metal-organic compounds

catena-Poly[[dibromidomercury(II)]-*μ*-3,6-bis(2-pyridylsulfanyl)pyridazine-$\kappa^2 N^3:N^6$]

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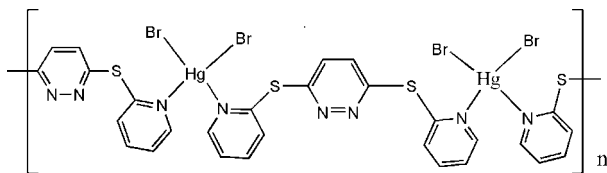Correspondence e-mail: songrf@mail.usts.edu.cn

In the title coordination polymer, $[HgBr_2(C_{14}H_{10}N_4S_2)]_n$, the Hg[II] atom is four-coordinated in a distorted tetrahedral geometry by the two N atoms of the pyridyl groups of different 3,6-bis(2-pyridylsulfanyl)pyridazine ligands and two Br atoms. The bridging function of the *cis* ligands leads to a helical chain structure along [100].

Related literature

For metal coordination compounds with 3,6-bis(2-pyridylthio)pyridazine, see: Chen *et al.* (1996); Mandal *et al.* (1987, 1988); Song *et al.* (2011); Woon *et al.* (1986).

Experimental

Crystal data

$[HgBr_2(C_{14}H_{10}N_4S_2)]$	V = 1775.1 (5) Å³
M_r = 658.78	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 16.393 (3) Å	μ = 13.41 mm⁻¹
b = 12.4954 (19) Å	T = 223 K
c = 9.7648 (16) Å	0.55 × 0.30 × 0.26 mm
β = 117.444 (3)°	

Data collection

Rigaku Saturn diffractometer	5341 measured reflections
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)	2013 independent reflections
	1688 reflections with $I > 2\sigma(I)$
T_{min} = 0.013, T_{max} = 0.030	R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038	107 parameters
$wR(F^2)$ = 0.080	H-atom parameters constrained
S = 1.00	$\Delta\rho_{max}$ = 1.56 e Å⁻³
2013 reflections	$\Delta\rho_{min}$ = −2.20 e Å⁻³

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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supporting information

catena-Poly[[dibromidomercury(II)]-*µ*-3,6-bis(2-pyridylsulfanyl)pyridazine-*κ²N³:N⁶*]

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S1. Comment

In recent years, metal complexes of N-containing heterocyclic flexible thioethers ligands especially attracted considerable interest. The ligand 3,6-bis(2-pyridylthio) pyridazine (PTP) is interesting bridging ligand and is able to act as bridges between metal centers to form dinuclear (Chen *et al.*, 1996; Mandal *et al.*, 1987, 1988; Woon *et al.*, 1986) and coordination polymer (Song *et al.* 2011). Herein, we report the crystal structure of Hg^{II} complex (I).

The title complex (I) is one-dimensional chain coordination polymer. Each Hg^{II} atom is in a distorted tetrahedral geometry with two N atoms from two different PTP ligands and two bromide (Fig. 1). Its structure is isomorphous with HgI$_2$ complex (Song *et al.*, 2011). Complex (I) has a compressed N—Hg—N angle of 98.8 (2)° and an expanded Br—Hg—Br angle of 140.84 (4)°, whereas for iodide structure the compressed N—Hg—N angle and expanded I—Hg—I angle are 96.6 (2)° and 144.01 (2)° (Song *et al.*, 2011), respectively. As HgI$_2$ complex (Song *et al.*, 2011), HgBr$_2$ units of the complex (I) are connected to each other by *cis*-PTP ligands through the pyridyl nitrogen atoms into a one-dimensional chain along [100] (Fig. 2). The ligand adopts a pronounced *syn* twist, creating an angle of 15.3 (1)° between the pyridine planes and angles of 83.2 (1)° between the pyridine planes and the pyridazine plane. The two pyridyl groups in PTP are not coplanar, and the bending of the ligand and its coordination at the Hg(II) center result in one-dimensional chains that adopt a helical twist. The isomorphous structure results from tetrahedral coordination geometry Hg^{II} ions.

