Polymeric μ-bromo-μ-pyridine-3-carboxylato-$\kappa^3 O,O'$:N-mercury(II)

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The asymmetric unit of the title polymeric complex, [HgBr-$(C_6H_4NO_2)]_n$ or HgBr(nic), contains mercury coordinated via two Br atoms [Hg—Br = 2.6528 (9) and 2.6468 (9) Å], two carboxylate O atoms, which form a characteristic four-membered chelate ring [Hg—O = 2.353 (6) and 2.478 (7) Å], and an N atom [Hg—N = 2.265 (5) Å], in the form of a very irregular (3+2)-coordination polyhedron. The pronounced irregularity of the effective Hg (3+2)-coordination is a result of the rigid stereochemistry of the nicotinate ligand. According to the covalent and van der Waals radii criteria, the strongest bonds are Hg—Br and Hg—N. These covalent interactions form a two-dimensional polymer. The puckered planes are connected by van der Waals interactions, and there are only two intermolecular C—H⋯O hydrogen bonds [3.428 (10) and 3.170 (10) Å].

Comment

Recently, we began an investigatoin of mercury(II) coordination chemistry with ligands containing N- and O-donor atoms, such as mono- and disubstituted pyridinecarboxylic acids, which form polymeric complexes of the Hg$X(L)$ and Hg$X(L)(LH)$ types, where L is deprotonated pyridinecarboxylic acid and LH is neutral pyridinecarboxylic acid (Popović et al., 1999; Matković-Čalogović et al., 2001, 2002).
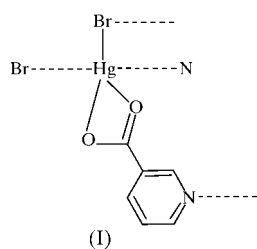

(I)

Interestingly, in all of these complexes, replacement of one halide atom occurred. Moreover, different coordination modes of mercury are observed, i.e. with COOH or COO⁻

Figure 1
The structure of HgBr(nic) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

groups as well as the pyridine N-donor atom. The COOH and COO⁻ groups can act as monodentate, chelating and/or bridging groups, while the pyridine N-donor atom acts in a monodentate manner. The tendency of the Hg atom to achieve effective coordination (Grdenić, 1981), which includes covalent bonds and van der Waals interactions (Pauling, 1960; Bondi, 1964; Grdenić, 1965; Nyburg & Faerman, 1985; Matković-Čalogović, 1994), along with the spatial arrangement of the donor atoms (i.e. the type of pyridinecarboxylic acid used), leads to various, mostly irregular, coordination polyhedra of mercury.

No structural data on mercury(II) complexes with nicotinic acid or the nicotinate ion are reported in the Cambridge Structural Database (CSD; Version 5.24 of November 2002; Allen, 2002). NicH (pyridine-3-carboxylic acid or nicotinic acid) and nic⁻ (the nicotinate ion) exhibit various coordination modes in metal complexes. Polymerization can occur by the formation of covalent bonds or via extensive hydrogen-bond networks. catena-[Bis[trans-bis(μ_2-thiocyanato)bis(nicotinic acid)cadmium(II)] bis(nicotinic acid) clatrate] is the only known complex of the group 12 metals with nicH as a ligand (Yang et al., 2001). NicH is coordinated by the Cd atom through the pyridine N atom, while the COOH group does not take part in coordination. There are a few other examples of nicH complexes of Cu (Goher & Mak, 1987; Aakeröy et al., 2000; Naumov et al., 2001) or Pd (Qin et al., 1999) in which
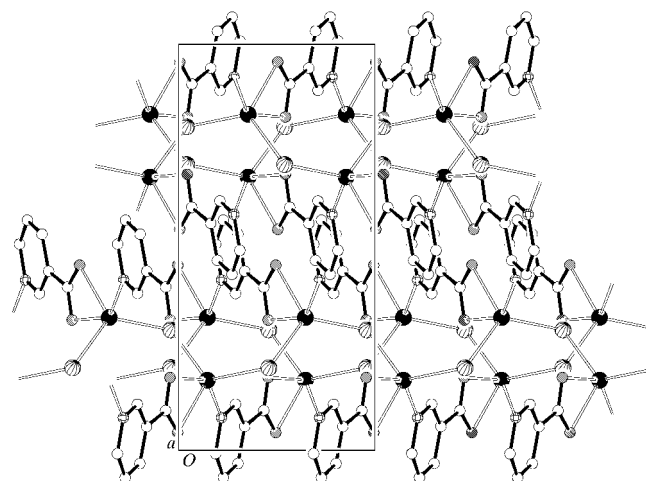

Figure 2
PLATON (Spek, 1998) view of the crystal structure of (I).

coordination also occurs *via* the N atom. The only complex that has a different coordination mode of nicH, through the keto O atom of the carboxyl group, is the trinuclear Cr complex, where the structure was solved from powder X-ray data (Mullica *et al.*, 1986).

