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Dibromidobis(pyrazine-2-carboxylic acid-κN^4)mercury(II) dihydrate

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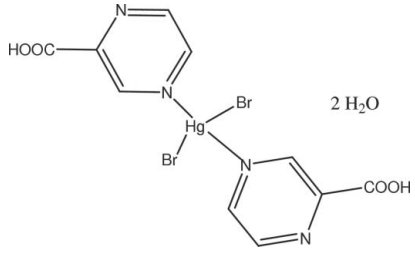
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.011 Å; R factor = 0.070; wR factor = 0.149; data-to-parameter ratio = 13.2.

The asymmetric unit of the title compound, $[HgBr_2(C_5H_4N_2O_2)_2]\cdot 2H_2O$, contains one half-molecule and one water molecule. The Hg^{II} ion, lying on a twofold rotation axis, is four-coordinated by two N atoms of pyrazine-2-carboxylic acid ligands and two bromide ions, forming a highly distorted tetrahedral geometry. In the crystal structure, intermolecular O—H···O and O—H···N hydrogen bonds link the molecules.

Related literature

For general background, see: O'Conner *et al.* (1982); Zhang (2005); Zou *et al.* (1999). For a related structure, see: Wang *et al.*(2007). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$[HgBr_2(C_5H_4N_2O_2)_2]\cdot 2H_2O$
M_r = 644.63
Monoclinic, $C2/c$
a = 13.895 (1) Å
b = 5.7176 (2) Å
c = 21.8753 (7) Å
β = 102.544 (2)°
V = 1696.42 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 13.82 mm^{-1}
T = 294 (2) K
0.4 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.048, T_{max} = 0.063
2775 measured reflections
1480 independent reflections
1287 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
3 standard reflections
every 200 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.150
S = 1.12
1480 reflections
112 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 2.85 e Å^{-3}
$\Delta\rho_{min}$ = −3.62 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1—Br1	2.4234 (15)	Hg1—N1	2.528 (13)
Br1—Hg1—Br1^{i}	153.72 (12)	Br1^{i}—Hg1—N1	101.2 (3)
Br1—Hg1—N1	97.8 (3)	N1—Hg1—N1^{i}	86.9 (6)

Symmetry code: (i) $-x+2, y, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O3^{ii}	0.82	1.75	2.56 (2)	166
O3—H3A···O1^{iii}	0.84 (2)	2.28 (3)	2.89 (2)	130 (2)
O3—H3B···N2	0.84 (2)	2.09 (3)	2.93 (2)	177 (3)

Symmetry codes: (ii) $-x+2, -y, -z+1$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2365).

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S1. Comment

Functional materials built up by organic ligands and metal ions, especially transition metals, have potential applications in optics, electronics, magnetics, biology, catalyst and medicine (Zhang, 2005; O′Conner *et al.*, 1982). Pyrazine-2,3-dicarboxylic acid, having six possible coordination sites, is a good ligand with versatile coordination types, which is widely used in the self-assembled polymeric coordination synthesis (Zou *et al.*, 1999; Wang *et al.*, 2007). The title compound, (I), was obtained unintentionally as the product of a hydrothermal synthesis of pyrazine-2,3-dicarboxylic acid and mercury(II) bromide. Under high temperature as 413 K and mercury(II) ion catalyst, pyrazine-2,3-dicarboxylic acid is likely to decarboxylate as 2-pyrazine carboxylic acid. We report herein the crystal structure of (I), a complex containing the ligand of 2-pyrazine carboxylic acid.

The asymmetric unit of (I), (Fig. 1), contains one half-molecule and one water molecule, in which the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The Hg^{II} ion lying on a twofold rotation axis, is four -coordinated (Table 1) by two N atoms of pyrazine carboxylic acid ligands and two bromide atoms. The two pyrazine rings are oriented at a dihedral angle of 78.4 (9)°.

The Hg—N [2.528 (13) Å] bond is slightly longer, while Hg—Br [2.4234 (15) Å] bond is slightly shorter than the corresponding values [2.270 (5) Å and 2.5269 (7) Å, respectively] in [Hg(bib)Br_2]0.5THF (where bib is 1-bromo-3,5 -bis(imidazol-1-ylmethyl)benzene) (Wang *et al.*, 2007).