S2. Experimental

The ligand 3,6-bis(2-pyridylthio) pyridazine (PTP) was prepared according to the general procedure reported by Woon *et al.* (1986). For preparation of the title compound, a solution of HgBr$_2$ (18.5 mg, 0.05 mmol) in acetone (2 ml) was slowly added to a solution of PTP (15 mg, 0.05 mmol) in CH$_3$OH (2 ml). The mixture was stirred for 0.5 h at room temperature, and then filtered and kept in the refrigerator (-18 C°). After 48 h, yellow prismatic single-crystals (I) of suitable for X-ray analysis was obtained in 67.2% yield. IR (cm^{-1}): 3039.81.w, 2368.58w, 1581.62*m*, 1450.47*m*, 1427.32*m*, 1396.46 s, 833.25w, 771.52 s, 632.65w, 578.64w. Anal. Found: C, 25.53; H, 1.51; N, 8.46. Calcd. For C$_{14}$H$_{10}$Br$_2$HgN$_4$S$_2$: C, 25.50; H, 1.32; N, 8.50.

S3. Refinement

H atoms were included in calculated positions refined as part of a riding with C—H distances of 0.94Å (aromatic H), and with U_{iso}= 1.2U_{eq}(C).
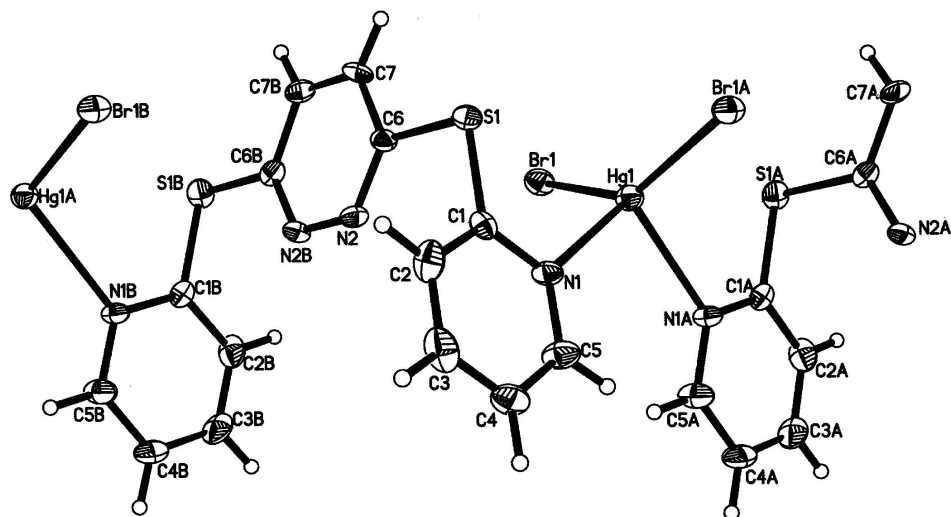
Figure 1

The the coordination environment of Hg^{II} center of complex(I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.
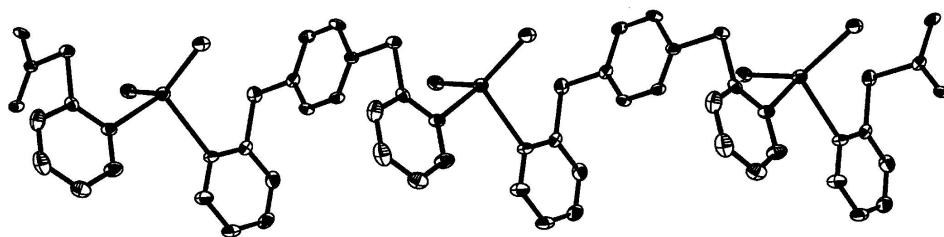

Figure 2

Perspective view of the 1-D helical chain structure of complex(I).