In the case of the deprotonated nic⁻ ligand, coordination can be achieved *via* the pyridine N atom, as in the structures of *trans*-tetraaquabis(pyridine-3-carboxylate-*N*)chromium(II) (Cooper *et al.*, 1984; Broderick *et al.*, 1986; Marsh & Spek, 2001), *trans*-tetraaquabis(nicotinate-*N*)zinc(II) (Broderick *et al.*, 1986), *trans*-tetraaquabis(pyridine-3-carboxylate-*N*)-nickel(II) (Batten & Harris, 2001) and *trans*-tetraaquabis-(pyridine-3-carboxylate-*N*)copper(II) (Kenar *et al.*, 1999). On the other hand, the nicotinate ion can act in a bidentate manner through carboxylate O,O'-donor atoms, as in the structure of *trans*-dichlorobis(*N*-methylpyridinium-3-car-boxylato)copper(II) (Nakagawa *et al.*, 1999), or through an *N,O*-donor set, as in the structure of the polymeric *catena*-[ammonium bis(pyridine-3-carboxylato-*O,N,N'*)silver(I)] complex (Smith *et al.*, 1994).

In the title polymeric complex, HgBr(nic), (I), the irregular five-coordination of mercury is strongly dictated by the rigid geometry of the nic⁻ ligand (Fig. 1). The Hg atom is surrounded by two carboxylic acid O atoms from the depro-tonated nic⁻ ligand, in the form of a characteristic four-membered chelate ring [where the Hg—O bonds (Table 1) are longer than the tetrahedral Hg—O covalent bond of 2.14 Å; Grdenić, 1965; Pauling, 1960], two symmetry-related bridging Br atoms [where the Hg—Br bonds (Table 1) are slightly longer than the tetrahedral Hg—Br covalent bond of 2.62 Å; Grdenić, 1965; Pauling, 1960] and the pyridine N atom [where the Hg—Nⁱ bond (see Table 1 for symmetry code) is slightly longer than the tetrahedral Hg—N covalent bond of 2.23 Å; Grdenić, 1965; Pauling, 1960]. Bond angles range from 53.7 (2)° for O1—Hg—O2 to 140.9 (2)° for O1—Hg—Nⁱ. The largest bond-angle value corresponds to the stronger Hg—O bond (Hg—O1), but the O1—Hg—Nⁱ bond-angle value is a result of the constraints of ligand geometry rather than an indication of a strong Hg—O bond. It is obvious that the strongest bonds are to the N and Br atoms, although the bond-angle values exhibit significant irregularity (compare Br—Hg—Nⁱ, Brⁱⁱ—Hg—Nⁱ and Br—Hg—Brⁱⁱ in Table 1) and therefore lead to a deformed (3+2)-coordination for mercury. The geometry of the nic⁻ ion is normal (Allen *et al.*, 1987). The crystal structure of nicH is known [CSD refcodes NICOAC (Wright & King, 1953), NICOAC01 (Gupta & Kumar, 1975) and NICOAC02 (Kutoglu & Scheringer, 1983)]. The molecules of nicH are linked through O—H⋯N intermolecular hydrogen bonds parallel to the *b* axis. The endocyclic C—N bonds within the pyridine ring in (I) are comparable to those in the structure of nicotinic acid itself [N—C3 and N—C4 of 1.334 (8) and 1.343 (9) Å, respectively, in (I) *versus* N—C1 and N—C5 of 1.348 (4) and 1.342 (4) Å in the acid; Kutoglu & Scheringer, 1983]. The deprotonation of the carboxyl group implies changes in the C—O bond lengths, which are 1.226 (11) and 1.259 (10) Å for bonds O1—C1 and O2—C1, respectively, in (I) compared with O1—C6 and O2—C6 of

1.308 (4) and 1.211 (4) Å in nicH (Kutoglu & Scheringer, 1983). The two-dimensional polymeric structure of (I) is formed by the covalent interactions of Br⁻ and nic⁻ ions with Hg atoms. The planes are connected by van der Waals contacts of the pyridine rings, and there are only two weak inter-molecular hydrogen bonds of the C—H⋯O type (Fig. 2 and Table 2).

