

Synthesis, Spectral and Thermal Characterization of Bis(pyridine-3-carboxy-2-thiolato-S)mercury(II). Crystal Structure of Dibromobis(3-metoxycarbonylpyridine-2-thiolato-S)mercury(II)[†]

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Abstract. 2-mercaptionicotinic acid ($H_2mna = 2-HS(C_5H_3N)COOH$) gave a thiolato compound of the formula $Hg(Hmna)_2$ by a reaction with various mercury(II) salts, HgX_2 ($X = Cl^-, Br^-, \Gamma^-, SCN^-$) in an ethanol or methanol solution irrespectively of the molar ratio of the reactants (1:1 or 1:2). The same compound was obtained from the reaction of mercury(II) acetate in an aqueous-ethanol solution. $Hg(Hmna)_2$ was characterized by vibrational spectroscopy and thermal analysis. 1H and ^{13}C NMR measurements provided additional information on the thiol-thione tautomerism in H_2mna and $Hg(Hmna)_2$ and also on the binding mode to mercury in the DMSO- d_6 solution. $HgBr_2(CH_3-Hmna)_2$ was obtained from the reaction of H_2mna with $HgBr_2$ in methanol after filtering off the main product $Hg(Hmna)_2$ ($CH_3-Hmna = 2-HS(C_5H_3N)COOCH_3$). The crystal structures of H_2mna and $HgBr_2(CH_3-Hmna)_2$ were determined by the X-ray structure analysis. 2-mercaptionicotinic acid exists in the crystalline state in the thione tautomeric form. Two bromine atoms and two S-bound CH_3-Hmna ligands form a tetrahedral coordination sphere around the mercury atom in $HgBr_2(CH_3-Hmna)_2$. (doi: 10.5562/cca2169)

Keywords: 2-mercaptionicotinic acid, mercury complex, thione-thiol tautomerism, X-ray single crystal structure analysis, intra- and intermolecular hydrogen bonds, 1H , ^{13}C NMR

INTRODUCTION

The coordination chemistry of polyfunctional ligands can be interesting from the point of view of their selective binding to different metal ions. They are widespread in biological systems, including amino acids and nucleic acids. It is a well known fact that mercury(II) ions interact with many biological molecules through coordination with a thiole, imidazole, amino or carboxylate group.¹ The biological chemistry of mercury is dominated by interactions with the cysteine thiolato group which is consistent with Pearson's hard and soft acids and bases (HSAB) principle.^{2,3} Mercury(II) complexes with sulphur-donor ligands can be used to imitate mercury interactions in biological systems.⁴

A common feature of nitrogen-containing heterocyclic thiones is the thione and thiol tautomerism as

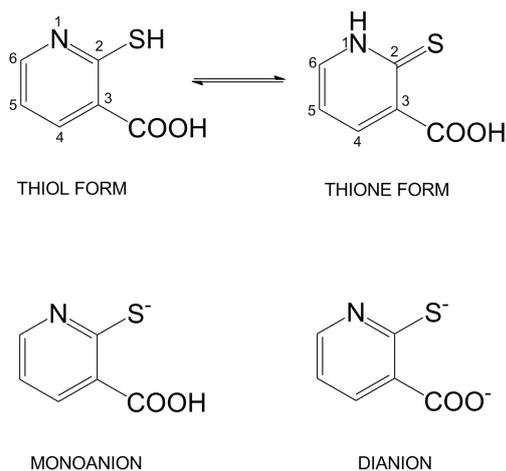
shown for H_2mna in Scheme 1. Furthermore the monoanion and dianion forms of H_2mna can be obtained by deprotonation (Scheme 1).

In the past years complexes of different transition metals with 2-mercaptionicotinic acid have been reported.^{5–16} H_2mna upon deprotonation exhibits three potential binding sites for metal centers. Deprotonated H_2mna can act through the pyridine nitrogen atom, carboxylate or thiolate groups as a monodentate, bidentate or bridging ligand, particularly for transition metal ions. Coordination modes found for the monoanion (a–e) and the dianion (f–h) are shown in Scheme 2.

As a part of our continuous study of mercury(II) complexes with heterocyclic thiones as polyfunctional ligands^{16–26} we investigated the reaction of H_2mna with mercury(II) halides and thiocyanate in ethanol or methanol solutions and in two molar ratios of reactants (1:1 and 2:1). The reaction of mercury(II)

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Scheme 1. Thiol, thione tautomers (with enumeration of atoms), monoanion and dianion forms of the 2-mercaptopyridine-3-carboxylic acid.

acetate and H_2mna in an aqueous-ethanol solution was also investigated. We report here the synthesis and characterization of $Hg(Hmna)_2$ by vibrational spectroscopy and thermal analysis and the crystal structures of uncoordinated H_2mna and of $HgBr_2(CH_3-Hmna)_2$ which were determined by single-crystal X-ray structure analysis.

The structure of free H_2mna was reported earlier in a *Note* describing a silver cluster with 2-mercaptopyridine-3-carboxylic acid, however, the description of H_2mna is very scarce.¹⁰ In addition, in the manuscript there is no mention of the Flack parameter and the absolute structure determination which we have done here.

