first prepared in 1977 (Krug *et al.*, 1977), reacts with $HgI_2$ to afford the coordination polymer $[Hg_4I_8(C_4S_6)]_n$ (**1**). As shown in Fig.1, the monomeric unit has a centrosymmetrical tetranuclear structure which is formed by one $\alpha,\alpha$-$C_4S_6$ ligand linking two $Hg_2I_4$ fragments with an inversion centre located at the mid-point of the central C═C bond. Each mercury(II) centre is arranged in a distorted tetrahedral manner. The Hg1 atom is coordinated by one terminal iodine atom (I1), two bridging iodine atoms (I2 and $I4^{iii}$) and the sulfur of the thiocarbonyl function S2 whereas the coordination sphere of Hg2 involves only bridging iodo ligands (I2, I3, $I3^{ii}$ and I4). Note however that the bridging contribution of I4 is weak since the $Hg1^{iii}$-I4 distance (3.423 (1) Å) is quite long compared to that of Hg2—I4 (2.6497 (8) Å). The C═S bond of $\alpha,\alpha$-$C_4S_6$ is weakly affected by coordination of the sulfur atom on Hg1 (1.671 (10) Å *versus* 1.645 (2) in the free ligand, Beck *et al.*, 2006). The Hg1—S2 distance of 2.697 (3) Å is somewhat longer than that reported for 4,5-bis(methylthio)-1,3-dithiole-2-thione on $HgI_2$ (Hameau *et al.*, 2006). The $\alpha,\alpha$-$C_4S_6$ ligands connect the inorganic chains built upon the alternance of 8-membered $Hg_4I_4$ and 4-membered $Hg_2I_2$ cycles to form a two-dimensional framework. Note that there are no S—S interactions inferior to the sum of the van der Waals radii of two S atoms in the solid state.

### S2. Experimental

The $\alpha,\alpha$-$C_4S_6$ ligand was prepared as described previously (Beck *et al.*, 2006). To the $\alpha,\alpha$-$C_4S_6$ dithione (14 mg, 58 $\mu$mol) dissolved in 13.5 ml of a solvent mixture (toluene/acetonitrile/chlorobenzene in 2/1/1 ratio) was added upon stirring a solution of $HgI_2$ (53 mg, 116 $\mu$mol) in toluene (10 ml). The resulting solution was refluxed for 0.2 h., then allowed to reach room temperature and filtered. Dark red crystals suitable for X-ray analysis were obtained by slow evaporation of the solution (yield 85%). IR (KBr): $\nu_{C=S}$ = 1036 cm$^{-1}$.

### S3. Refinement

The largest Fourier peak/hole (3.56 and –3.29 e/Å$^3$, respectively) are found 0.95 and 0.68Å from Hg1 (see even extra table).

