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Aquabromo(6-carboxypyridine-2-carboxylato-*O*,*N*,*O*′)mercury(II)

Dubravka Matković-Čalogović,* Jasminka Popović, Zora Popović, Igor Picek and Željka Soldin

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, HR-10000 Zagreb, Croatia
Correspondence e-mail: dubravka@chem.pmf.hr

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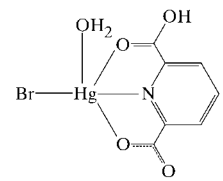
The title compound, [HgBr($C_7H_4NO_4$)(H_2O)], was obtained by the reaction of an aqueous solution of mercury(II) bromide and pyridine-2,6-dicarboxylic acid (picolinic acid, dipicH_2). The shortest bond distances to Hg are Hg—Br 2.412 (1) Å and Hg—N 2.208 (5) Å; the corresponding N—Hg—Br angle of 169.6 (1)° corresponds to a slightly distorted linear coordination. There are also four longer Hg—O interactions, three from dipicH^- [2.425 (4) and 2.599 (4) Å within the asymmetric unit, and 2.837 (4) Å from a symmetry-related molecule] and one from the bonded water molecule [2.634 (4) Å]. The effective coordination of Hg can thus be described as 2+4. The molecules are connected to form double-layer chains parallel to the *y* axis by strong O—H···O hydrogen bonds between carboxylic acid groups of neighbouring molecules, and by weaker hydrogen bonds involving both H atoms of the water molecule and the O atoms of the carboxylic acid groups.

Comment

The first report of dipicolinic acid in a biological system was by Udo (1936), who found dipicH_2 in the viscous matter of natto, a Japanese food made of steamed soybeans fermented with *Bacillus natto*. DipicH_2 is present in large amounts in bacterial spores of the *Bacillus* group (Powell & Strange, 1953). The crystal structure of dipicH_2, as the monohydrate, has been known for many years (Takusagawa *et al.*, 1973). DipicH_2 exhibits biological activity, such as inhibition of the zinc enzyme bovine carbonic anhydrase (Pocker & Fong, 1980) or of *E. coli* dihydropicolinate reductase (Scapin *et al.*, 1997). To date, no crystal structures of Hg complexes with dipicH_2 have been published. There are two structures of Zn complexes known, one with two deprotonated dipic^{2-} ligands (Hakansson *et al.*, 1993), and the other with two mono-deprotonated dipicH^- ligands bonded to the Zn atom (Hakansson *et al.*, 1993; Okabe & Oya, 2000). In an Fe^{III} complex with dipic^{2-}, one Cl ligand and two water molecules are also within the coordination sphere and form an octahedral complex (Lainé *et al.*, 1995). The ligand is tridentately bound in all of these structures and forms typical chelating complexes, with *M*—O and *M*—N bonds of similar length.

The Hg^{II} ion, as a soft Lewis acid, forms covalent complexes with various soft Lewis bases, mostly by binding to *S*-donor groups, or, if these are not available, to *N*- or *O*-donor groups. As part of a wider research programme, we are interested in the competition of halide or pseudo-halide ligands with *N*- and *O*-ligands towards Hg, and the structural characterization of Hg^{II} complexes with such ligands (Popović *et al.*, 1999; Matković-Čalogović, Picek *et al.*, 2001; Matković-Čalogović, Pavlovic *et al.*, 2001). We present here the crystal structure of the first complex of Hg with dipicH_2, the title compound, (I).



(I)

In (I), Hg is coordinated by a tridentate monodeprotonated dipicH^- ligand, a Br atom and a weakly bonded water molecule. Hg has a strong tendency to preserve linear coordination, as can be seen from the two shortest bonds, Hg—N 2.208 (5) Å and Hg—Br1 2.412 (1) Å, and from the N—Hg—Br1 angle of 169.6 (1)°. The Hg—Br distance is close to the sum of the covalent radii of Hg(linear) (Grdenić, 1965, 1981) and Br, while that of Hg—N is longer than the corresponding sum. This elongation, together with the deviation from linearity, may be attributed to additional contacts with the O atoms, two from the monoanion [Hg—O1 2.425 (4) Å and Hg—O4 2.599 (4) Å], the third from the water molecule [Hg—

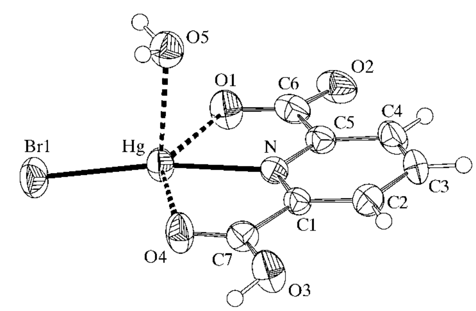


Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

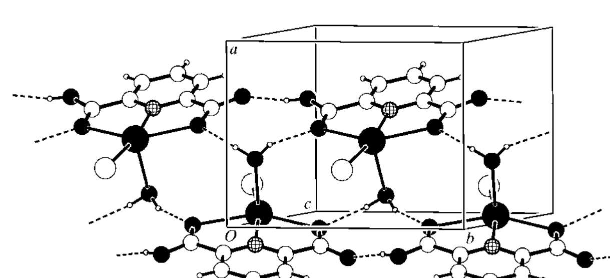


Figure 2
One double-layer chain formed by hydrogen bonding within the unit cell of (I). The hydrogen bonds are indicated by dashed lines.