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Crystal data

[HgBr$_2$(C$_{14}$H$_{10}$N$_4$S$_2$)]
$M_r = 658.78$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 16.393$ (3) Å
$b = 12.4954$ (19) Å
$c = 9.7648$ (16) Å
$\beta = 117.444$ (3)°
$V = 1775.1$ (5) Å^3
$Z = 4$

$F(000) = 1216$
$D_x = 2.465$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71075$ Å
Cell parameters from 2664 reflections
$\theta = 3.6$–27.5°
$\mu = 13.41$ mm^{-1}
$T = 223$ K
Prism, yellow
$0.55 \times 0.30 \times 0.26$ mm

Data collection

Rigaku Saturn
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 14.63 pixels mm^{-1}
ω scans

Absorption correction: multi-scan
  (*REQAB*; Jacobson, 1998)
$T_{min} = 0.013$, $T_{max} = 0.030$
5341 measured reflections
2013 independent reflections
1688 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$

$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$		$k = -9 \rightarrow 16$	
$h = -18 \rightarrow 21$		$l = -12 \rightarrow 10$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.080$	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
2013 reflections	$(\Delta/\sigma)_{max} < 0.001$
107 parameters	$\Delta\rho_{max} = 1.56$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -2.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.00186 (14)

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}
Hg1	0.5000	0.24799 (3)	0.2500	0.03257 (15)
Br1	0.37219 (4)	0.18078 (6)	0.00215 (7)	0.03794 (19)
S1	0.63765 (10)	0.19500 (16)	0.09685 (16)	0.0354 (4)
N1	0.5935 (3)	0.3774 (4)	0.1882 (5)	0.0300 (11)
N2	0.5304 (3)	0.2847 (4)	−0.1745 (5)	0.0282 (11)
C1	0.6470 (3)	0.3344 (5)	0.1311 (6)	0.0272 (13)
C2	0.7060 (4)	0.3982 (7)	0.0995 (7)	0.0438 (18)
H2A	0.7442	0.3669	0.0625	0.053*
C3	0.7083 (4)	0.5050 (8)	0.1218 (7)	0.051 (2)
H3	0.7469	0.5486	0.0984	0.062*
C4	0.6537 (4)	0.5493 (6)	0.1790 (7)	0.0440 (16)
H4	0.6530	0.6236	0.1937	0.053*
C5	0.6000 (4)	0.4815 (6)	0.2142 (8)	0.0427 (16)
H5	0.5657	0.5113	0.2598	0.051*
C6	0.5593 (3)	0.1942 (5)	−0.1028 (6)	0.0284 (12)
C7	0.5306 (4)	0.0926 (6)	−0.1734 (7)	0.0411 (15)
H7	0.5525	0.0287	−0.1176	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0342 (2)	0.0283 (2)	0.0378 (2)	0.000	0.01890 (15)	0.000

Br1	0.0372 (3)	0.0317 (4)	0.0401 (3)	−0.0041 (3)	0.0137 (3)	0.0007 (3)
S1	0.0382 (7)	0.0330 (10)	0.0332 (7)	0.0155 (7)	0.0148 (6)	0.0078 (7)
N1	0.029 (2)	0.021 (3)	0.041 (2)	−0.003 (2)	0.018 (2)	0.000 (2)
N2	0.030 (2)	0.019 (3)	0.031 (2)	0.000 (2)	0.0111 (19)	−0.004 (2)
C1	0.018 (2)	0.035 (4)	0.025 (2)	0.003 (2)	0.007 (2)	0.008 (2)
C2	0.032 (3)	0.063 (6)	0.043 (3)	−0.013 (3)	0.023 (3)	−0.009 (3)
C3	0.050 (4)	0.059 (6)	0.045 (3)	−0.032 (4)	0.022 (3)	−0.004 (4)
C4	0.045 (3)	0.029 (4)	0.054 (4)	−0.012 (3)	0.019 (3)	−0.002 (3)
C5	0.041 (3)	0.028 (4)	0.066 (4)	−0.003 (3)	0.030 (3)	−0.004 (3)
C6	0.028 (3)	0.026 (4)	0.036 (3)	0.008 (2)	0.019 (2)	0.008 (3)
C7	0.066 (4)	0.015 (3)	0.048 (3)	0.005 (3)	0.030 (3)	0.010 (3)