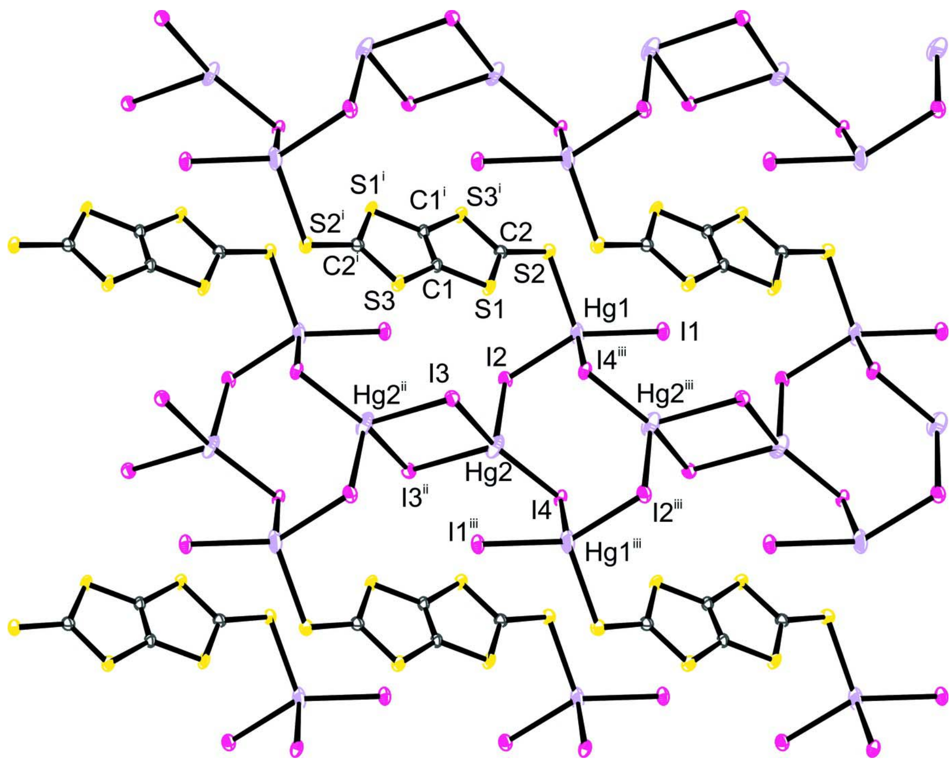


**Figure 1**

A view of the title compound along (001). Displacement ellipsoids are drawn at the 50% probability level. Symmetry operations: (i) -x, -y+2, -z+2; (ii) -x, -y+1, -z+2; (iii) -x+1, -y+1, -z+2.

## Poly[($\mu_2$-2*H*,5*H*-1,3-dithiolo[4,5-*d*][1,3]dithiole- 2,5-dithione)hexa-$\mu_2$-iodido-diiodidotetramercury(II)]

### *Crystal data*

[$Hg_4I_8(C_4S_6)$]
$M_r$ = 1028.98
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a$ = 8.5502 (6) Å
$b$ = 11.2156 (8) Å
$c$ = 13.4634 (9) Å
$\beta$ = 91.343 (1)°
$V$ = 1290.73 (16) Å$^3$
$Z$ = 4
$F(000)$ = 1728
$D_x$ = 5.295 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 8987 reflections
$\theta$ = 2.4–26°
$\mu$ = 33.76 mm$^{-1}$
$T$ = 173 K
Needle, dark red
0.30 × 0.10 × 0.10 mm