Experimental

An aqueous solution of HgBr₂ (0.3 g, 0.83 mmol) and nicH (0.1 g, 0.82 mmol) was mixed and left to stand for a few days. Colourless crystals (0.17 g, yield 50.73%) precipitated and were filtered off and dried. The compound is soluble in dimethyl sulfoxide, dimethylfor-mamide, γ-picoline and py. Analysis calculated for HgBr(nic): C 17.90, H 1.00, N 3.48, Hg 49.82%; found: C 18.02, H 1.21, N 3.51, Hg 49.87%. IR spectral data supported the presence of the deprotonated nicotinate ion, which displaced one Br ion from HgBr₂. Absorption bands around 2600 and 1900 cm⁻¹, which are typical for inter-molecular O—H⋯O hydrogen bonds of free pyridine acids, were not observed in the IR spectrum of HgBr(nic). A shift of the carbonyl band from 1655 cm⁻¹ in free nicH to 1631 cm⁻¹ in HgBr(nic) was observed. The pyridine-ring N-atom coordination to Hg in the 1600–1400 cm⁻¹ spectrum area is indicated by a splitting of the C=C and C=N vibration bands.

Crystal data

[HgBr(C₆H₄NO₂)]	$D_x = 3.502$ Mg m⁻³
$M_r = 402.60$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 55
$a = 14.2021\,(12)$ Å	reflections
$b = 7.2102\,(16)$ Å	$\theta = 10.0$–$18.0°$
$c = 15.368\,(3)$ Å	$\mu = 25.33$ mm⁻¹
$\beta = 103.945\,(9)°$	$T = 293\,(2)$ K
$V = 1527.3\,(5)$ Å³	Irregular block, colourless
$Z = 8$	$0.13 \times 0.09 \times 0.08$ mm

Data collection

Philips PW1100 diffractometer,	$R_{\text{int}} = 0.024$
updated by Stoe	$\theta_{\max} = 30.0°$
ω scans	$h = -19 \rightarrow 19$
Absorption correction: ψ scan	$k = -2 \rightarrow 10$
(*X-RED*; Stoe & Cie, 1995)	$l = -1 \rightarrow 21$
$T_{\min} = 0.019$, $T_{\max} = 0.065$	4 standard reflections
5692 measured reflections	frequency: 90 min
2216 independent reflections	intensity decay: 3.1%
1426 reflections with $I > 2\sigma(I)$	

Table 1
Selected geometric parameters (Å, °).

Hg—Nⁱ	2.265 (5)	O1—C1	1.226 (11)
Hg—O1	2.353 (6)	O2—C1	1.259 (10)
Hg—O2	2.478 (7)	N—C3	1.334 (8)
Hg—Brⁱⁱ	2.6468 (9)	N—C4	1.343 (9)
Hg—Br	2.6528 (9)		
Nⁱ—Hg—O1	140.9 (2)	O2—Hg—Brⁱⁱ	106.69 (15)
Nⁱ—Hg—O2	88.6 (2)	Nⁱ—Hg—Br	98.65 (16)
O1—Hg—O2	53.7 (2)	O1—Hg—Br	95.13 (17)
Nⁱ—Hg—Brⁱⁱ	106.38 (15)	O2—Hg—Br	123.15 (15)
O1—Hg—Brⁱⁱ	95.30 (17)	Brⁱⁱ—Hg—Br	124.27 (2)

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C3—H3$\cdots$O1^{iii}	0.93	2.60	3.428 (10)	149
C4—H4$\cdots$O2^{iv}	0.93	2.47	3.170 (10)	132

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

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{max} = 0.001$
2216 reflections	$\Delta\rho_{max} = 0.98$ e Å^{-3}
100 parameters	$\Delta\rho_{min} = -2.02$ e Å^{-3}

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]. Because of the irregular shape of the crystal block, the applied absorption correction was semi-empirical (calculated with *X-RED*; Stoe & Cie, 1995). Four reflections were used for the φ-scan absorption correction ($\overline{5}15$, $\overline{5}16$, $\overline{9},\overline{1},12$ and $9,1,\overline{12}$). The value of μR was taken to be 2.533.

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*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1998); software used to prepare material for publication: *SHELXL*97.

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