EXPERIMENTAL

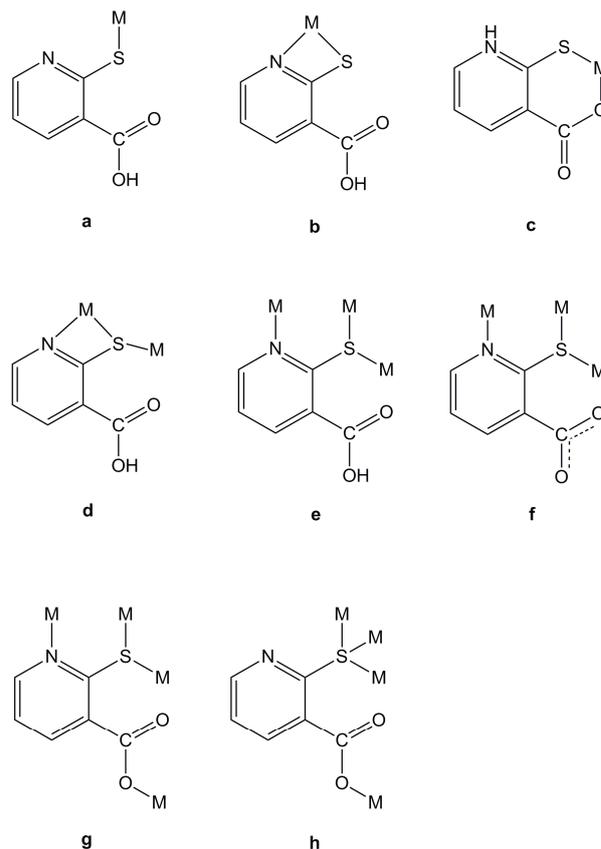
Mercury(II) halides, HgX_2 ($X = Cl^-, Br^-, I^-, SCN^-$), thiocyanate and acetate were supplied by Kemika (Zagreb, Croatia) while 2-mercaptopyridine-3-carboxylic acid was supplied by Aldrich and used without further purification.

Synthesis of Bis(3-carboxypyridine-2-thiolato-S)mercury(II), $Hg(Hmna)_2$

i) from mercury(II) acetate

A solution of 2-mercaptopyridine-3-carboxylic acid (0.97 g, 6.26 mmol) in 200 ml of ethanol was added drop wise to a solution of mercury(II) acetate (1 g, 3.13 mmol) in 50 ml of water (with a few drops of glacial acetic acid). A pale yellow microcrystalline product was filtered off, washed with cold ethanol and dried in air. Yield: 1.49 g (90 %).

Elemental analysis; found (calculated) for $Hg(C_6H_4NO_2S)_2$: C 28.32 (28.46); H 1.71 (1.58); N 5.68 (5.50); S 12.54 (12.60); Hg 39.52 (39.41).



Scheme 2. Coordination modes of 2-mercaptopyridine-3-carboxylic acid found in transition metal complexes.

ii) from mercury(II) salts, HgX_2 ($X = Cl^-, Br^-, I^-, SCN^-$)

An ethanolic or methanolic solution of 2-mercaptopyridine-3-carboxylic acid was added drop wise to an ethanolic or methanolic solution of the corresponding mercury(II) salt in an appropriate molar ratio. A pale yellow microcrystalline product was filtered off, washed with cold ethanol and dried in air. Yield: 85–90 %. Results of the elemental analysis confirmed that the reaction product is always $Hg(C_6H_4NO_2S)_2$.

Synthesis of Dibromobis(3-methoxycarbonylpyridine-2-thiolato-S)mercury(II), $HgBr_2(CH_3-Hmna)_2$

A solution of 2-mercaptopyridine-3-carboxylic acid (0.26 g, 1.69 mmol) in 150 ml of methanol was added drop wise to a solution of the mercury(II) bromide (0.30 g, 0.83 mmol) in 5 mL methanol. $Hg(Hmna)_2$ was filtered off, washed with cold methanol and dried in air. Yield: 0.39 g (90 %). From the filtrate a few crystals of $HgBr_2(CH_3-Hmna)_2$ were obtained in the form of thin needle-shaped stellar conglomerates after two weeks. Unfortunately, the amount was insufficient for elemental and spectroscopic analysis.

Methods

IR and Raman spectroscopy

IR-spectra of KBr pellets were recorded on a Perkin-Elmer FTIR 1600 spectrometer in the 4500–450 cm^{-1} region. The Raman spectra in the range 600–100 cm^{-1} were obtained with a Bruker Equinox 55 spectrometer.

^1H and ^{13}C NMR spectroscopy

The one- and twodimensional homo- and heteronuclear ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini spectrometer, operating at 300.08 MHz for the ^1H nucleus and 75.46 MHz for the ^{13}C nucleus. Samples were measured from DMSO- d_6 solutions at 20 °C (293 K) in 5 mm NMR tubes. Chemical shifts, in ppm, are referred to TMS as internal standard. FID resolution in ^1H NMR and ^{13}C NMR spectra was 0.20 Hz and 0.60 Hz per point, respectively. The following measurement techniques were used: standard ^1H , ^{13}C broadband decoupling, ^{13}C gated proton decoupling, COSY, COSY-45, LRCOSY-45, NOESY and HETCOR.

