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1,1′-(Butane-1,4-diyl)bis(1H-benzimidazol-3-ium) diiodo(pyridine-2,6-dicarboxylato-κ^3O,N,O')-mercurate(II)

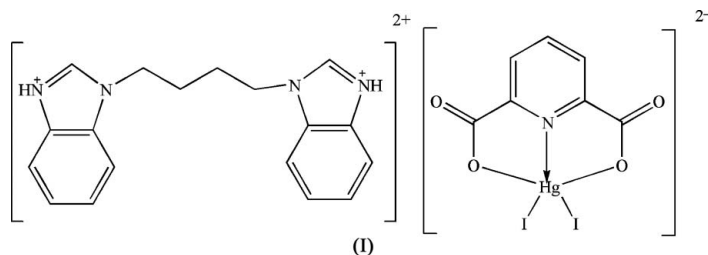In the title complex, $(C_{18}H_{20}N_4)[HgI_2(C_7H_3NO_4)]$, the Hg atom exists in a distorted trigonal–bipyramidal geometry formed by two I atoms, one pyridine N and two carboxylate O atoms from a chelating 2,6-pyridinedicarboxylate ligand. Extensive hydrogen bonding between the carboxylate groups and the 1,1′-(butane-1,4-diyl)bis(1H-benzimidazol-3-ium) ion is present in the structure, as well as π–π stacking interactions. The cation has a crystallographic centre of symmetry. In the anion, a crystallographic twofold rotation axis coincides with the Hg–N bond.

Comment

Interesting structures and properties have been reported for a number of proton-transfer metal complexes of pyridine-2,6-dicarboxylic acid (H_2pdc), which were isolated from the reaction of the reagent with lanthanides and transition metals in the presence of Lewis bases such as pyridine-2,6-diamine, 1,10-phenanthroline, creatinine and imidazole (Fu *et al.*, 2004; MacDonald *et al.*, 2000; Moghimi *et al.*, 2002; Moghimi, Sharif *et al.*, 2005; Moghimi, Sheshmani *et al.*, 2005). In these structures, H_2pdc acts as an *N*– and *O*-donor ligand to the metal ions, forming stable chelates. Previously, we have reported a novel proton-transfer iron(III) complex incorporating pyridine-2,6-dicarboxylate ligands and the flexible *N*-heterocycle 1,1′-(butane-1,4-diyl)bis(1H-benzimidazol-3-ium) ion [$(H_2$bbbm$)^{2+}$; Hou *et al.*, 2006]. As an extension of our work on this series of complexes, we report here the crystal structure of the title mercury(II) complex, (I).

(I)

Complex (I) consists of discrete mononuclear $[HgI_2(pdc)]^{2-}$ anions and $[H_2$bbbm$]^{2+}$ cations (Fig. 1). The central Hg atom is five-coordinated by two I atoms, one pyridine N and two carboxylate O atoms from the deprotonated pdc^{2-} ligand, completing a distorted trigonal–bipyramidal geometry. The Hg^{II} atom lies in the plane of the pdc ligand, with the two I atoms lying above and below the plane. In the anion, a crystallographic twofold rotation axis coincides with the Hg–N bond.
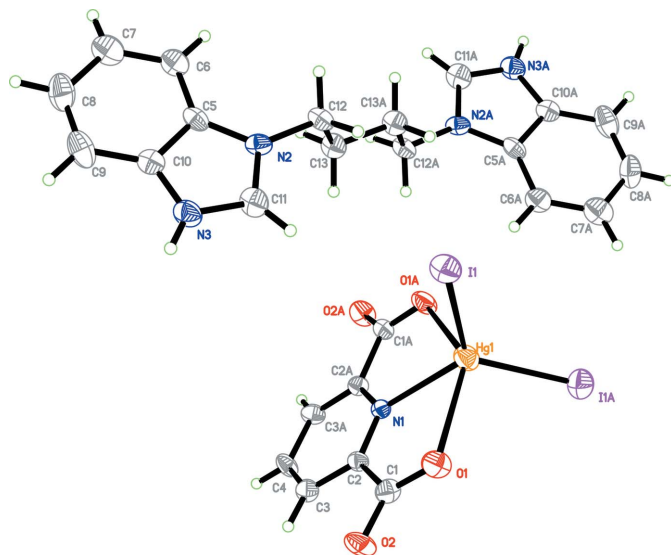
Figure 1
A view of (I), showing the numbering scheme employed. Displacement ellipsoids are drawn at the 30% probability level. H atoms are drawn with arbitrarily small radii. Atoms with the suffix A are related by the symmetry code ($1 - x, y, \frac{3}{2} - z$) in the [HgI₂(pdc)]²⁻ anion and by ($\frac{1}{2} - x, -y - \frac{1}{2}, 1 - z$) in the [H₂bbbm]²⁺ cation.

Anions interact with the [H₂bbbm]²⁺ cations to produce a hydrogen-bonded sheet structure by N—H···O hydrogen bonds (Table 2 and Fig. 2). A face-to-face separation of 3.552 (5) Å between the N2-containing imidazolium rings from two neighbouring [H₂bbbm]²⁺ dications suggests the existence of π–π stacking interactions.

