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Original Scientific Paper

Binding of Mercury(II) by *N*-(2-mercaptopropionyl)glycine. Synthesis, IR and NMR Characterization. Crystal Structure of the 1:2 Solvate of Bis[*N*-(propionyl-2-thiolato)-glycine]mercury(II) with 4-Methylpyridine*

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Bis[*N*-(propionyl-2-thiolato)glycine]mercury(II), $Hg[SCH(CH_3)CONHCH_2COOH]_2$, was obtained by the reaction of an aqueous solution of *N*-(2-mercaptopropionyl)glycine and mercury(II) acetate. From the 4-methylpyridine (γ-picoline) solution it crystallizes as a 1 : 2 solvate, $Hg[SCH(CH_3)CONHCH_2COOH]_2 \cdot 2C_6H_7N$, in the triclinic system, space group $P\bar{1}$ with a = 4.810(5) Å, b = 9.711(4) Å, c = 15.615(8) Å, α = 105.76(4)°, β = 103.44(4)°, γ = 94.01(4)°, Z = 1, R = 0.027. Two *N*-(propionyl-2-thiolato)glycine molecules are bonded centrosymmetrically to mercury over sulfur atoms as mercaptide at a distance of 2.341(2) Å. $Hg(mpgH)_2$ molecules are connected by centrosymmetrically related hydrogen bonds N1–H···O3 of 2.922(5) Å into chains along [100]. Each molecule also forms two hydrogen bonds O1–H···N2 of 2.612(6) Å with two γ-picoline molecules. The structure of complexes and binding to sulfur were substantiated by ^1H and ^{13}C NMR spectroscopy on the basis of mercury induced chemical shifts, H–H and C–H coupling constants and connectivities in twodimensional homo- and heteronuclear correlated spectra.

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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Key words: mercury(II), *N*-(2-mercaptopropionyl)glycine, bis[*N*-(propionyl-2-thiolato)glycine]mercury(II), X-ray crystal structure, IR spectra, one- and twodimensional homo- and heteronuclear ^{1}H and ^{13}C NMR spectra.

INTRODUCTION

The binding of metal ions by peptides and proteins is of fundamental interest in view of the importance of metal ions in biological systems. Peptides and proteins are composed of a number of functional groups, many of which are potential coordination sites, as shown by studies on metal binding of simple amino acids and other model compounds. *N*-(2-mercaptopropionyl)-glycine, $mpgH_2$, in the complex with Ni^{2+} acts as a terdentate ligand with the coordination sites being the sulfur, the peptide nitrogen and also the carboxylate group.[1]

Later investigation revealed extensive polynuclear complex formation in equimolar solutions with sulfhydryl bridging.[2] The most outstanding feature of $mpgH_2$ ligand is the ability to chelate Cu^{2+} without reduction to Cu^{+} and oxidation to disulfide.[3] Sulfhydryl ligands have an extremely high affinity for mercury. It is thought that all the inorganic mercury in the blood and tissues of humans is bound to sulfhydryl groups of cysteine-containing peptides and proteins. However, even though the thermodynamic stability of Hg(II)-thiol complexes is high, Hg(II) in biological systems must be labile since exchanging among multitude of sulfhydryl groups occurs. It combines with sulfhydryl groups of enzymes and other molecules that are dependent on free thiol groups for their activity. The labile nature of Hg(II)-thiol binding in biological systems is also evidenced from the fact that sulfhydryl compounds like 2,3-dimercaptopropanol (British anti-Lewisite, BAL), penicillamine (β,β-dimethylcysteine) and *N*-(2-mercaptopropionyl)glycine extract Hg(II) from its thiolate complexes in the fluids and tissues of the body.[4,5] These compounds are known as antidotes against mercury poisoning. The lability of Hg-thiol binding in cells is evidenced also from ^{1}H NMR studies of Hg(II) binding in intact human erythrocytes,[6] and from ^{13}C NMR studies of the coordination chemistry and kinetics of Hg(II) with cysteine, penicillamine and glutathione ligands.[7] The stability constants of some mercury(II) complexes with sulfhydryl ligands were found to be of the order $10^{35} - 10^{44}$,[8,9] with BAL being the most stable and *N*-acetyl-D,L-penicillamine the least stable.[8] The stability of the complex with BAL is thought to be connected to the fact that it has two –SH groups which can bind to mercury.

