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Iodo(picolinato-κ^2N,O)(picolinic acid-κ^2N,O)mercury(II)

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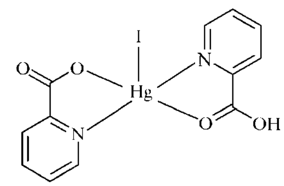
The title compound, $[Hg(C_6H_4NO_2)I(C_6H_5NO_2)]$, has twofold symmetry along the Hg—I bond. The Hg^{II} ion coordinates one I atom [at 2.6045 (4) Å], two N and two O atoms [at 2.298 (3) and 2.481 (2) Å] from one picolinate ion, and one picolinic acid molecule in a very irregular trigonal–bipyramidal coordination. The single hydroxy H atom required for chemical neutrality is both statistically (by crystal symmetry) and structurally disordered, and is involved in an intermolecular O—H···O hydrogen bond [O···O = 2.455 (4) Å], connecting the molecules into one-dimensional infinite chains along the [101] direction.

Comment

We started recently to investigate mercury(II) coordination chemistry with ligands containing N- and O-atom donors, such as monopyridine carboxylic acids acting as *N*,*O*- or *O*,*O*-chelating ligands (Popović *et al.*, 1999; Matković-Čalogović *et al.*, 2001, 2002). The focus of our research is the competition between halide ions and ligands containing N,O-atom donors for the coordination sites of the mercury(II) ion. Interestingly, we have found that the replacement of only one halide atom occurs with the above ligands when the complexes are derived from $HgCl_2$ or $HgBr_2$. The tendency of mercury to achieve effective coordination (Grdenić, 1965, 1981) including both covalent bonds and van der Waals interactions, along with the spatial arrangement of donor atoms (such as that provided by pyridinecarboxylic acids), leads to various, mostly irregular, coordination polyhedra of mercury. We distinguish between covalent bonds and van der Waals interactions in mercury(II) compounds by geometrical criteria using published covalent and van der Waals radii of mercury and corresponding atoms (Pauling, 1960; Bondi, 1964; Nyburg & Faerman, 1985; Matković-Čalogović, 1994).

In a survey of the Cambridge Structural Database (CSD; Version 5.26 of August 2005; Allen, 2002), 34 structural fragments are found containing only one Hg—I covalent bond. There are five structures containing, in addition to one or more Hg—I covalent bonds, Hg—O and Hg—N contacts [CSD refcodes NEJXEF and NEJXIJ (Pickardt & Wiese, 1997), HGTXZO (Malmsten, 1979), VAQHOK (González-Duarte *et al.*, 1998) and XANBIX (Pickardt & Wiese, 2000)]. These latter compounds contain different coordination environments of mercury and have 'bond' distance ranges Hg—I = 2.601–2.758 Å, Hg—N = 2.21–2.72 Å and Hg—O = 2.62–2.91 Å.



(I)

By contrast, there are only three structures of mercury complexes with picolinic acid or its derivatives but none similar to the title complex. In the structure of mercury(II) picolinate (Álvarez-Larena *et al.*, 1994), with the characteristic bridging coordination mode for carboxylates, a linear polymer is formed, and the mercury achieves (2+4) octahedral coordination with shorter Hg—N [2.125 (2) Å] and longer Hg—O distances [2.470 (2) and 2.756 (2) Å]. González-Duarte *et al.* (1998) reported the complexes with the isopropyl ester of picolinic acid and $HgBr_2$ and HgI_2 (VAQHOK). These complexes are centrosymmetric dimers with irregular square–pyramidal mercury coordination (4+1 effective coordination) formed by one Hg—N [2.455 (6) Å], one Hg—O [2.658 (6) Å] and three Hg—I [2.601 (6), 2.638 (2) and 3.411 (2) Å] (or Hg—Br) bonds.

In the title compound, (I) (Fig. 1), the Hg and I atoms are situated on a crystallographic twofold axis. The Hg^{II} atom is coordinated *via* one I atom, two N atoms and two O atoms (the *N*,*O*-chelate bidentate mode of the ligand) in the form of a very irregular trigonal–bypiramidal (3+2)-coordination (Table 1), rather than the (4+1)-coordination mode. The Hg—I distance is at the shorter end of the range noted above (2.601–2.758 Å) and smaller than that predicted for covalent Hg—I distances in mercury(II) compounds with diagonal

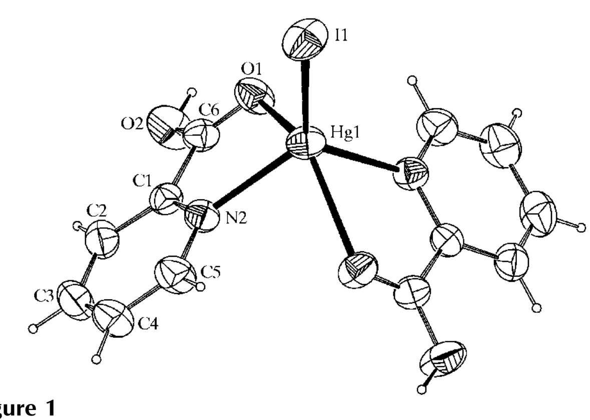


Figure 1
The structure of HgI(pic)(picH), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydroxy H atom is disordered.