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O5 2.635 (4) Å] and the fourth, the weakest, from the monoanion of a neighbouring complex molecule [Hg···O2($-\frac{1}{2}-x$, $y-\frac{1}{2}, \frac{1}{2}-z$) 2.837 (4) Å]. These four O atoms are at distances greater than the sum of the covalent radii but less than the sum of van der Waals radii, so the effective coordination can be described as 2+4. The Hg—N distance is comparable with that in ethylenediaminemercury(II) dibromide, where two Hg—N bonds are 2.19 (2) Å, yet in this structure four Br atoms are weakly bound at distances of 3.012 (2) Å (2+4 coordination; Matković-Čalogović & Sikirica, 1990). The weak bonding of the water molecule to Hg in (I) can be recognized in comparison with the much stronger Hg—OH_2 bond in [Hg(H_2OHg)(NO_3Hg)- CCOO]NO_3, regarded as a monomercurated oxonium ion (Grdenić *et al.*, 1986), where the bond length is 2.17 (3) Å.

The molecules in (I) are interconnected by O—H···O intermolecular hydrogen bonds (Table 2). The shortest is between the protonated and deprotonated carboxylic acid groups and joins the molecules into chains. The two longer hydrogen bonds join H atoms from the water molecule to the carboxylic acid groups of two neighbouring molecules from the parallel chain. In this way, a double-layer chain is formed parallel to the *y* axis (Fig. 2).

Experimental

Crystals of (I) were obtained by slow evaporation from an aqueous solution of a mixture containing pyridine-2,6-dicarboxylic acid (0.14 g, 83.8 mmol, in 10 ml H_2O) and mercury(II) bromide (0.3 g, 83.3 mmol, in 25 ml H_2O) at room temperature.

Crystal data

[HgBr($C_7H_4NO_4$)(H_2O)]	D_x = 3.052 Mg m^{-3}
M_r = 464.63	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 56 reflections
a = 6.967 (3) Å	θ = 10–19°
b = 9.068 (3) Å	μ = 19.17 mm^{-1}
c = 16.007 (5) Å	T = 293 (2) K
β = 91.05 (3)°	Parallelepiped, colourless
V = 1011.1 (6) Å^3	0.28 × 0.28 × 0.22 mm
Z = 4	

Table 1
Selected geometric parameters (Å, °).

Hg—N	2.208 (5)	Hg—O4	2.599 (4)
Hg—Br1	2.4120 (10)	Hg—O5	2.634 (5)
Hg—O1	2.425 (4)		
N—Hg—Br1	169.57 (11)	O1—Hg—O4	141.10 (13)
N—Hg—O1	71.98 (15)	N—Hg—O5	82.31 (16)
Br1—Hg—O1	117.29 (11)	Br1—Hg—O5	101.33 (11)
N—Hg—O4	69.22 (14)	O1—Hg—O5	92.44 (14)
Br1—Hg—O4	101.16 (9)	O4—Hg—O5	85.32 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H31···O2^{i}	0.85 (5)	1.81 (7)	2.591 (6)	153 (9)
O5—H51···O4^{ii}	0.85 (7)	2.14 (7)	2.938 (7)	157 (7)
O5—H52···O1^{iii}	0.86 (7)	1.99 (7)	2.798 (7)	159 (8)

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

Data collection

Philips PW1100 diffractometer updated by Stoe	R_{int} = 0.030
ω scans	θ_{max} = 30°
Absorption correction: by integration (*X-RED*; Stoe & Cie, 1995)	$h = -9 \rightarrow 9$
T_{min} = 0.031, T_{max} = 0.091	$k = -5 \rightarrow 12$
4339 measured reflections	$l = 0 \rightarrow 17$
2658 independent reflections	5 standard reflections frequency: 90 min intensity decay: 2.2%
1907 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.6877P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.028	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.066	$\Delta\rho_{max}$ = 0.98 e Å^{-3}
S = 0.99	$\Delta\rho_{min}$ = −0.97 e Å^{-3}
2658 reflections	Extinction correction: *SHELXL*97
149 parameters	Extinction coefficient: 0.00157 (14)
H atoms: see below	

H atoms of the water molecule and the carboxylic acid group were located in the difference Fourier map and were refined isotropically with restrained bond lengths. Pyridine H atoms were generated geometrically and refined using a riding model.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1482). Services for accessing these data are described at the back of the journal.

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