### *Data collection*

Bruker APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min}$ = 0.035, $T_{max}$ = 0.133
24415 measured reflections
2543 independent reflections
2337 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.086
$\theta_{max}$ = 26.0°, $\theta_{min}$ = 2.4°
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.114$
$S = 1.03$
2543 reflections
100 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 7.1937P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 3.56$ e Å$^{-3}$
$\Delta\rho_{min} = -3.29$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.0263 (12) | 0.9542 (9) | 1.0288 (7) | 0.029 (2) |
| C2 | 0.2439 (12) | 0.9942 (9) | 0.9076 (8) | 0.033 (2) |
| Hg1 | 0.51629 (6) | 0.77041 (5) | 0.83365 (5) | 0.05585 (19) |
| Hg2 | 0.22624 (7) | 0.46970 (6) | 0.97826 (5) | 0.0672 (2) |
| I1 | 0.82359 (9) | 0.77867 (6) | 0.83985 (5) | 0.0374 (2) |
| I2 | 0.25603 (8) | 0.64475 (6) | 0.79810 (5) | 0.0372 (2) |
| I3 | 0.08558 (9) | 0.60123 (6) | 1.11662 (5) | 0.03616 (19) |
| I4 | 0.45656 (8) | 0.32667 (6) | 0.92556 (5) | 0.03444 (19) |
| S1 | 0.2076 (3) | 0.8973 (2) | 1.0033 (2) | 0.0374 (6) |
| S2 | 0.4123 (3) | 0.9968 (3) | 0.8465 (2) | 0.0427 (6) |
| S3 | −0.0987 (3) | 0.9043 (2) | 1.1185 (2) | 0.0363 (6) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.025 (5) | 0.035 (5) | 0.028 (5) | −0.001 (4) | 0.003 (4) | 0.002 (4) |
| C2 | 0.031 (5) | 0.029 (5) | 0.039 (5) | −0.002 (4) | 0.003 (4) | −0.001 (4) |
| Hg1 | 0.0325 (3) | 0.0672 (4) | 0.0682 (4) | −0.0029 (2) | 0.0078 (2) | 0.0044 (3) |
| Hg2 | 0.0477 (4) | 0.0668 (4) | 0.0881 (5) | 0.0157 (3) | 0.0243 (3) | −0.0110 (3) |
| I1 | 0.0303 (4) | 0.0452 (4) | 0.0369 (4) | −0.0012 (3) | 0.0048 (3) | −0.0032 (3) |
| I2 | 0.0332 (4) | 0.0424 (4) | 0.0359 (4) | −0.0019 (3) | 0.0013 (3) | 0.0038 (3) |
| I3 | 0.0351 (4) | 0.0365 (4) | 0.0369 (4) | −0.0014 (3) | 0.0029 (3) | −0.0047 (3) |
| I4 | 0.0305 (4) | 0.0404 (4) | 0.0326 (4) | 0.0048 (3) | 0.0041 (3) | −0.0024 (3) |
| S1 | 0.0310 (14) | 0.0406 (14) | 0.0410 (14) | 0.0074 (11) | 0.0101 (11) | 0.0073 (11) |
| S2 | 0.0350 (15) | 0.0365 (13) | 0.0576 (17) | 0.0020 (11) | 0.0205 (13) | 0.0038 (12) |
| S3 | 0.0339 (14) | 0.0372 (13) | 0.0383 (13) | 0.0051 (10) | 0.0128 (11) | 0.0067 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C1$^{i}$ | 1.36 (2) | Hg1—S2 | 2.697 (3) |
| C1—S1 | 1.718 (11) | Hg2—I4 | 2.6496 (9) |
| C1—S3 | 1.724 (11) | Hg2—I3 | 2.6828 (9) |
| C2—S2 | 1.675 (11) | Hg2—I3$^{ii}$ | 3.0353 (10) |
| C2—S3$^{i}$ | 1.715 (11) | Hg2—I2 | 3.1357 (10) |
| C2—S1 | 1.720 (11) | I3—Hg2$^{ii}$ | 3.0353 (10) |
| Hg1—I1 | 2.6285 (9) | S3—C2$^{i}$ | 1.715 (11) |
| Hg1—I2 | 2.6678 (9) | | |
| | | | |
| C1$^{i}$—C1—S1 | 117.1 (11) | I4—Hg2—I3$^{ii}$ | 112.31 (3) |
| C1$^{i}$—C1—S3 | 116.3 (11) | I3—Hg2—I3$^{ii}$ | 91.87 (3) |
| S1—C1—S3 | 126.6 (6) | I4—Hg2—I2 | 95.60 (3) |
| S2—C2—S3$^{i}$ | 121.0 (6) | I3—Hg2—I2 | 103.81 (3) |
| S2—C2—S1 | 123.4 (6) | I3$^{ii}$—Hg2—I2 | 85.70 (3) |
| S3$^{i}$—C2—S1 | 115.5 (6) | Hg1—I2—Hg2 | 105.93 (3) |
| I1—Hg1—I2 | 148.57 (3) | Hg2—I3—Hg2$^{ii}$ | 88.13 (3) |
| I1—Hg1—S2 | 107.19 (7) | C1—S1—C2 | 95.4 (5) |
| I2—Hg1—S2 | 103.53 (7) | C2—S2—Hg1 | 107.7 (4) |
| I4—Hg2—I3 | 150.11 (4) | C2$^{i}$—S3—C1 | 95.7 (5) |

Symmetry codes: (i) $-x, -y+2, -z+2$; (ii) $-x, -y+1, -z+2$.