Experimental

1,1′-(Butane-1,4-diyl)bis(1*H*-benzimidazole) (bbbm) was prepared according to a literature method (Xie *et al.*, 2000). A methanol solution (5 ml) of H₂pdc (16.7 mg, 0.1 mmol) was added dropwise to a methanol solution (5 ml) of HgI₂ (22.7 mg, 0.05 mmol) and bbbm (29.0 mg, 0.1 mmol) to give a clear solution. Pink block-like crystals (52% yield) suitable for X-ray diffraction were obtained after one week. Analysis calculated for C₂₅H₂₃HgI₂N₅O₄: C 32.93, H 2.54, N 7.68%; found: C 32.74, H 2.65, N 7.55%.

Crystal data

(C₁₈H₂₀N₄)[HgI₂(C₇H₃NO₄)]
$M_r = 911.87$
Monoclinic, $C2/c$
$a = 21.696 (4)$ Å
$b = 15.158 (3)$ Å
$c = 8.9959 (18)$ Å
$\beta = 107.16 (3)°$
$V = 2826.8 (11)$ Å³
$Z = 4$

$D_x = 2.143$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1415 reflections
$\theta = 2.1–25.7°$
$\mu = 7.67$ mm⁻¹
$T = 291 (2)$ K
Block, pink
$0.20 \times 0.17 \times 0.17$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.24$, $T_{max} = 0.27$
7241 measured reflections

2786 independent reflections
2157 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 26.0°$
$h = -26 \rightarrow 26$
$k = -18 \rightarrow 18$
$l = -11 \rightarrow 11$
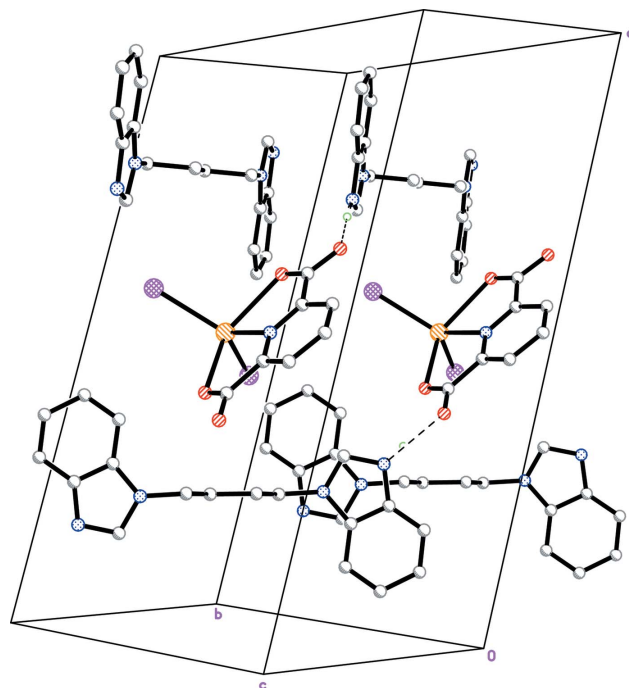
Figure 2
A view of the packing of (I). Thin dashed lines indicate the hydrogen-bonding interactions. H atoms have been omitted.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.129$
$S = 1.03$
2786 reflections
170 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 1.94P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.66$ e Å⁻³
$\Delta\rho_{min} = -1.56$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Hg1—N1	2.364 (8)	N2—C12	1.466 (10)
Hg1—I1	2.6755 (11)	N3—C11	1.341 (12)
N1—C2	1.318 (8)	N3—C10	1.373 (11)
N2—C11	1.341 (11)	O1—C1	1.239 (10)
N2—C5	1.379 (11)	O2—C1	1.291 (10)
N1—Hg1—O1	67.39 (13)	C5—N2—C12	127.5 (6)
O1—Hg1—O1ⁱ	134.8 (3)	C11—N3—C10	108.4 (7)
N1—Hg1—I1	118.95 (2)	C1—O1—Hg1	114.4 (5)
O1—Hg1—I1	99.28 (16)	O1—C1—O2	124.3 (7)
O1ⁱ—Hg1—I1	102.18 (16)	O1—C1—C2	119.5 (7)
I1—Hg1—I1ⁱ	122.10 (4)	O2—C1—C2	116.2 (7)
C2—N1—C2ⁱ	120.8 (9)	N1—C2—C3	121.8 (7)
C2—N1—Hg1	119.6 (4)	N1—C2—C1	118.9 (7)
C11—N2—C5	109.2 (7)	N3—C11—N2	108.4 (9)
C11—N2—C12	123.1 (7)		

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···O2ⁱⁱ	0.86	1.71	2.568 (9)	174

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

All H atoms were placed in calculated positions and were refined isotropically, with $U_{iso}(H)$ values constrained to $1.2U_{eq}(C,N)$ or $1.5U_{eq}(C)$, using a riding model with C—H = 0.93–0.97 Å and N—H = 0.86 Å. The maximum electron-density peak in the final difference map lies 1.78 Å from atom C7.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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