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Coordination modes of 3-hydroxypicolinic acid: Synthesis and structural characterization of polymeric mercury(II) complexes

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Abstract

Novel mercury(II) compounds of 3-hydroxypicolinic acid (HpicOH; IUPAC name: 3-hydroxy-2-pyridinecarboxylic acid) were synthesized and characterized. HgCl(picOH) (**1**) and $HgBr_2$(HpicOH) (**2**) were obtained as reaction products from the reaction of the corresponding mercury(II) halide with HpicOH, irrespective of the molar ratio of the reactants. From the reaction of HpicOH and mercury(II) acetate, $Hg(picOH)_2$ (**3**) was obtained, while mercury(II) nitrate monohydrate gave the 1/1 solvate with water $Hg(picOH)_2 \cdot H_2O$ (**3a**). Infrared, ^1H and ^{13}C NMR spectroscopic data were analyzed for complexes **1**, **2** and **3**. X-ray crystal structure analysis of **1** and **2** revealed their polymeric nature and different coordination modes of HpicOH. In **1** the deprotonated picolinic acid is *N*,*O*-chelating and bridging, while in **2** HpicOH is a *O*-monodentate weakly bound ligand. Compound **1** consists of HgCl(picOH) moieties with two linear covalent bonds, Hg–N 2.143(4) and Hg–Cl 2.298(1) Å, and four additional Hg···O contacts (2.460(3)–2.904(3) Å) in which both oxygen atoms from the carboxylic group are bridging and involved in coordination to three neighboring mercury atoms, thus forming infinite layers. The coordination of mercury is 2 + 4. **2** consists of $\{HgBr_2(HpicOH)\}$ moieties, which are linked into chains by means of mercury to bromine secondary long range interactions. The coordination sphere of mercury can be described as irregular 2 + 3 formed by two covalently bonded bromine atoms (Hg–Br 2.277(1) and 2.366(1) Å), two bridging bromine atoms (Hg···Br 3.309(1) and 3.247(1) Å) and by the HpicOH ligand attached to mercury in the zwitterionic form via the carboxylic oxygen atom (Hg···O 2.602(7) Å).

Keywords: Mercury(II) compounds; 3-Hydroxy-2-pyridinecarboxylic acid; IR and NMR spectra; X-ray diffraction

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1. Introduction

3-Hydroxypicolinic acid (HpicOH) is widely used as a DNA matrix system in matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) [1]. Because of its physiological activity [2] and rich coordination modes, many metal complexes have been investigated. As a ligand, 3-hydroxypicolinic acid, HpicOH, shows the following coordination modes: (i) *O*-monodentate via the deprotonated carboxylic group, as we found in this work in the structure of $HgBr_2$(HpicOH); (ii) non-symmetrical $picO_2^{2-}$ bridging through the oxygen of the deprotonated carboxylic and hydroxyl groups and pyridine nitrogen atom, as found in the binuclear complex $\{\mu\text{-picO-}[Ru(bipy)_2]_2\}^{2+}$ [3]; (iii) *N*,*O*-chelating through the pyridine nitrogen and the carboxylate group, forming a five-member ring; and (iv) *O*,*O*-chelating through the carboxylate group and deprotonated hydroxyl group, forming a six-membered ring [4] (Scheme 1). The *N*,*O*-chelation is the most common mode for $picOH^-$ and was reported for rhenium [5,6], vanadium [7], palladium and platinum [5], molybdenum and tungsten [8], and zinc,

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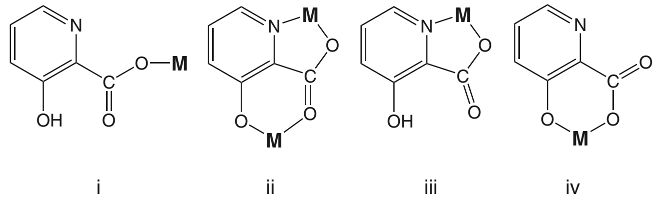


Scheme 1.

manganese and copper [9,10]. In [CdX(picOH)(HpicOH)(H_2O)]$_2$ (X = Cl^-, Br^-) we established two modes of HpicOH binding: *N*,*O*-chelating and *O*-monodenate with the pyridine nitrogen atom protonated [11].

Our former investigations pointed out that the mercury(II) ion is capable of forming various binding coordination modes with *N*,*O*-donor atoms when provided by suitable ligands [12–16]. Our present interest on mercury(II) coordination complexes has been directed towards the understanding of the competition between halide ions and ligands containing *N*,*O*-donors for coordination sites of the mercury(II) ion. So far, we found that the tendency of mercury to achieve effective coordination by spatial arrangement of donor atoms of different types of acids, leads to various, mostly highly irregular, coordination polyhedra of mercury. Mono- and dicarboxylic acids containing a pyridine ring, or their hydroxy derivatives, are good ligand systems with *N*,*O*-donor atoms at appropriate sites for modelling various mercury coordination polyhedra in discrete or polymeric complexes of the formulas HgXL, HgX_2L or HgX(L)(LH) (LH and L stand for the protonated and deprotonated form of the ligand, respectively, X = Cl^-, Br^-, I^-, SCN^-).