Thermal analysis

Thermogravimetric analyses were performed using a simultaneous TGA-DTA analyser (Mettler-Toledo TGA/SDTA 851 $^{\circ}$). The samples of about 5 mg in mass were placed in aluminium pans (40 μL). The TGA and DTA curves were obtained with a heating rate of 10 °C min^{-1} and nitrogen flowing at rate of 200 mL min^{-1} . The samples were heated from room temperature up to 600 °C. DSC measurements were performed on a Mettler-Toledo DSC823 $^{\circ}$ module in aluminium pans (40 μL), heated in flowing nitrogen (200 mL min^{-1}) at a rate of 10 °C min^{-1} . The samples were heated from room temperature up to 500 °C. The data collection and analysis was performed using the program package STARE Software 9.01.²⁷

X-ray structural analysis

Single crystals of H₂mna suitable for X-ray diffraction were obtained by recrystallization from dimethylsulfoxide. Data collection was performed on a Philips PW 1100 four circle diffractometer with graphite monochromator and controlled by the program STADI4.²⁸ The data were corrected for Lorentz-polarization effects by the program X-RED.²⁹

It was difficult to obtain single crystals of HgBr₂(CH₃-Hmna)₂ since they had to be broken from stellar conglomerates of thin needle-shaped crystals. Many crystals had to be tested before finding one of good quality for diffraction. The single-crystal X-ray diffraction data were collected by ω -scans on an Oxford Diffraction Xcalibur 3 CCD diffractometer. Data reduction that included an empirical absorption correction using spherical harmonics was performed using the CrysAlisPro software package.³⁰

Solution, refinement and analysis of the structures were done using the programs integrated in the WinGX

system.³¹ The structure of H₂mna was solved by direct methods while that of HgBr₂(CH₃-Hmna)₂ was solved by the Patterson method using SHELXS.³² The refinement procedure was performed by the full-matrix least-squares method based on F^2 against all reflections using SHELXL.³² The non-hydrogen atoms were refined anisotropically. The Flack parameter confirmed the correct absolute structures.³³ Graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) was used for both data collections at room temperature. Details of data collection and crystal structure refinement are given in Table 1.

The hydrogen atoms belonging to the oxygen O2 atom of the COOH group and to the pyridine nitrogen N atom in H₂mna were found in the difference electron-density maps at the end of the refinement procedure as a small electron density with appropriate geometry (O1–H1O 0.90(3) Å, N–H1N 0.86(2) Å). Location of the hydrogen atom at O1 was supported further by the geometry of the COOH group (C6–O2 1.213(2) Å and C6–O1 1.321(3) Å) clearly making difference between single C–O and double C=O bonds.³⁴ The positions of hydrogen atoms belonging to the Csp² atoms were geometrically optimized applying the riding model (Csp²–H 0.93 Å, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$). All hydrogen atoms on the pyridine ring in HgBr₂(CH₃-Hmna)₂ were located in the difference Fourier maps. Because of poor geometry for some of them they were placed in calculated positions and refined using the riding model.

The geometrical calculations and molecular graphics were done with PLATON98³⁵ and Mercury 3.0.³⁶

RESULTS AND DISCUSSION

The reaction of 2-mercaptonicotinic acid with various mercury(II) salts, HgX₂ (X = Cl[−], Br[−], I[−], SCN[−]) in an ethanol or methanol solution irrespectively of the molar ratio of the reactants (1:1 or 1:2) resulted in a thiolato compound of the formula Hg(Hmna)₂. The same compound was obtained from the reaction of mercury(II) acetate in an aqueous-ethanol solution. Unfortunately all attempts to get single crystals by means of recrystallization and by varying experimental conditions have failed. Quite unexpectedly, HgBr₂(CH₃-Hmna)₂ was obtained from the reaction of H₂mna with HgBr₂ in methanol after filtering off the principle product Hg(Hmna)₂. In this complex the ester of 2-mercaptonicotinic acid occurred. Such esterification was observed in solutions containing molybdenum complexes.^{9,37,38}

IR, Raman and NMR spectra

Fundamental vibrational modes for H₂mna and Hg(Hmna)₂ were assigned in accordance with the literature data regarding metal complexes with H₂mna.^{7,8,10,13,39}

Table 1. General and crystal data and summary of intensity data collection and structure refinement for H₂mna and HgBr₂(CH₃-Hmna)₂