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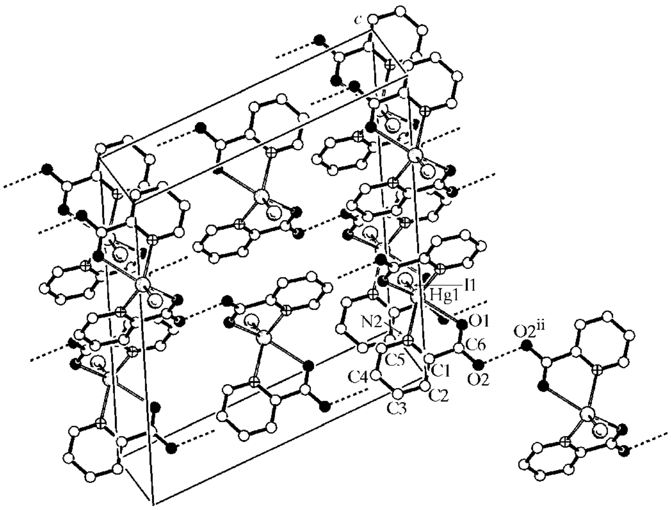

Figure 2
A *PLATON98* (Spek, 1998) view of the crystal structure of (I), with H atoms omitted for clarity. The disordered H2 atom is not shown, but the hydrogen bonds (Table 2) linking molecules along the [101] direction are shown as dashed lines.

coordination (2.66 Å; Pauling, 1960; Bondi, 1964; Nyburg & Faerman, 1985; Matković-Čalogović, 1994). It is also comparable to the Hg—I bond in the yellow form of mercury(II) iodide (Jeffrey & Vlasse, 1967), where mercury is diagonally coordinated [2.615 (6) and 2.620 (6) Å]. The shortest Hg—I covalent bond in mercury(II) complexes with one Hg—I bond is found in bis(ethylenediamine)triiododimercury(II) triiodomercurate(II) (Grdenić *et al.*, 1977), which contains a trigonal–bipyramidal cation and a Hg—I bond distance of 2.571 (3) Å.

The Hg—N distances are within the range noted above and should be considered stronger than van der Waals contacts but longer than a normal covalent bond. An example of the latter is the Hg—N bond in mercury(II) picolinate of 2.125 (2) Å. A similar scenario exists for the Hg—O distances; the value here is shorter than the range noted above but also longer than that in the structure of mercury(II) picolinate [Hg—O = 2.470 (2) Å].

The chelate ring defined by atoms Hg1, O1, C6, C1 and N2 is approximately planar, with a maximum deviation out of the plane of 0.039 (3) Å for atom C6. This plane makes a small angle of 1.7 (2)° with the planar pyridine ring (atoms C1–C5 and N2). The carboxylate plane (atoms C1, C6 and O2) is not coplanar with the chelate ring mean plane, the interplanar angle being 6.0 (4)°.

The molecules are connected into one-dimensional infinite chains along the [101] direction *via* an O—H···O intermolecular hydrogen bond (Fig. 2 and Table 2). The H atom involved (H2) is structurally disordered.

Experimental

A solution of picolinic acid (0.084 g, 0.682 mmol) in ethanol (10 ml) was added dropwise to a solution of HgI_2 (0.30 g, 0.660 mmol) in tetrahydrofuran (THF, 10 ml). After two weeks, pale-yellow crystals were filtered off, washed with THF and dried in air (yield 0.14 g, 70%). Analysis calculated for $C_{12}H_9HgIN_2O_4$: C 25.17, H 1.58, N 4.89%; found: C 25.19, H 1.73, N 4.81%.

Crystal data

$[Hg(C_6H_4NO_2)I(C_6H_5NO_2)]$
M_r = 572.70
Monoclinic, $C2/c$
a = 14.2329 (8) Å
b = 7.3321 (4) Å
c = 14.9255 (10) Å
β = 109.030 (6)°
V = 1472.46 (15) Å^3
Z = 4
D_x = 2.579 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 12.56 mm^{-1}
T = 296 (2) K
Prism, pale yellow
0.27 × 0.26 × 0.13 mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer with Sapphire-3 CCD detector
ω scans
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2004)
T_{min} = 0.096, T_{max} = 0.201
18474 measured reflections
2149 independent reflections
2117 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 30.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.047
S = 1.11
2149 reflections
94 parameters
All H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 3.3936P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.70 e Å^{-3}
$\Delta\rho_{min}$ = −1.36 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00199 (9)

Table 1
Selected geometric parameters (Å, °).

Hg1—N2	2.298 (3)	O1—C6	1.233 (4)
Hg1—O1	2.481 (2)	O2—C6	1.271 (4)
Hg1—I1	2.6045 (4)		
N2^i—Hg1—N2	109.78 (13)	O1^i—Hg1—O1	131.23 (12)
N2^i—Hg1—O1^i	69.91 (8)	N2^i—Hg1—I1	125.11 (6)
N2—Hg1—O1^i	82.45 (9)	O1^i—Hg1—I1	114.38 (6)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O2^{ii}	0.869 (3)	1.591 (3)	2.455 (4)	172 (1)

Symmetry code: (ii) $-x - \frac{1}{2}, -y + \frac{5}{2}, -z$.

H atoms bonded to C atoms were introduced at calculated positions and refined by applying a riding model [$U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.93 Å]. To maintain complex neutrality, the H2 atom (on O2) is statistically disordered (by crystal symmetry) between the two ligands in each complex. The refinement models that were tried are noted in the CIF. The maximum and minimum electron densities in the final difference Fourier map are located 1.97 and 0.71 Å, respectively, from the I1 and Hg1 atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON98* (Spek, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3005). Services for accessing these data are described at the back of the journal.

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