Our wider interest includes investigation of toxicity effects of various metal complexes of the 12th group of elements on microbial communities. For such a study well characterized complexes are needed. This paper describes new mercury(II) complexes with 3-hydroxypicolinic acid. They were synthesized, identified by chemical analysis, characterized by the appropriate spectroscopic methods, both in solution and in the solid state, and two crystal structures were determined by the X-ray diffraction method.

2. Experimental

2.1. Materials and physical measurements

All reagents were supplied by Aldrich Chemical Co. and were used as received without further purification. The CHN-microanalyses were measured by the Central Analytical Service of the Ruđer Bošković Institute, Zagreb. The mercury content in the complexes was determined by complexometric titration with sodium diethyldithiocarbamate of the solution obtained after decomposition of the specimen in *aqua regia* [17].

Pressed KBr pellets were used for IR measurements within the range 4000–400 cm^{-1} with a Perkin–Elmer FT-IR spectrometer 1600 Series.

The one- and two-dimensional homo- and heteronuclear ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV 600 spectrometer, operating at 600.133 MHz for the ^{1}H nucleus and 150.917 MHz for the ^{13}C nucleus. Samples were measured from DMSO-d_6 solutions at 22 °C (295 K) in 5 mm NMR tubes. Chemical shifts, in ppm, are referred to TMS as internal standard. FID resolution in ^{1}H NMR and ^{13}C NMR spectra was 0.29 and 0.54 Hz per point, respectively. The following measurement techniques were used: standard ^{1}H, ^{13}C gated proton decoupling, APT, COSY, HMQC and HMBC. The 2D NMR spectra were measured in the pulsed field gradient mode (*z*-gradient).

X-ray and NMR data are given in Tables 1 and 2, respectively.

Table 1
General and crystal data, summary of intensity data collection and structure refinement of compounds **1** and **2**

	1	**2**
Formula	$C_6H_4ClHgNO_3$	$C_6H_5Br_2HgNO_3$
M_r	374.14	499.52
Temperature (K)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Color	colorless	colorless
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell parameters		
a (Å)	10.4838(19)	10.0030(13)
b (Å)	7.9647(12)	4.1601(5)
c (Å)	9.8583(16)	23.720(3)
β (°)	106.206(18)	97.378(10)
V (Å^3)	790.5(2)	978.9(2)
Z	4	4
D_{calc} (g cm^{-3})	3.144	3.389
F(000)	672	888
Crystal size (mm^3)	0.173 × 0.111 × 0.022	0.412 × 0.111 × 0.070
θ Range for data collection (°)	4.8, 30.0	4.66, 26.98
Number of measured reflections	27,119	12,503
Number of independent reflections	2295	2114
Number of observed reflections, $I \geqslant 2\sigma(I)$	2092	2006
Number of parameters	110	123
Absorption correction	integration	integration
μ (mm^{-1})	19.769	23.859
Range of transmission factors	0.027, 0.427	0.050, 0.191
R[a], wR[b] [$I \geqslant 2\sigma(I)$]	0.0266, 0.0308	0.0506, 0.0525
R, wR (all data)	0.0621, 0.0639	0.1320, 0.1347
g_1, g_2 in w[c]	0.0344, 0.9218	0.0768, 5.3103
Goodness-of-fit on F^2, S[d]	1.124	1.134
Minimum and maximum electron density (e Å)[e]	−1.68, 2.61	−3.185, 1.831

[a] $R = \sum||F_o| - |F_c|/\sum|F_o|$.

[b] $wR = \left[\sum(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\right]^{1/2}$.

[c] $w = 1/[\sigma^2(F_o^2)] + [g_1P + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$.

[d] $S = \sum[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

[e] The maximum electron density in the last difference Fourier map is near Hg.

2.2. HgCl(picOH) (**1**)

To an aqueous solution of mercury(II) chloride (0.30 g; 1.1 mmol in 15 ml H_2O) an aqueous solution of 3-hydroxypicolinic acid was added dropwise (0.16 g; 1.15 mmol in 15 ml H_2O). The reaction mixture was allowed to stand for a few days at room temperature to crystallize. The crystalline product was filtered off, washed with cold water and dried in a desiccator. Yield: 0.31 g (75.6%). *Anal.* Calc. for $C_6H_4ClHgNO_3$ (mol. wt. 374.14): C, 19.26; H, 1.08; N, 3.74; Hg, 53.61. Found: C, 19.38; H, 1.18; N, 3.67; Hg, 53.81%. IR max. (cm^{-1}): 3087w, 1621vs, 1601s, 1570s, 1527m, 1476s, 1456vs, 1375vs, 1312vs, 1249s, 1229s, 1149m, 1064w, 893m, 872m-w, 829s, 805m-s, 692s, 578m.

When the same reaction is performed in ethanol **1** is also obtained, however the yield is better from aqueous solution.