Compound	H ₂ mna	HgBr ₂ (CH ₃ -Hmna) ₂
Formula	C ₆ H ₅ NO ₂ S	C ₁₄ H ₁₄ Br ₂ HgN ₂ O ₄ S ₂
<i>M_r</i>	155.17	698.80
Habit and colour	Prism, yellow	Needle, light yellow
Crystal dimension / mm ³	0.36 x 0.28 x 0.22	0.01 x 0.01 x 0.12
Crystal system, space group	Orthorhombic, <i>P na</i> 2 ₁	Orthorhombic, <i>F dd</i> 2
<i>a</i> / Å	8.4075(7)	34.8053(7)
<i>b</i> / Å	13.2916(9)	20.6894(6)
<i>c</i> / Å	5.9031(4)	5.03488(15)
<i>V</i> / Å ³	659.67(8)	3625.62(17)
<i>Z</i>	4	8
<i>D_c</i> / g cm ⁻³	1.562	2.560
<i>μ</i> / mm ⁻¹	0.42	13.151
Temperature / K	298(2)	293(2)
2θ range for data collection / °	3–27	4.2–29.0
<i>h</i> , <i>k</i> , <i>l</i> range	-10 to 10 ; -16 to 16; -7 to 7	-46 to 45, -28 to 26, -6 to 6
<i>F</i> (000)	320	2608
No. independent reflections (<i>R</i> _{int})	1446 (0.020)	2268 (0.049)
No. observed reflections, <i>I</i> ≥ 2σ(<i>I</i>)	1159	1915
<i>R</i> ^a , <i>wR</i> ^b [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0272, 0.0762	0.0329, 0.0565
<i>R</i> , <i>wR</i> [all data]	0.0424, 0.0698	0.0469, 0.0527
Goodness of fit on <i>F</i> ² , <i>S</i> ^c	1.056	1.018
<i>g</i> ₁ , <i>g</i> ₂ in <i>w</i> ^d	0.0373, 0.0638	0.217, 0
Flack parameter	-0.02(9)	-0.030(8)
Max., min. electron density / e Å ⁻³	0.138, -0.167	0.877, -0.485
Maximum Δ/σ	0.001	0.001

$$^{(a)} R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

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

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

$$^{(d)} w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P] \text{ where } P = (F_o^2 + 2F_c^2)/3$$

By comparing the IR and Raman spectra of the free ligand molecule and its metal complex we could conclude about the coordination mode of H₂mna. Characteristic IR bands of H₂mna and Hg(Hmna)₂ are listed in Table 2 (IR spectra can be requested from the authors as supplementary material). The IR spectra shows vibrational bands which have been assigned mainly to C–N modes of the thioamide group (thioamide I and thioamide II) and C–S modes of the thioamide group (thioamide III and thioamide IV).

Absence of the ν(S–H) absorption at ca. 2500 cm⁻¹ in the IR-spectrum of free H₂mna, and presence of the ν(N–H) band at 3187 cm⁻¹ and ν(C=S) at 1143 cm⁻¹, suggests that H₂mna in the solid state exists in the thione rather than the thiol form (Scheme 1). This was also determined by the X-ray structural determination of H₂mna. Position of the band assigned to the ν(C=O)

Table 2. Characteristic IR bands (cm⁻¹) in H₂mna and Hg(Hmna)₂

Assignment	H ₂ mna	Hg(Hmna) ₂
ν(N–H)	3187m	-
ν(C=O)	1688vs	1686vs
δ(N–H)	1621s	-
Thioamide I	1580vs	1572m
ν(C=S)	1143m	1133m
Thioamide II	1320s	1305s
Thioamide III	1075m	1051w
Thioamide IV	639w	650w

carbonyl stretching, in the IR-spectrum of Hg(Hmna)₂ at 1686 cm⁻¹, clearly indicates that the carboxyl group

Table 3. ¹H and ¹³C NMR chemical shifts (δ / ppm)^a, H–H and C–H coupling constants (J / Hz)^b and difference in chemical shifts ($\Delta\delta$ / ppm)^c in thiol and thione tautomers of H₂mna

Molecule Atom		Thiol (TL)	Thione (TN)
H-4	δ	8.26 (1)	8.52 (1)
	J_{HH}	6.8 (d)	6.2 (d)
	$\Delta\delta$		-0.26
H-5	δ	7.29 (1)	7.13 (1)
	J_{HH}	7.5 (d)	6.8 (d)
	$\Delta\delta$		0.16
H-6	δ	8.52 (1)	8.15 (1)
	J_{HH}	4.8 (d)	4.8 (d)
	$\Delta\delta$		0.37
NH	δ		14.57 (1)
	J_{HH}	n.e. ^d	s
	$\Delta\delta$		
COOH	δ	14.57 (1)	14.57 (1)
	J_{HH}	s	s
	$\Delta\delta$		
SH	δ	4.63 (1)	
	J_{HH}	s	n.e. ^d
	$\Delta\delta$		
C-2	δ	159.21	173.62
	J_{CH}	s	s
	$\Delta\delta$		-14.41
C-3	δ	124.54	129.87
	J_{CH}	s	s
	$\Delta\delta$		-5.33
C-4	δ	139.50	144.32
	J_{CH}	167.7 (d)	167.1 (d)
	$\Delta\delta$		-4.82
C-5	δ	120.90	115.41
	J_{CH}	168.9 (d)	176.5 (d)
	$\Delta\delta$		5.49
C-6	δ	152.73	143.58
	J_{CH}	182.8 (d)	187.6 (d)
	$\Delta\delta$		9,15
COOH	δ	167.30	165.71
	J_{CH}	s	s
	$\Delta\delta$		1,59

^a Recorded in DMSO-d₆ solution. Referred to TMS. Number of protons in brackets.

^b (s) singlet, (d) doublet

^c Sign (+) denotes deshielding effect, while (-) denotes shielding effects.