Mercury(II) complexes of $mpgH_2$ and related compounds have been isolated already but their structures have been studied only with infrared spectroscopy.[10]

We report here on the preparation and characterization by IR and ^{1}H and ^{13}C NMR spectroscopies of $Hg[SCH(CH_3)CONHCH_2COOH]_2$, ($Hg(mpgH)_2$) and its 1:2 solvate with γ-picoline $Hg[SCH(CH_3)CONHCH_2COOH]_2 \cdot 2C_6H_7N$, ($Hg(mpgH)_2 \cdot 2\gamma$-pic). The X-ray crystal structure of $Hg(mpgH)_2 \cdot 2\gamma$-pic is described.

EXPERIMENTAL

Reagents and Apparatus

N-(2-mercaptopropionyl)glycine and mercury(II) acetate (Aldrich) were used as received. The IR spectra were recorded on a Perkin-Elmer 1600 Fourier transform spectrophotometer, with samples compressed in KBr discs in the region of 4000–450 cm^{-1}.

The ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini 300 spectrometer, operating at 75.46 MHz for the ^{13}C nucleus. The samples were dissolved in DMSO-d_6 and measured at 20 °C in 5 mm NMR tubes. Concentrations of samples were 0.1 mol dm^{-3} for ^{1}H and 0.3 mol dm^{-3} for ^{13}C measurments. Chemical shifts (δ/ppm) are referred to TMS. Digital resolution was 0.3 Hz per point in ^{1}H and 0.7 Hz per point in ^{13}C NMR onedimensional spectra. The techniques used were: ^{13}C broadband proton decoupling, normal and inverse ^{13}C gated decoupling, COSY-45, long-range COSY-45, NOESY and HETCOR. The COSY-45 spectra were recorded in the magnitude mode with 1024 points in F2 dimension and 256 increments in F1 dimension, zero-filled to 1024 points. Increments were measured with 16 scans, 4500 Hz spectral width and a relaxation delay of 1 s. The resolution was 8.9 Hz/point and 17.6 Hz/point in F2 and F1 dimensions, respectively. The long-range COSY-45 was measured with 5000 Hz spectral width. Digital resolution was 9.8 Hz/point in F2 and 19.5 Hz/point in F1, while delay time (*D*3) was 0.2 s. The NOESY spectra were recorded in phase-sensitive mode with mixing times 0.4–0.6 s and all other measurement parameters as for COSY spectra. The HETCOR spectra were recorded with 2048 points in F2 dimension and 256 increments in F1 dimension, which were zero-filled to 512 points. Increments were obtained using 128 scans, relaxation delay of 1 s and spectral widths of 19000 Hz in F2 and 4500 Hz in F1 dimensions, respectively. The resolution was 18.6 Hz/point in F2 dimension and 17.6 Hz/point in F1 dimension. The proton decoupling was performed with Waltz-16 modulation.

Synthesis and Characterization of Complexes

Preparation of $Hg[SCH(CH_3)CONHCH_2COOH]_2$, $Hg(mpgH)_2$

Aqueous solution of *N*-(2-mercaptopropionyl)glycine (0.65 g, 4 mmol in 10 ml) was slowly added to an aqueous solution of mercuric acetate (0.64 g, 2 mmol in 20 ml with a few drops of 2 mol dm^{-3} acetic acid). The reaction mixture was left overnight. The colourless microcrystalline needles were collected by filtration, washed with ethanol and dried in air. Yield: quantitative.

Anal. calcd. for $C_{10}H_{16}S_2N_2O_6Hg$ (M_r = 524.97): C, 22.88; H, 3.07; S, 12.21; N, 5.33; Hg, 38.21%. Found: C, 22.64; H, 3.17; S, 12.14; N, 5.27; Hg, 38.29%. Unfortunately, these needles were not of good quality for X-ray structure analysis.

Preparation of Hg[SCH(CH$_3$)CONHCH$_2$COOH]$_2$ · 2C$_6$H$_7$N, Hg(mpgH)$_2$ · 2γ-pic

Beautiful transparent prismatic crystals of Hg(mpgH)$_2$ · 2γ-pic, suitable for X-ray determination, crystallize from the γ-picoline solution of Hg[SCH(CH$_3$)-CONHCH$_2$COOH]$_2$.

Anal. calcd. for $C_{22}H_{30}S_2N_4O_6Hg$ (M_r = 711.21): C, 37.15; H, 4.25; S, 9.02; N, 7.88; Hg, 28.20%. Found: C, 37.22; H, 4.37; S, 9.10; N, 7.91; Hg, 28.33%.