Geometric parameters (Å, º)

Hg1—N1	2.485 (5)	C2—C3	1.350 (12)
Hg1—N1^i	2.485 (5)	C2—H2A	0.9400
Hg1—Br1	2.5056 (6)	C3—C4	1.371 (10)
Hg1—Br1^i	2.5056 (6)	C3—H3	0.9400
S1—C1	1.767 (7)	C4—C5	1.373 (9)
S1—C6	1.773 (5)	C4—H4	0.9400
N1—C5	1.321 (9)	C5—H5	0.9400
N1—C1	1.349 (7)	C6—C7	1.417 (9)
N2—C6	1.299 (8)	C7—C7^{ii}	1.365 (12)
N2—N2^{ii}	1.347 (9)	C7—H7	0.9400
C1—C2	1.394 (9)		
N1—Hg1—N1^i	98.8 (2)	C1—C2—H2A	120.0
N1—Hg1—Br1	108.55 (10)	C2—C3—C4	119.4 (6)
N1^i—Hg1—Br1	96.77 (10)	C2—C3—H3	120.3
N1—Hg1—Br1^i	96.77 (10)	C4—C3—H3	120.3
N1^i—Hg1—Br1^i	108.55 (10)	C3—C4—C5	117.8 (7)
Br1—Hg1—Br1^i	140.84 (4)	C3—C4—H4	121.1
C1—S1—C6	99.7 (3)	C5—C4—H4	121.1
C5—N1—C1	117.4 (5)	N1—C5—C4	124.4 (6)
C5—N1—Hg1	126.8 (4)	N1—C5—H5	117.8
C1—N1—Hg1	115.6 (4)	C4—C5—H5	117.8
C6—N2—N2^{ii}	119.5 (4)	N2—C6—C7	124.2 (5)
N1—C1—C2	120.9 (6)	N2—C6—S1	119.1 (5)
N1—C1—S1	117.0 (4)	C7—C6—S1	116.7 (5)
C2—C1—S1	122.0 (5)	C7^{ii}—C7—C6	116.4 (3)
C3—C2—C1	120.0 (6)	C7^{ii}—C7—H7	121.8
C3—C2—H2A	120.0	C6—C7—H7	121.8
N1^i—Hg1—N1—C5	11.6 (4)	S1—C1—C2—C3	177.5 (5)
Br1—Hg1—N1—C5	111.9 (5)	C1—C2—C3—C4	1.5 (10)
Br1^i—Hg1—N1—C5	−98.4 (5)	C2—C3—C4—C5	1.3 (10)
N1^i—Hg1—N1—C1	−172.8 (4)	C1—N1—C5—C4	3.8 (9)
Br1—Hg1—N1—C1	−72.5 (3)	Hg1—N1—C5—C4	179.3 (5)

Br1^i—Hg1—N1—C1	77.2 (3)	C3—C4—C5—N1	−4.1 (10)
C5—N1—C1—C2	−0.7 (8)	N2^{ii}—N2—C6—C7	−0.2 (9)
Hg1—N1—C1—C2	−176.7 (4)	N2^{ii}—N2—C6—S1	−178.8 (5)
C5—N1—C1—S1	180.0 (4)	C1—S1—C6—N2	1.6 (4)
Hg1—N1—C1—S1	3.9 (5)	C1—S1—C6—C7	−177.1 (4)
C6—S1—C1—N1	96.6 (4)	N2—C6—C7—C7^{ii}	0.6 (10)
C6—S1—C1—C2	−82.8 (5)	S1—C6—C7—C7^{ii}	179.2 (6)
N1—C1—C2—C3	−1.9 (9)		

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