2.3. $HgBr_2$(HpicOH) (**2**)

To an ethanolic solution of mercury(II) bromide (0.3 g; 0.83 mmol in 15 ml of EtOH) an ethanolic solution of 3-hydroxypicolinic acid was added dropwise (0.12 g; 0.86 mmol in 25 ml EtOH). The reaction mixture was left to stand for a few days. The crystalline product was filtered off, washed with cold ethanol and dried. Yield: 0.37 g (90.5%). *Anal.* Calc. for $C_6H_5Br_2HgNO_3$ (mol. wt. 499.52): C, 14.43; H, 1.01; N, 2.80; Hg, 40.16. Found: C, 14.13; H, 1.07; N, 3.15; Hg, 40.07%. IR max. (cm^{-1}): 3585m, sharp, 3526m, sharp, 3065m-w, 2856w, br, 1655s, 1613s, 1534s, 1470s, 1412s, 1377m, 1335s, 1283s, 1252m, 1214m, 1152m, 1120m-w, 1048m-w, 874s, 816vs, 802s, 682s, 667vs, 576w, 549w, 446m.

The same reaction performed in an aqueous solution also results in **2**, but with traces of unreacted $HgBr_2$ which is less soluble in water than ethanol.

2.4. $Hg(picOH)_2$ (**3**) and $Hg(picOH)_2 \cdot H_2O$ (**3a**)

To an aqueous solution of mercury(II) acetate (0.3 g; 0.94 mmol in 15 ml H_2O with a few drops of 2 M acetic acid) an aqueous solution of 3-hydroxypicolinic acid was added (0.3 g; 2.15 mmol in 15 ml H_2O). The yellowish product was filtered off, washed with water and dried. Yield (**3**): 0.40 g (88.9%). From the reaction of 3-hydroxypicolinic acid (0.24 g; 1.72 mmol in 15 ml H_2O) and mercury(II) nitrate monohydrate (0.3 g; 0.86 mmol in 15 ml H_2O with a few drops of 20% nitric acid) the 1/1 solvate of $Hg(picOH)_2$ with water was obtained. Yield (**3a**): 0.38 g (87.8%). *Anal.* Calc. for $C_{12}H_8HgN_2O_6$ (mol. wt.

Table 2
^1H and ^{13}C NMR chemical shifts (δ/ppm)[a] and mercury induced chemical shifts ($\Delta\delta$/ppm),[b] H–H coupling constants ($^nJ_{HH}$/Hz)[c] and C–H coupling constants ($^nJ_{CH}$/Hz)[c] of 3-hydroxypicolinic acid (HpicOH) and its mercury compounds

Molecule		HpicOH	HgCl(picOH)	$HgBr_2$(HpicOH)	$Hg(picOH)_2$
Atom			**1**	**2**	**3**
H-2,3	δ	14.81 (bs)	15.42 (bs)	14.34 (bs)	15.31 (bs)
	$\Delta\delta$		0.61	−0.47	0.50
H-4	$\mathit{\Delta}$	7.76	7.65	7.74	7.78
	$^3J_{HH}$	8.55 (d)	8.44 (d)	8.43 (d)	8.46 (d)
	$\Delta\delta$		−0.11	−0.02	0.02
H-5	$\mathit{\Delta}$	7.70	7.74	7.76	7.88
	$^3J_{HH}$	8.61; 5.07 (dd)	8.19; 5.02 (dd)	8.55; 4.93 (dd)	8.05; 5.10 (dd)
	$\Delta\delta$		0.04	0.06	0.18
H-6	$\mathit{\Delta}$	8.05	8.26	8.13	8.29 (bs)
	$^3J_{HH}$	4.94 (d)	4.20 (d)	4.80 (d)	
	$\Delta\delta$		0.21	0.08	0.24
C-2	δ	129.42 (s)	131.21 (s)	129.55 (s)	131.11 (s)
	$\Delta\delta$		1.79	0.13	1.69
C-3	δ	160.17 (s)	160.62 (s)	159.87 (s)	160.63 (s)
	$\Delta\delta$		0.45	−0.30	0.46
C-4	δ	131.92	129.98	131.73	130.04
	J_{CH}	168.06 (d)	169.90 (d)	168.19 (d)	167.34 (d)
	$\Delta\delta$		−1.94	−0.19	−1.88
C-5	$\mathit{\Delta}$	129.63	130.01	129.83	130.41
	J_{CH}	170.48 (d)	167.61 (d)	171.11 (d)	170.25 (d)
	$\Delta\delta$		0.38	0.20	0.78
C-6	$\mathit{\Delta}$	133.56	139.94	135.16	140.02
	J_{CH}	189.93 (d)	190.64 (d)	190.94 (d)	189.94 (d)
	$\Delta\delta$		6.38	1.60	6.46
COOH	δ	165.93 (s)	168.03 (s)	165.93 (s)	168.09 (s)
	$\Delta\delta$		2.46	0.36	2.52

[a] Recorded in DMSO-d_6 solutions. Referred to TMS.