In the crystal structure, intermolecular O—H···O and O—H···N hydrogen bonds (Table 2, Fig. 2) link the molecules, in which they seem to be effective in the stabilization of the structure.

S2. Experimental

For the preparation of the title compound, mercury(II) bromide (360 mg, 1 mmol) and 2,3-pyrazine dicarboxylic acid (168 mg, 1 mmol) were dissolved in a mixed solvent of ethanol (5 ml) and acetonitrile (5 ml). Then the mixture was added into a Teflon-lined stainless steel autoclave at 413 K for 2 d. The green crystals were obtained after cooling to room temperature and was filtrated. Elemental analysis calcd: C 19.58%, H 4.40%, N 45.60%; Found: C 19.51%, H 4.35%, N 45.53%.

S3. Refinement

H atoms (for H_2O) were located in a difference map and refined [O—H = 0.84 (2) and 0.84 (2) Å, U_{iso}(H) = 1.5U_{eq}(O)]. The remaining H atoms were positioned geometrically, with O—H = 0.82 Å (for OH) and C—H = 0.93 Å, for aromatic H atoms and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,*O*), where x = 1.2 for aromatic H and x = 1.5 for OH H atoms.

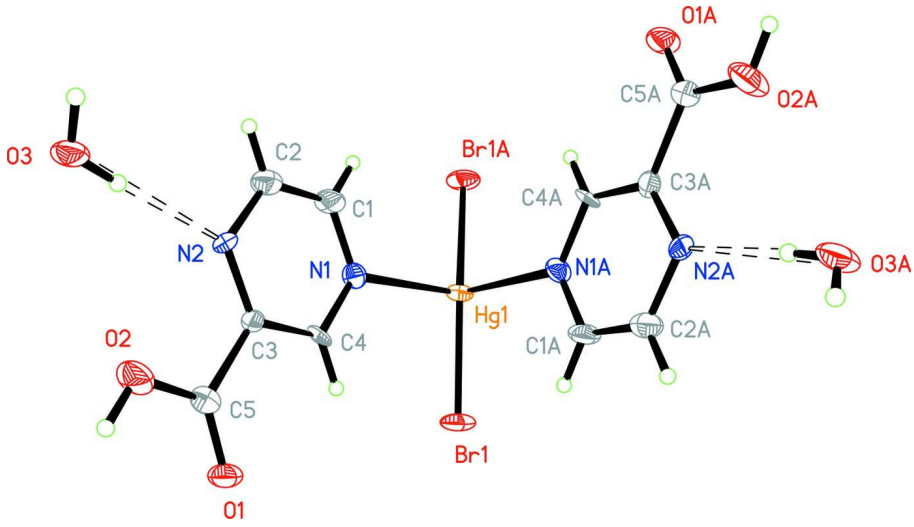

Figure 1

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level [symmetry code A: 2 - *x*, *y*, 3/2 - *z*]. Hydrogen bonds are shown as dashed lines.