^d Not existing proton in thiol or thione tautomer.

remained protonated and therefore is not coordinated to the mercury atom. Low wavenumbers of the $\nu(\text{C}=\text{O})$ carbonyl stretching bands in the IR spectra of free H₂mna and Hg(Hmna)₂ (1688 cm⁻¹ and 1686 cm⁻¹, respectively) are probably caused by hydrogen bonding

Table 4. ¹H and ¹³C NMR chemical shifts (δ / ppm)^a, H–H and C–H coupling constants (J /Hz)^b and difference in the chemical shifts ($\Delta\delta$ / ppm)^c of bis(pyridine-3-carboxy-2-thiolato-S)mercury and the thiol form of H₂mna

Atom	δ / ppm	J / Hz	$\Delta\delta_{\text{TL}}^{\text{d}}$
H-4	8.12 (1)	7.7 (d)	-0.14
H-5	7.17 (1)	7.7 (d)	-0.12
H-6	8.32 (1)	4.8 (d)	-0.20
COOH	13.24 (1)	s	0
C-2	165.50	12.8 (d)	6.29
C-3	126.32	6.7 (d)	1.78
C-4	139.62	166.4 (d)	0.12
C-5	119.77	168.9 (d)	-1.13
C-6	150.57	182.8 (d)	-2.16
COOH	167.21	s	-0.09

^a Recorded in DMSO-d₆ solution. Referred to TMS. Number of protons in brackets.

^b (s) singlet, (d) doublet

^c Sign (+) denotes deshielding effect, while (-) denotes shielding effects.

^d $\Delta\delta_{\text{TL}}$ means difference between chemical shifts of the complex and the ligand in thiol (TL) form.

in the crystal structure of the compounds. Disappearance of the $\delta(\text{N-H})$ band (1621 cm⁻¹) in the IR-spectrum of Hg(Hmna)₂ indicates that the thiolate is bound to the metal ion.⁴⁰ The thioamide bands I and II are shifted to a lower wavenumber in the IR-spectrum of Hg(Hmna)₂ indicating that the nitrogen atom does not participate in coordination.⁷ The thioamide band III at 1075 cm⁻¹ shifts to a lower wavenumber upon coordination (1051 cm⁻¹). The most significant change has been observed for the thioamide band III and $\nu(\text{C}=\text{S})$, supporting coordination through the ligand sulphur atom.^{10,41}

Information on the Hg–S vibrational modes can be obtained from low frequency Raman spectra. The frequency range of the Raman active Hg–S stretching vibration for mercury(II) thiolates is 400–180 cm⁻¹.⁴² Position of the Hg–S stretching mode depends on the coordination number of mercury. In the Raman spectrum of Hg(Hmna)₂ the medium band at 378 cm⁻¹ is observed. This band can be assigned to a $\nu(\text{Hg-S})$ stretching vibration. One Raman active stretching mode is consistent with the linear coordination of mercury(II). The medium band at 175 cm⁻¹ can be tentatively assigned to $\delta(\text{S-Hg-S})$ bending.

Assignment of the NMR spectra of the free ligand in both tautomeric forms and its mercury(II) complex are shown in Tables 3 and 4, respectively. The enumeration of carbon atoms are displayed in Scheme 1.

Signals in the ¹H NMR spectra of 2-mercaptopyridine-3-carboxylic acid in DMSO-d₆ correspond to the thione tautomer form, what is in agreement with literature

data⁴³ for similar compounds. The very broad ¹H signal belongs to both NH and COOH protons of 2-mercaptionicotinic acid. This was proven by addition of a small amount of Na₂CO₃ which neutralizes the acid and interrupts the hydrogen bonding as was revealed by an upfield shift of the NH proton.

The thiol form appears after a few weeks in a DMSO-d₆ solution or immediately by addition of HCl.

As expected, the chemical shifts of thiol and thione forms are different. The shielding effect of the C=S group upon the H-5 atom in the thione form is greater than that of the C-SH group upon H-5 atom in the thiol form, both being in the *para* position to the H-5.

The chemical shifts (δ /ppm) and the C-H coupling constants (J_{CH}/Hz) in ¹³C NMR spectra of 2-mercaptionicotinic acid in DMSO-d₆ solution also correspond to the thione form. Two-bond deuterium isotope effect from N-D to C-6 is observed, amounting to 40 ppb, while four-bond deuterium isotope effect on the carboxyl carbon atom is not detected.

The ¹H and ¹³C NMR spectra of bis(pyridine-3-carboxy-2-thiolato-*S*)mercury(II), Hg(Hmna)₂ in DMSO-d₆ solution are similar to the spectra of the ligand molecule in the thiol form, which corroborates that the ligand in the mercury complex is in the thiol rather than in the thione form. The NMR data display that both a number of hydrogen and carbon atoms in complex are sensitive to mercury binding.⁴⁴ Thus in the mercury complex the COOH proton is shifted upfield, which can be clearly seen since there is no NH proton in the thiol form to overlap with COOH. A considerable downfield shift, amounting to 6.3 ppm at the C-2 carbon in Hg(Hmna)₂ and upfield shifts at C-6 and C-5 atoms, with the fact that the chemical shift of the COOH carbon barely changed, is consistent with *S*-bonded ligand to mercury. In the case of *N,S*-chelation, a downfield shift of C-6 should be observed.^{7,9}