X-ray Data Collection and Structure Determination of Hg(mpgH)$_2$ · 2γ-pic

Data Collection

Data were collected at 293 K on the Philips PW1100 diffractometer (updated by Stoe) with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). Four standard reflections monitored every 2 h indicated decay amounting to 3.7%. Cell dimensions were based on setting angles of 34 reflections ($13.4 \leq \theta \leq 19.6°$). Data were corrected for decay, Lorentz, polarization and absorption effects.[11] Additional data are given in Table I.

Crystal Structure Determination

The structure was solved by Patterson and Fourier methods. It was refined by the full-matrix least-squares procedure on F^2 with anisotropic temperature factors for all non-hydrogen atoms and isotropic for the hydrogen atoms in the mpgH$^-$ ligand. All hydrogen atoms in mpgH$^-$ were located in the difference Fourier map, while those from 2γ-pic were generated geometrically using the riding model with the isotropic factor set at 1.2 U_{eq} or 1.5 U_{eq} of the parent C sp^2 or C sp^3 atom, respectively. The atomic coordinates and equivalent isotropic displacement parameters are given in Table II. All calculations were performed on an IBM compatible computer using SHELXS-97,[12] SHELXL-97,[13] PLATON[14] and ORTEPIII[15] programs. ORTEP presentation of the Hg(mpgH)$_2$ molecule with the atom numbering scheme is shown in Figure 1.

RESULTS AND DISCUSSION

Soft mercury(II) ions are known to show a strong affinity for sulfhydryl groups. From the observed absorption bands in infrared spectra of Hg(mpgH)$_2$ and Hg(mpgH)$_2$ · 2γ-pic, (selected ones are presented in Table III), one can presume that mercury atom is linked with the mpgH$_2$ molecules through the sulfur atoms as mercaptide due to disappearance of ν(SH). In the spectra of both complexes no significant shift of the amide bands was observed with respect to the free mpgH$_2$ molecule (see Table III), which indicates non-participation of peptide nitrogen in coordination. IR bands of weak to medium intensity, indicative of hydrogen bonding,[16–19] are found between 3000 and 1900 cm^{-1}. A closer inspection reveals several relatively broad bands centered at about 1900, 2500 and 2900 cm^{-1}.

TABLE I

Crystal data and structure refinement parameters for $Hg(mpgH)_2 \cdot 2\gamma$-pic

Empirical formula	$C_{22}H_{30}HgN_4O_6S_2$
Formula weight	711.21
Temperature / K	293(2)
Wavelength / Å	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a /Å	4.810(5)
b /Å	9.711(4)
c /Å	15.615(8)
α /°	105.76(4)
β /°	103.44(4)
γ /°	94.01(4)
V / Å^3	675.8(8)
Z	1
D_{calc} / g cm^{-3}	1.748
D_{exp} / g cm^{-3}	1.76
μ / mm^{-1}	5.891
F(000)	350
Face indices, distancesfrom centroid / mm	(110), (–1–10) 0.1982
	(011), (0–1–1) 0.1699
	(001), (00–1) 0.0637
Transmission coeff. (min., max.)	0.1007; 0.5297
Theta range for data collection /°	2.81 to 30.00
Index ranges	$-6 \le h \le 6$, $-13 \le k \le 13$, $0 \le l \le 21$
Reflections collected	4071
Independent reflections	3937 [R_{int} = 0.0149]
Refinement method	Full-matrix least-squares on F^2
Data [$I > 2\sigma(I)$] / restraints / parameters	3797 / 0 / 193
Goodness of fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0273, $wR2$ = 0.0705
R indices (all data)	$R1$ = 0.0295, $wR2$ = 0.0718
Largest diff. peak and hole	1.315 and –1.428 e Å^{-3}

TABLE II

Atomic coordinates and equivalent isotropic displacement parameters, U_{eq},[a] for $Hg(mpgH)_2 \cdot 2\gamma$-pic

	x	*y*	*z*	U_{eq} / Å^2
Hg	0.0000	0.0000	0.0000	0.03988(6)
S	0.37814(18)	–0.05761(8)	0.10307(5)	0.0398(2)
C1	0.5466(11)	–0.3146(5)	0.1197(3)	0.0533(9)
C2	0.3391(7)	–0.2553(3)	0.0538(2)	0.0342(5)
C3	0.4020(6)	–0.2874(3)	–0.0401(2)	0.0312(5)
O3	0.6514(5)	–0.2791(3)	–0.0486(2)	0.0420(5)
N1	0.1717(6)	–0.3246(3)	–0.1127(2)	0.0391(5)
C4	0.2024(9)	–0.3516(6)	–0.2054(3)	0.0543(10)
C5	–0.0369(7)	–0.4619(4)	–0.2752(2)	0.0429(7)
O1	–0.0171(10)	–0.4811(5)	–0.3588(2)	0.0897(16)
O2	–0.2244(9)	–0.5216(5)	–0.2555(2)	0.0904(15)
N2	0.5856(8)	0.3230(4)	0.5162(2)	0.055(1)
C6	0.581(2)	0.2838(9)	0.4292(4)	0.126(4)
C7	0.4037(14)	0.1665(7)	0.3632(3)	0.078(2)
C8	0.2343(12)	0.0823(6)	0.3870(3)	0.070(1)
C9	0.240(3)	0.1268(13)	0.4782(5)	0.209(8)
C10	0.4184(18)	0.2459(9)	0.5407(4)	0.116(3)
C11	0.045(2)	–0.0493(10)	0.3176(5)	0.136(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