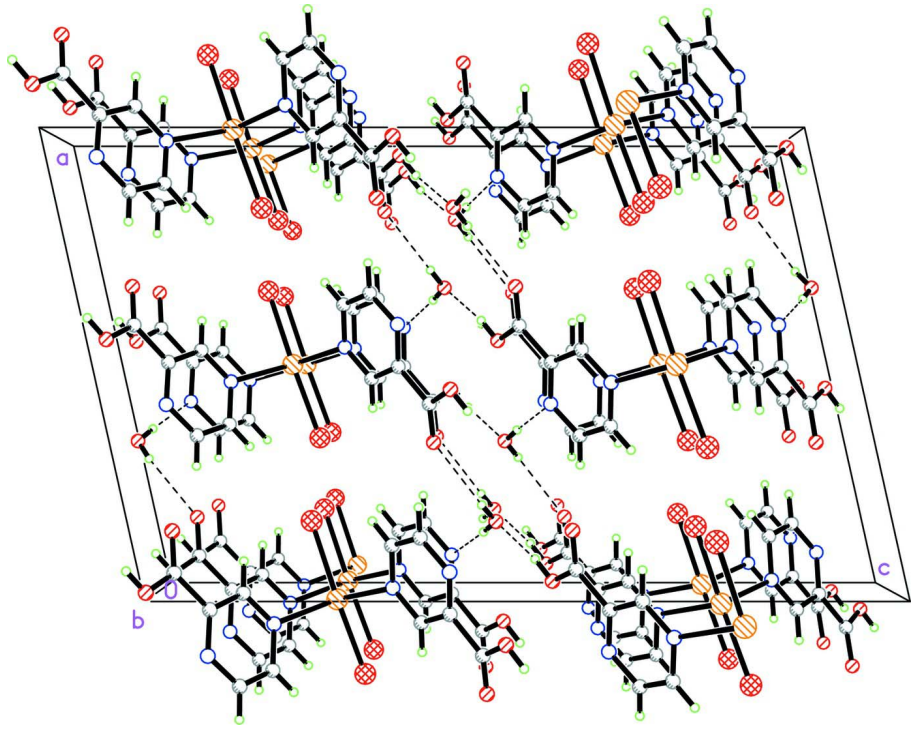

Figure 2

A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

Dibromidobis(pyrazine-2-carboxylic acid-κN^4)mercury(II) dihydrate

Crystal data

$[HgBr_2(C_5H_4N_2O_2)_2]\cdot 2H_2O$
$M_r = 644.63$

Monoclinic, *C*2/*c*
Hall symbol: -C 2yc

a = 13.895 (1) Å
b = 5.7176 (2) Å
c = 21.8753 (7) Å
β = 102.544 (2)°
V = 1696.42 (15) Å^3
Z = 4
F(000) = 1192
D_x = 2.524 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–13°
μ = 13.82 mm^{-1}
T = 294 K
Block, green
0.4 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.048, T_{max} = 0.063
2775 measured reflections

1480 independent reflections
1287 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 25.1°, θ_{min} = 1.9°
h = −16→8
k = −6→5
l = −20→26
3 standard reflections every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.150
S = 1.12
1480 reflections
112 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1015P)^2 + 4.7441P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.85 e Å^{-3}
$\Delta\rho_{min}$ = −3.62 e Å^{-3}
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0045 (4)

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	1.0000	1.10939 (9)	0.7500	0.0355 (4)
Br1	1.16422 (12)	1.2057 (6)	0.73701 (9)	0.0525 (6)
C1	0.8717 (5)	0.6941 (4)	0.6566 (4)	0.039 (4)
H1	0.8234	0.7561	0.6754	0.047*
C2	0.8499 (5)	0.5080 (4)	0.6166 (4)	0.041 (4)
H2	0.7871	0.4427	0.6093	0.050*

C3	1.0047 (6)	0.5069 (4)	0.6006 (6)	0.030 (3)
C4	1.0302 (6)	0.6941 (6)	0.6411 (6)	0.043 (5)
H4	1.0940	0.7538	0.6490	0.051*
C5	1.0825 (6)	0.4040 (4)	0.5701 (5)	0.029 (3)
N1	0.9628 (7)	0.7881 (7)	0.6688 (6)	0.033 (3)
N2	0.9161 (7)	0.4188 (7)	0.5885 (5)	0.034 (3)
O1	1.1642 (8)	0.4862 (6)	0.5761 (6)	0.046 (3)
O2	1.0514 (10)	0.2121 (5)	0.5379 (6)	0.060 (4)
H2A	1.0954	0.1606	0.5221	0.090*
O3	0.8315 (9)	0.0042 (3)	0.5179 (6)	0.051 (3)
H3A	0.794 (2)	−0.090 (3)	0.531 (2)	0.077*
H3B	0.857 (2)	0.123 (2)	0.537 (2)	0.077*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0234 (5)	0.0443 (7)	0.0442 (6)	0.000	0.0149 (3)	0.000
Br1	0.0263 (10)	0.0587 (14)	0.0617 (13)	−0.0056 (8)	0.0225 (9)	0.0088 (10)
C1	0.029 (9)	0.045 (10)	0.047 (10)	0.007 (8)	0.017 (7)	−0.011 (8)
C2	0.031 (8)	0.050 (11)	0.045 (10)	0.000 (9)	0.014 (7)	−0.004 (9)
C3	0.027 (7)	0.044 (10)	0.021 (7)	−0.011 (7)	0.005 (6)	0.003 (7)
C4	0.029 (8)	0.051 (13)	0.027 (8)	0.004 (9)	0.020 (7)	−0.009 (8)
C5	0.035 (9)	0.032 (8)	0.033 (7)	0.001 (7)	0.012 (6)	0.006 (7)
N1	0.037 (7)	0.034 (8)	0.032 (7)	0.000 (6)	0.012 (6)	−0.012 (6)
N2	0.033 (6)	0.053 (9)	0.028 (6)	−0.012 (6)	0.002 (5)	−0.008 (6)
O1	0.030 (6)	0.054 (8)	0.051 (7)	−0.011 (6)	0.016 (5)	−0.020 (6)
O2	0.050 (8)	0.061 (9)	0.057 (9)	−0.010 (7)	0.033 (7)	−0.039 (8)
O3	0.039 (7)	0.052 (9)	0.052 (9)	−0.014 (7)	0.033 (6)	−0.030 (7)