Thermal Analysis

TG and DSC analysis of H₂mna and Hg(Hmna)₂ were also performed. The samples were heated from room temperature to 600 °C (TG) and from room temperature to 500 °C (DSC). TG curve of H₂mna show two degradation steps. Small mass loss (approx. 5 %) due to the sublimation of H₂mna is observed in the first step. This step is represented by an endothermic peak at 233 °C on the DSC curve. Endothermic minima at 261 °C with a corresponding mass loss of 90 % represents almost complete degradation of H₂mna. Degradation of Hg(Hmna)₂ proceeds over two overlapping steps in the range 253–555 °C. The first step corresponding to the elimination of both ligands without the sulphur atoms is represented by two endothermic DSC peaks at 254 and 261 °C. A broad endothermic peak at 408 °C on the DSC curve of Hg(Hmna)₂ corresponds to the thermal

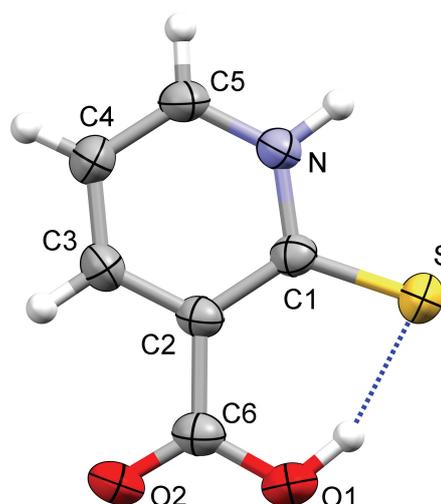


Figure 1. Molecular structure of 2-mercaptionicotinic acid, H₂mna, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are drawn as small circles of arbitrary radius. The intramolecular hydrogen bond is shown as a blue dashed line.

degradation of HgS followed by evaporation of mercury.

Crystal Structure of H₂mna

2-mercaptionicotinic acid (Scheme 1, Figure 1) exists in the crystalline state in the thione tautomeric form as it was previously established by vibrational spectroscopy according to the absence of the SH vibration characteristic for the thiol form, by the presence of the NH vibration band⁹ and also from the previously reported crystal structure.¹⁰ The thione tautomer is established to be the dominant form in the crystalline state for heterocyclic thiones.

Bond distances and valence angles are given in Tables 5 and 6, respectively. The molecule is planar with the greatest deviation of the atom O2 of 0.059(2) Å

Table 5. Selected bond distances/Å in H₂mna and HgBr₂(CH₃-Hmna)₂

H ₂ mna			
O1–C6	1.321(3)	S–C1	1.7034(18)
O2–C6	1.217(3)	N–C1	1.369(3)
		N–C5	1.343(3)
HgBr ₂ (CH ₃ -Hmna) ₂			
Hg–Br	2.7602(7)	S–C1	1.710(6)
Hg–S	2.4587(14)	N–C1	1.366(7)
O1–C6	1.188(7)	N–C5	1.330(7)
O2–C6	1.331(6)		
O2–C7	1.465(8)		

Table 6. Selected bond angles/^o in H₂mna and HgBr₂(CH₃-Hmna)₂

H ₂ mna			
C1–N–C5	125.03(19)	S–C1–C2	127.60(18)
N–C1–C2	115.43(17)	S–C1–N	116.97(17)
N–C5–C4	120.2(2)	O1–C6–C2	118.87(19)
		O2–C6–C2	121.33(19)
		O1–C6–O2	119.8(2)
HgBr ₂ (CH ₃ -Hmna) ₂			
Br–Hg–S	100.35(4)	S–C1–C2	124.8(4)
Br–Hg–Br ⁱ	98.87(2)	S–C1–N	120.6(3)
Br–Hg–S ⁱ	110.87(4)	O1–C6–C2	126.2(5)
S–Hg–S ⁱ	131.33(5)	O2–C6–C2	110.0(5)
Hg–S–C1	110.01(18)	O1–C6–O2	123.8(5)
C1–N–C5	125.7(4)	C6–O2–C7	115.3(5)
N–C1–C2	114.7(5)		
N–C5–C4	120.4(5)		

ⁱ Symmetry transformation used to generate equivalent atoms: (i) 3/2 – x, 1/2 – y, z

from the least-squares plane through the ring atoms. The C_{ar}–S bond distance of 1.703(2) Å corresponds to a C–S bond of significant π-character within the structures of heterocyclic thiones (the average value is 1.671 Å for the Csp²=S bond distance type in the structural fragment (X)₂–C=S where X = C, N, O, S)³⁴ and can be regarded as a thioketo bond. According to the literature⁴⁵ the bond length of 1.703(2) Å possesses 50 % of π-character. The pyridine ring C_{ar}–C_{ar} bond lengths exhibit a quinoid character with the longest C1–C2 bond distance of 1.421(3) Å.