[b] Mercury induced chemical shifts ($\Delta\delta$/ppm) are obtained by subtracting the chemical shifts of the parent compound (HpicOH) from the chemical shifts of the Hg-compounds. Sign (+) denotes deshielding effect, while (−) denotes shielding effect of mercury.

[c] n Denotes the number of bonds between nuclei in spin–spin coupling; (s) singlet, (d) doublet.

476.80): C, 30.23; H, 1.69; N, 5.88; Hg, 42.07. Found: C, 30.37; H, 1.75; N, 5.92; Hg, 42.18%. IR max. (cm^{-1}): 3435m, br, 3100m, br, 2935w, 1647vs, 1597s, 1572m, 1470s, 1455s, 1400s, 1380s, 1314s, 1248m, 1230s, 1147m, 1066w, 991w, 939w, 917w-m, 890s, 821s, 691s, 579m-w, 561w. *Anal.* Calc. for $C_{12}H_{10}HgN_2O_7$ (mol. wt. 494.82): C, 29.13; H, 2.04; N, 5.66; Hg, 40.54. Found for: C, 29.25; H, 1.93; N, 5.62; Hg, 40.24%. IR max. (cm^{-1}): 3436m, br, 3030w, 2924w, 1636s, 1590m-s, 1470m, 1455s, 1381s, 1312s, 1229m, 1144m-w, 1040w, 1000w, 980vw, 918w, 886m, 819m, 800m, 687m, 670w, 578w, 542w, 448w.

2.5. X-ray crystallographic structure determination of 1 and 2

The general and crystal data, and summary of intensity data collection and structure refinement for compounds **1** and **2** are given in Table 1.

The data collection for both structures was carried out on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire 3 CCD detector, by applying the CrysAlis Software system [18]. A crystal-detector distance of 60 mm and ω scan type was used for both structures. Data reduction, including absorption correction, was done by the CrysAlis RED application of the CrysAlis Software system [18]. Coordinates of the non-hydrogen atoms were determined by direct methods using the SHELXS program [19]. The coordinates and anisotropic thermal displacement parameters for all non-hydrogen atoms were refined by the least-squares methods based on F^2 using the SHELXL97 program [20]. The coordinates of the hydrogen atom belonging to the nitrogen atom in **2** were found by examination of the electron-density Fourier map at the final stages of refinement and were refined freely [the bond distance is 0.8(1) Å]. The other hydrogen atoms which belong to the pyridine carbon atoms, as well as the hydroxyl hydrogen atom, were generated at ideal geometrical positions [Csp^2–H 0.93 Å, $U_{iso}(H) = 1.2\ U_{eq}(C)$; O–H 0.82 Å; $U_{iso}(H) = 1.5\ U_{eq}(O)$], and were refined applying the riding model. The molecular graphics were created by means of the PLATON98 program [21].

3. Results and discussion

3.1. Preparation

Compound **1** HgCl(picOH) was obtained from the reaction of 3-hydroxypicolinic acid (HpicOH) with mercury(II) chloride in an aqueous solution. Similarly, reaction with $HgBr_2$ in ethanolic solution gave $HgBr_2$(HpicOH) (**2**). In both cases the reaction products were not influenced by the molar ratio of reactants (1:1 or 2:1). Both mercury(II) acetate and nitrate monohydrate react with HpicOH in aqueous media giving typical metal carboxylates i.e. $Hg(picOH)_2$ (**3**) and $Hg(picOH)_2 \cdot H_2O$ (**3a**), respectively. All the isolated compounds are soluble in solvents with pronounced coordination properties such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl formamide (DMF) or pyridine. Crystals suitable for X-ray diffraction studies were obtained from the mother liquor for compounds **1** and **2**, but all our attempts to prepare crystals of compounds **3** and **3a** failed.

3.2. Structural description of 1 and 2

In **1** the shortest bonds to Hg are from nitrogen and chlorine atoms (Hg–N 2.143(4) and Hg–Cl 2.298(1) Å) giving a