Geometric parameters (Å, º)

Hg1—Br1	2.4234 (15)	C3—C4	1.381 (6)
Hg1—Br1^{i}	2.4234 (15)	C3—C5	1.510 (7)
Hg1—N1	2.528 (13)	C4—N1	1.334 (10)
Hg1—N1^{i}	2.528 (13)	C4—H4	0.9300
C1—N1	1.351 (7)	C5—O1	1.209 (18)
C1—C2	1.369 (8)	C5—O2	1.327 (19)
C1—H1	0.9300	O2—H2A	0.8200
C2—N2	1.310 (6)	O3—H3A	0.84 (2)
C2—H2	0.9300	O3—H3B	0.84 (2)
C3—N2	1.303 (8)		
Br1—Hg1—Br1^{i}	153.72 (12)	C4—C3—C5	118.4 (6)
Br1—Hg1—N1	97.8 (3)	N1—C4—C3	119.6 (7)
Br1^{i}—Hg1—N1	101.2 (3)	N1—C4—H4	120.2
Br1—Hg1—N1^{i}	101.2 (3)	C3—C4—H4	120.2
Br1^{i}—Hg1—N1^{i}	97.8 (3)	O1—C5—O2	124.8 (7)
N1—Hg1—N1^{i}	86.9 (6)	O1—C5—C3	123.1 (8)

N1—C1—C2	120.3 (8)	O2—C5—C3	112.1 (6)
N1—C1—H1	119.8	C1—N1—C4	118.1 (7)
C2—C1—H1	119.8	C1—N1—Hg1	118.0 (10)
N2—C2—C1	121.3 (8)	C4—N1—Hg1	123.7 (11)
N2—C2—H2	119.4	C2—N2—C3	118.7 (8)
C1—C2—H2	119.4	C5—O2—H2A	109.5
N2—C3—C4	122.0 (7)	H3A—O3—H3B	125 (4)
N2—C3—C5	119.6 (8)		

N1—C1—C2—N2	−1.0 (12)	C3—C4—N1—Hg1	175.2 (12)
N2—C3—C4—N1	−0.3 (13)	Br1—Hg1—N1—C1	−174.8 (12)
C5—C3—C4—N1	−179.9 (15)	Br1^{i}—Hg1—N1—C1	−13.0 (13)
N2—C3—C5—O1	175.2 (15)	N1^{i}—Hg1—N1—C1	84.4 (13)
C4—C3—C5—O1	−4.8 (12)	Br1—Hg1—N1—C4	10.9 (13)
N2—C3—C5—O2	−7.1 (11)	Br1^{i}—Hg1—N1—C4	172.7 (13)
C4—C3—C5—O2	173.3 (15)	N1^{i}—Hg1—N1—C4	−89.9 (14)
C2—C1—N1—C4	0.3 (9)	C1—C2—N2—C3	1.8 (12)
C2—C1—N1—Hg1	−175.1 (5)	C4—C3—N2—C2	−1.1 (11)
C3—C4—N1—C1	1.2 (9)	C5—C3—N2—C2	178.5 (14)

Symmetry code: (i) −*x*+2, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O3^{ii}	0.82	1.75	2.56 (2)	166
O3—H3*A*···O1^{iii}	0.84 (2)	2.28 (3)	2.89 (2)	130 (2)
O3—H3*B*···N2	0.84 (2)	2.09 (3)	2.93 (2)	177 (3)

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