Hydrogen bond geometry is listed in Table 7. The thione S atom forms a six-membered pseudo-aromatic chelate ring by an intramolecular hydrogen bond of the O–H...S type with the OH group of the carboxyl moiety (2.895(2) Å). The molecules are connected by the intermolecular N–H1...O2 (1/2 + x, 1/2 – y, –1 + z) hydrogen bonds into infinite chains (Figure 2) spreading parallel to the [102] direction alternating along the b-axis (shifted by b/2) with chains parallel to the [10-2] direction. The formation of such intra- and intermolecular

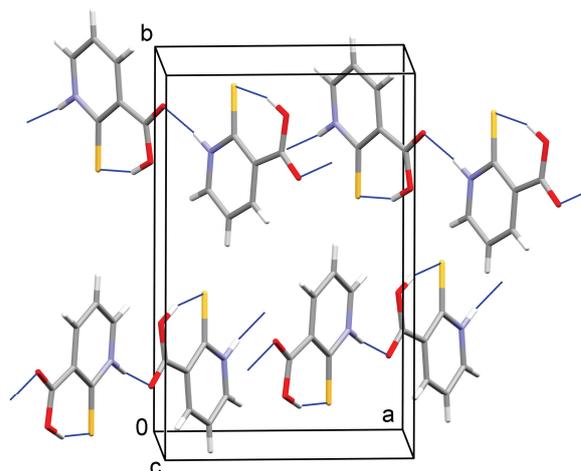


Figure 2. H₂mna molecules connected into chains by hydrogen bonds. The dotted blue lines indicate intramolecular O1–H...S and intermolecular N–H...O2ⁱ (i = 1/2 + x, 1/2 – y, –1 + z) hydrogen bonds.

hydrogen bonds compensate the energetically less favoured thione form. Namely, the SH group is less acidic than the NH group *i.e.* it is not such a good proton donor group in the hydrogen bond formation.

Crystal Structure of HgBr₂(CH₃-Hmna)₂

In the crystal structure of HgBr₂(CH₃-Hmna)₂ the mercury atom lies on a two-fold axis and is coordinated by two sulphur atoms from two 3-methoxycarbonylpyridine-2-thiolato ligands and by two bromine atoms in a deformed tetrahedral arrangement (Figure 3, Tables 5 and 6). The smallest angle within the tetrahedron is that of Br–Hg–Br (3/2 – x, 1/2 – y, z) of 98.87(2)^o, while the greatest one is S–Hg–S (3/2 – x, 1/2 – y, z) of 131.33(5)^o. The *Cambridge Structural Database*⁴⁶ search gave 28 structures with the mercury atom tetrahedrally coordinated by two sulphur atoms and two bromine atoms. In these structures the bond lengths vary significantly and appear in a wide range, Hg–S 2.45 to 3.19 Å and Hg–Br 2.38 to 3.01 Å. In the present structure the Hg–S

Table 7. Hydrogen bonds in H₂mna and HgBr₂(CH₃-Hmna)₂

D–H...A	D–H / Å	H...A / Å	D...A / Å	∠D–H...A / °	Symmetry code
H ₂ mna					
N–H1...O2	0.94(3)	1.88(3)	2.813(3)	172(2)	
O1–H1...S	0.97(3)	1.98(3)	2.8952(19)	157(3)	
C5–H5...O1	0.93	2.567	3.279(3)	134	1/2 + x, 1/2 – y, –1 + z
HgBr ₂ (CH ₃ -Hmna) ₂					
N–H1...Br	0.86	2.43	3.274(4)	167	
C5–H5...O1	0.93	2.48	3.245(8)	140	5/4 – x, 1/4 + y, 5/4 + z

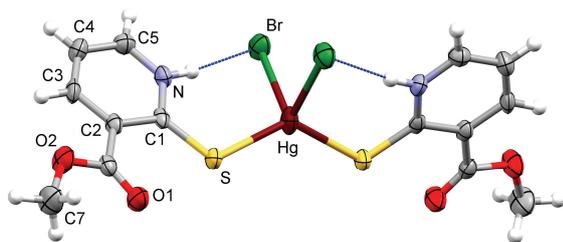


Figure 3. Molecular structure of $\text{HgBr}_2(\text{CH}_3\text{-Hmna})_2$, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are drawn as small circles of arbitrary radius. Intramolecular hydrogen bonds are shown as blue dotted lines.

distance of 2.4587(14) Å is among the shortest values. This bond distance is shorter than the sum of covalent radii of S and tetrahedral Hg (2.53 Å) but longer than the linear Hg–S bond (2.34 Å).^{47,48} Similar values we have observed previously¹⁸ in the structure of dibromobis(1,3-imidazole-2-thione), (Hg–S 2.453(2) Å, Hg–Br 2.7815(9) Å, S–Hg–S 134.80(10)° and Br–Hg–Br 95.25(4)°) and in dibromobis(3,4,5,6-tetrahydropyrimidine-2-thione)²¹ (Hg–S 2.431(2) and 2.467(2) Å, Hg–Br 2.734(1) and 2.732(1) Å, S–Hg–S 138.82°, Br–Hg–Br 105.56(3)°). In dibromobis(1,3-benzothiazole-2-thione)mercury(II)²⁶ the two Hg–Br distances are significantly different with the bromine atom forming

the longer bond being involved in hydrogen bonding (Hg–Br 2.758(1) and 2.546(2) Å, Hg–S 2.493(3) and 2.494(3) Å, S–Hg–S of 124.42(10)°, Br–Hg–Br 113.63(4)°). In the present structure the bromine atoms are involved in intramolecular hydrogen bonding (Table 7, Figure 4). There are only weak contacts of the C–H···O type between the molecules.