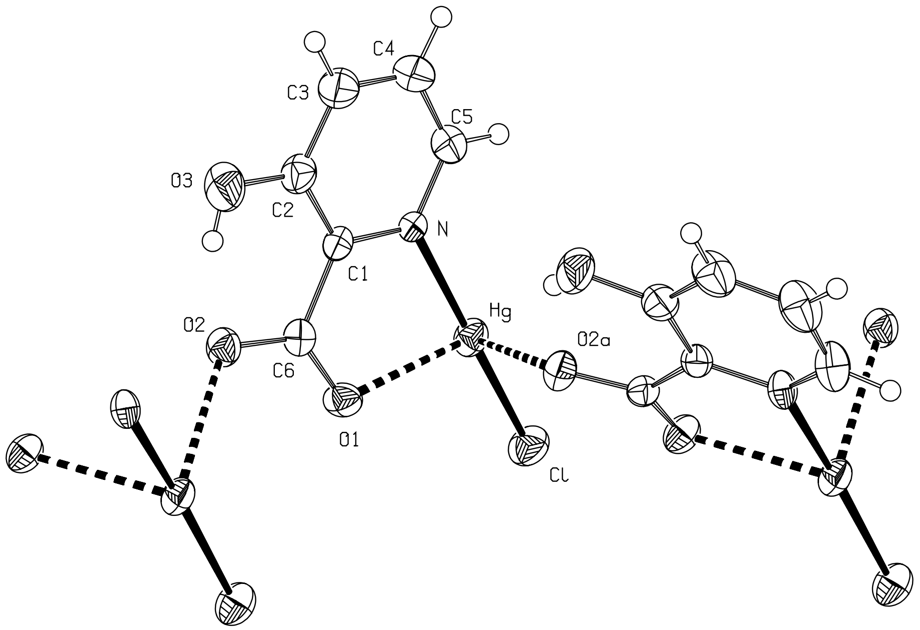


Fig. 1. Drawing of HgCl(picOH) (**1**) with the atom labelling scheme. The thermal ellipsoids are at the 50% probability level. Dashed lines represent Hg···O contacts. Symmetry operation: *a* = *x*, 0.5 − *y*, *z* − 0.5.

Table 3
Selected interatomic distances (Å) and angles (°) for **1**

Interatomic distances		Bond angles	
Hg–N	2.143(4)	N–Hg–Cl	172.68(10)
Hg–Cl	2.2975(13)	N–Hg–O1	73.47(12)
Hg···O1	2.460(3)	Cl–Hg–O1	109.95(8)
Hg···O2^{i}	2.609(3)	N–Hg–O2^{i}	85.13(12)
Hg···O2^{ii}	2.888(3)	Cl–Hg–O2^{i}	101.40(8)
Hg···O1^{iii}	2.904(3)	O1–Hg–O2^{i}	83.38(10)
N–C1	1.345(5)		
N–C5	1.331(6)		
O1–C6	1.248(5)		
O2–C6	1.266(5)		
O3–C2	1.339(6)		

Symmetry transformations used to generate equivalent atoms: (i) x, $0.5 - y$, $z - 0.5$; (ii) $1 - x$, $1 - y$, $2 - z$; (iii) $1 - x$, $1/2 + y$, $3/2 - z$.

Table 4
Selected interatomic distances (Å) and angles (°) for **2**

Bond distances		Bond angles	
Hg–Br1	2.2766(10)	Br1–Hg–Br2	168.22(4)
Hg–Br2	2.3660(10)	Br1–Hg–O1	87.99(18)
Hg···O1	2.602(7)	Br2–Hg–O1	103.63(18)
Hg···Br1^{i}	3.3093(10)		
Hg···Br2^{ii}	3.2469(10)		
Hg···Br2^{iii}	3.8475(10)		
N–C5	1.324(12)		
N–C1	1.492(13)		
O1–C6	1.405(12)		
O2–C6	1.211(12)		
O3–C2	1.481(13)		

Symmetry transformations used to generate equivalent atoms: (i) x, $y - 1$, z; (ii) x, $1 + y$, z; (iii) $-x$, $1/2 + y$, $-1/2 - z$.

slightly distorted characteristic linear coordination, N–Hg–Cl 172.7(1)° [22,23]. These bonds are slightly longer than the sum of the covalent radii of the corresponding atoms because of the additional Hg···O contacts. Both carboxylate oxygen atoms of the deprotonated picolinic acid are involved in coordination to two neighboring mercury atoms (Hg···O1 2.460(3) and Hg···O2 (x, $0.5 - y$, $z - 0.5$) 2.609(3) Å) thus bridging them and forming infinite zigzag chains along the b axis, Fig. 1. Relevant bond distances and bond angles are shown in Tables 3 and 4. Besides the two already mentioned, there are two more long Hg···O contacts (Hg···O2 ($1 - x$, $1 - y$, $2 - z$) 2.888(3) Å and Hg···O1 ($1 - x$, $0.5 + y$, $1.5 - z$) 2.904(3) Å), still shorter than the sum of van der Waals radii ($r_{\mathrm{VDW}}(\mathrm{Hg}) = 1.55$–$1.65$ Å; $r_{\mathrm{VDW}}(\mathrm{O}) = 1.40$–$1.52$ Å) [22–25]. All contacts fulfill the effective coordination sphere of mercury, which is therefore 2 + 4. This behavior is in agreement with Grdenić's classification of a characteristic and effective coordination sphere of mercury in crystal structures [22,23]. Through these contacts (Fig. 2), infinite two-dimensional layers are formed. There is an intramolecular hydrogen bond connecting the hydroxyl and carboxylic group, O3–H···O2 of 2.542(5) Å. The intermolecular hydrogen bonds are very weak (Table 5). A similar coordination, yet with slightly longer covalent Hg–N and Hg–Cl bonds than in **1**, is found in the structure of $(\mathrm{pyda \cdot H})_2[\mathrm{Hg(pydc)Cl_2 \cdot 2H_2O}]$ (pyda = 2,6-pyridinediamine; pydc = 2,6-pyridinedicarboxylic acid). In this structure the distances amount to 2.198(6)

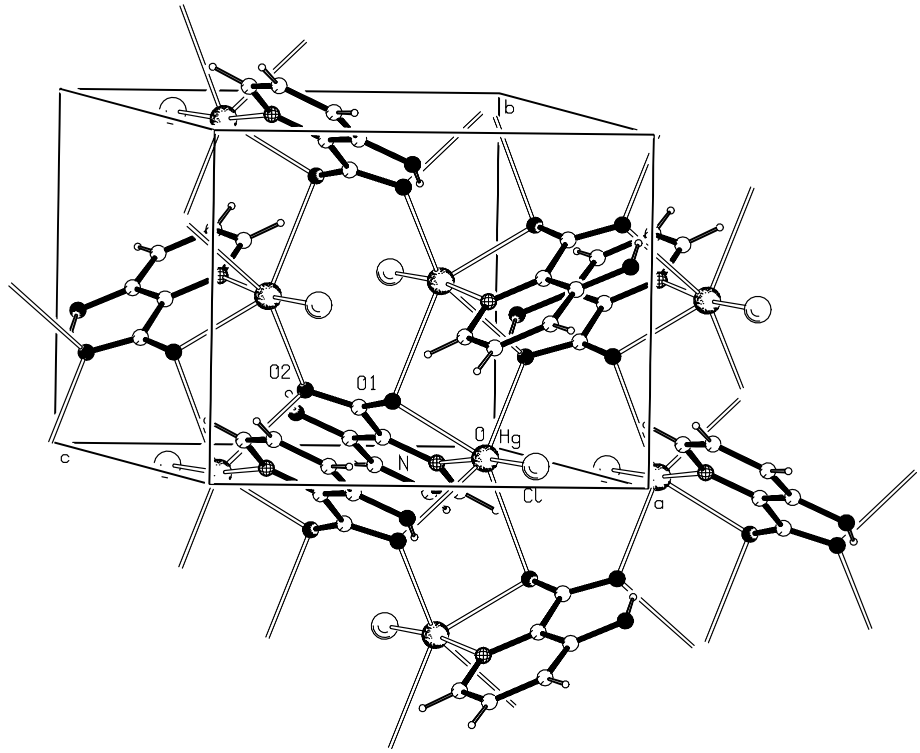


Fig. 2. Packing of molecules of HgCl(picOH) (**1**) in the unit cell, including one polymeric layer. The deformed octahedral geometry around Hg is shown by double lines.

Table 5
Hydrogen bond geometry (distances (Å), angles (°)) in **1** and **2**

D–H···A	D···A	D–H···A
1		
O3–H···O2	2.542(5)	143
C4–H···O3^{i}	3.443(7)	165
C5–H···Cl^{ii}	3.414(5)	131
2		
O3–H···O1	2.334(11)	138
N–H···O2	2.662(10)	116(13)
N–H···O2^{iii}	2.737(12)	133(14)
C3–H···Br2^{iv}	3.495(12)	140

Symmetry transformations used to generate equivalent atoms: (i) $-x$, $1/2+y$, $3/2-z$; (ii) $1-x$, $1-y$, $1-z$; (iii) $-1-x$, $-y$, $-z$; (iv) $-x$, $1-y$, $-z$.

and 2.310(2) Å, respectively [26]. The greater elongation is caused by four Hg···O contacts that are in the range 2.488(5)–2.659(5) Å.

Structure of **2** consists of polymeric chains (Fig. 3). There are two covalent bonds, Hg–Br1 2.277(1) and Hg–Br2 2.366(1) Å forming the linear characteristic coordination, Br1–Hg–Br2 168.22(4)° (Table 4). The effective coordination sphere of mercury can be described as irregular 2 + 3, consisting of three weak additional contacts, two with bromine atoms from adjacent molecules (Hg–Br1 (x, $1+y$, z) 3.309(1) and Hg–Br2 (x, $-1+y$, z) 3.247(1) Å), and one with the carboxylic oxygen of HpicOH in the zwitterionic form (Hg–O1 2.602(7) Å). Interestingly, both covalent Hg–Br bonds are shorter than the sum of the covalent radii for Hg(digonal) and Br atoms (1.30 and 1.14 Å, respectively) [22–25] and also shorter than in the brucite structural type of $HgBr_2$ (Hg–Br of 2.444(7) and 2.445(7) Å, 2 × Hg···Br of 3.240(5) and 2 × Hg···Br 3.243(5) Å) [27]. The two bridging mercury to bromine contacts as well as the mercury to oxygen contact are longer than the covalent bond, but shorter than the van der Waals interactions ($r_{VDW}(Br) = 1.85–1.95$ Å) [22–25]. The coordination polyhedron is best described as very deformed square-pyramidal with an O atom at the apex. The Hg to Br distance at the sixth coordination site of 3.8475(11) Å is too long to be considered as a contact. Analysis of all structures deposited with the Cambridge Crystallographic Data Centre [28] that contain a mercury to bromine bond, showed that the short Hg–Br1 bond in **2** is similar to the shortest one found so far in κ-(d_8-ET)$_4$[$HgBr_2 \cdot Hg_2Br_6$] (d_8-ET = wholly deuterated bis(ethylenediothio)tetrathiafulvalene) where Hg–Br is 2.28(2) Å and Br–Hg–Br is 169.7(7)°. There are two additional contacts of 3.41(2) Å at one side of this linear bond, yet the Hg–Br distance of 3.77(2) Å at the other side points to an absence of any additional interactions to Hg [29].