The $\text{Csp}^2\text{-S}$ bond distance of 1.710(6) Å is lengthened in relation to the distance found in free H_2mna due to metal coordination. The lengthening is caused by reduction of the π character of the C–S bond. The $\text{CH}_3\text{-Hmna}$ ligand is more distorted from planarity, the deviation of the atom O2 is 0.298(4) Å from the least-squares plane through the ring atoms.

CONCLUSION

The reaction of 2-mercaptonicotinic acid with various mercury(II) salts, HgX_2 ($\text{X} = \text{Cl}^-$, Br^- , I^- , SCN^-) in an ethanol or methanol solution irrespectively of the molar ratio of the reactants (1:1 or 1:2) resulted in the mercury complex, $\text{Hg}(\text{Hmna})_2$, with two ligands of 2-mercaptonicotinic acid linearly bound through the S-atom. The same compound was obtained from the reaction of mercury(II) acetate in an aqueous-ethanol solution.

The absence of the $\nu(\text{S-H})$ absorption at 2500 cm^{-1} in the IR-spectrum of the free H_2mna , and pres-

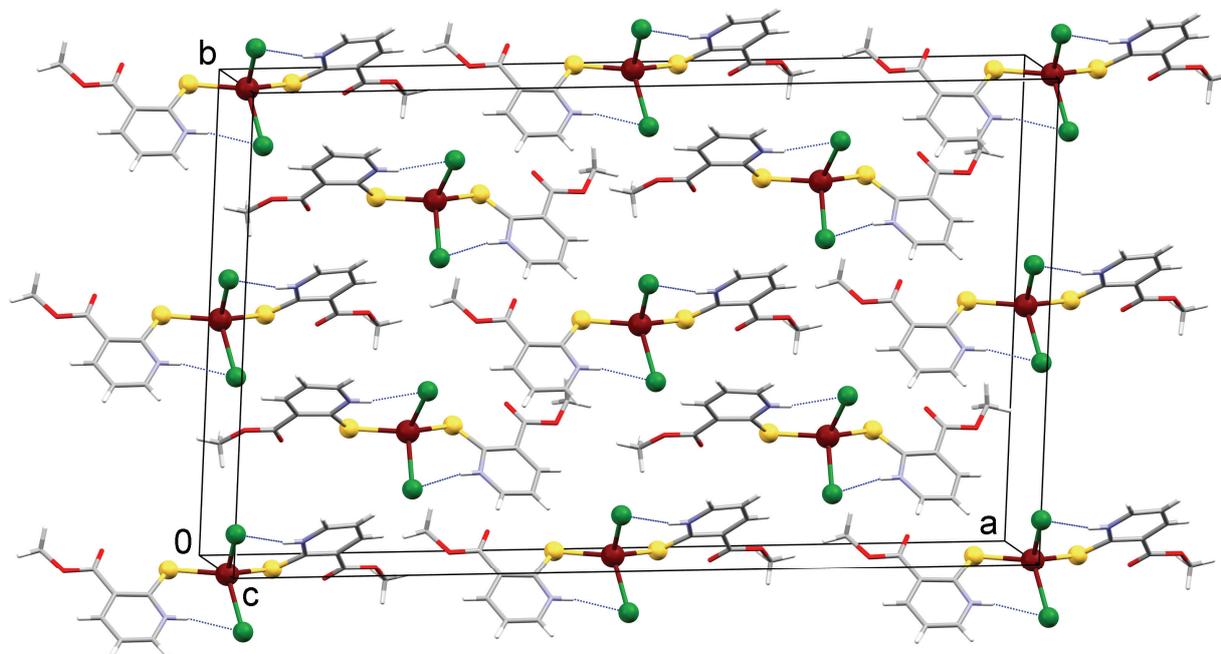


Figure 4. Packing of $\text{HgBr}_2(\text{CH}_3\text{-Hmna})_2$ molecules in the unit cell. The dotted blue lines indicate intramolecular N–H···Br hydrogen bonds.

ence of the $\nu(\text{N-H})$ band at 3187 cm^{-1} and $\nu(\text{C=S})$ band at 1143 cm^{-1} indicates that the H_2mna exists as thione tautomer in the solid state as revealed by the X-ray structure analysis. ^1H and ^{13}C NMR spectra of the free H_2mna confirm that the thione form is the dominant form in the DMSO solution. The thiol form forms after a few weeks in a DMSO- d_6 solution or immediately by addition of HCl. $\text{HgBr}_2(\text{CH}_3\text{-Hmna})_2$ was obtained from the reaction of H_2mna with HgBr_2 in methanol after filtering off the main product $\text{Hg}(\text{Hmna})_2$. The crystal structure of $\text{HgBr}_2(\text{CH}_3\text{-Hmna})_2$ revealed a tetrahedral coordination sphere around the mercury atom consisting of two bromine atoms and two S-bound 3-metoxycarbonylpyridine-2-thiolato ligands. IR and NMR spectroscopic data are consistent with coordination of the H_2mna through sulphur atom in the solid state, and also in the DMSO solution of the $\text{Hg}(\text{Hmna})_2$.

Supplementary Materials. – The crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary material with the deposition numbers: CCDC 649287 for H_2mna and CCDC 891562 for $\text{HgBr}_2(\text{CH}_3\text{-Hmna})_2$. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/const/retrieving.html>.

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