A similar polymeric structural motif to that of **2** was found in the structure of $HgCl_2$(tolnapH), (tolnapH = *N*-*p*-tolyl-2-oxo-1-napthylideneamine) [30]. In the structure of the polymeric HgBr(nic) (nic$^-$ = nicotinate anion, pyridine-3-carboxylate) [15] the effective Hg coordination is a 3 + 2 irregular polyhedron with Hg–Br bond distances of 2.6528(9) and 2.6468(9) Å, which are longer than in **2** and slightly longer than the tetrahedral Hg–Br covalent bond of 2.62 Å [22,23,25].

As in **1**, the O3 hydroxyl atom forms an intramolecular hydrogen bond O3–H···O1 of 2.334(11) Å, yet there is another one involving the protonated nitrogen (N–H···O2

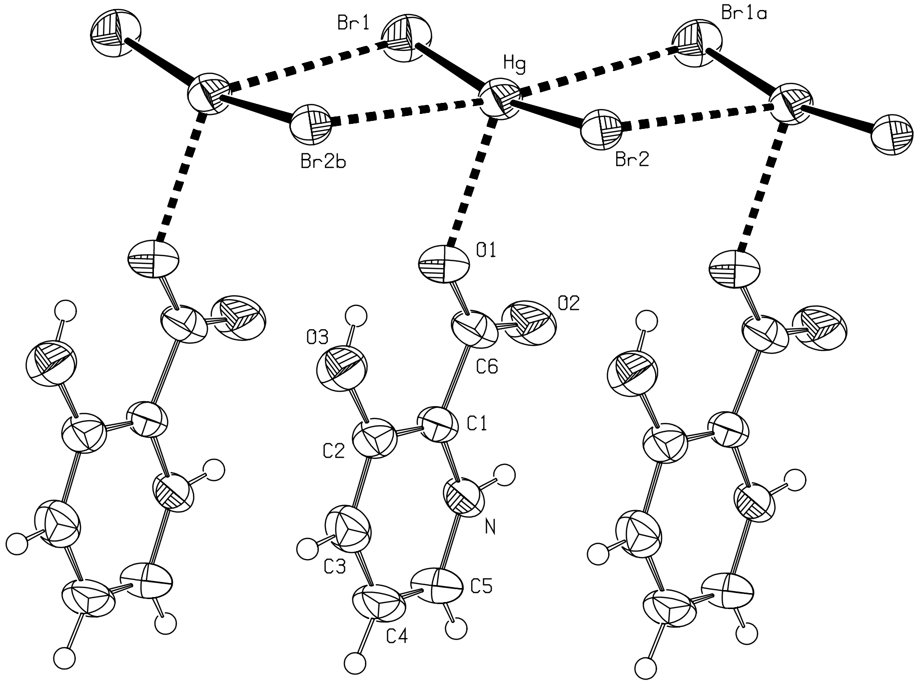


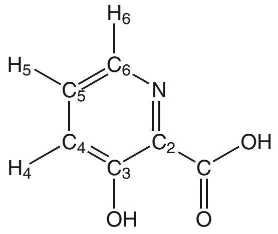
Fig. 3. Drawing of $HgBr_2$(HpicOH) (**2**) with the atom labelling scheme. The thermal ellipsoids are at the 50% probability level. Dashed lines represent Hg···Br and Hg···O contacts. Symmetry operations: $a = x, y-1, z$; $b = x, 1+y, z$.

2.662(10) Å). Two polymeric chains are mutually connected by centrosymmetric pairs via intermolecular hydrogen bonds N–H···O2 ($-1-x$, $-y$, $-z$) of 2.737(12) Å (Fig. 4, Table 5). In such a manner three-center hydrogen bonds are formed and the N–H group is distributed between two proton acceptors.

3.3. Spectral analysis

The infrared spectra of the complexes proved that 3-hydroxypicolinic acid is bound to the mercury(II) ion in the deprotonated form in all the isolated compounds (see ν_a(COO) in the experimental data), however different modes of ligand coordination in **1** and **2** were unambiguously confirmed by X-ray structure analysis. Unfortunately, due to overlaping of maxima and vibrational coupling, the observed shifts of absorption bands sensitive to metal coordination relatively to those of the free ligands could not be unambigously assigned.

^{1}H and ^{13}C NMR data of 3-hydroxypicolinic acid and its mercury(II) compounds are given in Table 2 while Scheme 2 shows the labelling of the atoms. The NMR spectra of **1**, **2** and **3** in DMSO solution revealed narrow signals and a lack of long range couplings, which is characteristic of the monomeric form of the molecules. This is not unexpected since in solution the polymers almost certainly break up into monomeric units. On the other hand, the NMR data showed that the ligand is bound as in the solid state with a deprotonated N and O in **1** and **3**, while a neutral O in **2**. The obtained ^{1}H spectra of **1**, **2** and **3** display four groups of signals. The assignments of the protons were supported by COSY spectra. In the ^{1}H NMR spectra, the greatest shifts ($\Delta\delta$) after complexation are observed for OH-protons which are five or six bonds remote from mercury. Interestingly, the OH-proton of compounds **1** and **3** is found to be deshielded, in comparison to the one in **2** which is a shielded proton. Such behavior arises from the different mode of mercury coordination. In all ^{1}H spectra the multiplicity of the signals is alike. The mercury binding does not influence significantly the other protons in the molecules of both compounds **1** and **2**. A small shielding effect is observed on the H-4 atom in complexes **1** and **2**, however deshielding effects are observed on H-5 and H-6 atoms in all three complexes.



Scheme 2.

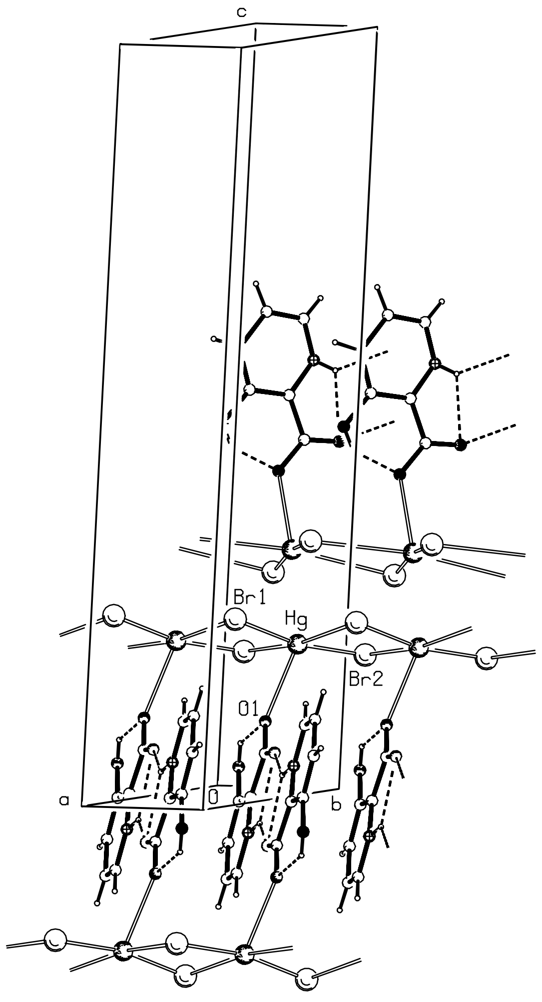


Fig. 4. Packing of $HgBr_2$(HpicOH) (**2**) molecules into polymeric layers. The deformed square pyramidal geometry around Hg is shown by double lines. Hydrogen bonds are shown by dashed lines.

The assignments of all the carbon atoms are confirmed by HMQC and HMBC measurements. In the ^{13}C NMR spectra, the greatest change upon complexation with mercury was observed for the chemical shifts of the C-6 atom. In **1** and **3**, C-6 is more deshielded than in **2**, since in complexes **1** and **3** the mercury atom is bonded to the nitrogen atom and the carboxyl group, while in **2** only to the carboxyl group. In all three compounds, carboxyl carbon atom was found to be not so deshielded as the C-6 atom. Shielding effects are observed on C-3 and C-4 atoms (−0.30 and −0.19 ppm, respectively) in complex **2**, and on the C-4 atom in **1** and **3** (−1.94 and −1.88 ppm, respectively). The carbon atom C-2 is deshielded in all three complexes (0.13–1.79 ppm) as expected, since it is close to the mercury binding site. The mercury binding induces electronic redistribution throughout the molecule which makes all the carbon atoms sensitive to mercury binding even if they are distant from mercury.

4. Conclusion

The competition reaction of halide (X = Cl^-, Br^-) with the 3-hydroxypyridine-2-carboxylate ligand (picOH$^-$) toward the mercury(II) ion was investigated. It was established that the molar ratio of the reactants did not influence the type of reaction product, and polymeric $\{HgCl(picOH)\}_n$ or $\{HgBr_2(HpicOH)\}_n$ was always obtained. X-ray crystal structural analysis of these polymeric compounds showed interesting $2+4$ and $2+3$ coordination polyhedra around the mercury atom, and confirmed two different coordination modes of HpicOH. The NMR spectra of all the isolated mercury compounds in DMSO solutions revealed that they exist in the monomeric form.

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Appendix A. Supplementary material

CCDC 602643 and 602642 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.09.094.

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