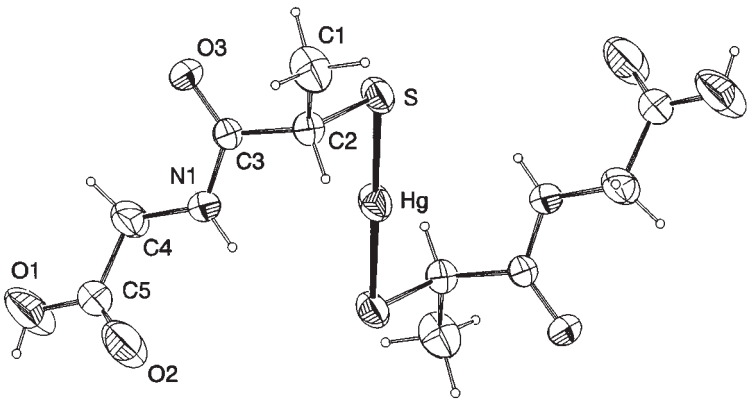

Figure 1. ORTEP presentation of the $Hg(mpgH)_2$ molecule in $Hg(mpgH)_2 \cdot 2\gamma$-pic with the atom numbering scheme. Ellipsoids are drawn at the 50% probability level.

TABLE III

Characteristic infrared absorption bands of *N*-(2-mercaptopropionyl)glycine and its mercury(II) complexes

	Observed bands[a] / cm^{-1}			
	ν(NH)	ν(SH)	ν(COOH)	ν(C=O) + ν(CN)
$mpgH_2$	3317 (s,br)	2529 (m)	1754 (vs)	1620 (vs), 1556 (vs)
$Hg(mpgH)_2$	3296 (s,br)	–	1732 (vs)	1620 (vs), 1556 (vs)
$Hg(mpgH)_2 \cdot 2\gamma$-pic	3294 (m,br)	–	1724 (m)	1626 (vs), 1554 (m)

[a] Intensity designations: vs, very strong; s, strong; m, medium; br, broad.

The structure of *N*-(2-mercaptopropionyl)glycine (**1**) and its mercury complexes $Hg[SCH(CH_3)CONHCH_2COOH]_2$ (**2**), and $Hg[SCH(CH_3)CONHCH_2COOH]_2 \cdot 2C_6H_7N$ (**3**) was determined in solution by ^1H and ^{13}C spectroscopy. Introduction of mercury into organic molecules is often studied on the basis of ^{199}Hg–^1H and ^{199}Hg–^{13}C satellites in ^1H and ^{13}C NMR spectra. However, this was not possible here due to the binding of mercury to the sulfur atom.[20,21] Namely, these satellites cannot be detected if heteroatoms (O, S, N, *etc.*) are involved in the coupling pathway between mercury and hydrogen or carbon.[22] Therefore, the site of mercury binding in the complexes investigated here was deduced from the change of the ^1H and ^{13}C chemical shifts, H–H and C–H multiplicities and coupling constants as well as connectivities in twodimensional homo- and heteronuclear correlated spectra. The ^1H and ^{13}C NMR data for the parent molecule **1**, and its complexes **2** and **3**, measured in dimethylsulphoxide solution, are collected in Tables IV and V, respectively.

The ^1H NMR spectrum of *N*-(2-mercaptopropionyl)glycine displays six signals. The signal of the COOH proton is significantly broadened and of low intensity, due to the fast proton exchange with water, present in the dimethylsulphoxide solution, as well as with other solute molecules. Contrary to that, the NH proton does not participate in H-bonding at concentrations used here since its signal is sharp, displaying triplet splitting. It is due to the spin-spin coupling with protons of methylene group, though they show slight chemical non-equivalency. The latter arises because of hindered rotation of glycine moiety with respect to the 2-mercaptopropionyl group. The methine proton diplays a complex H–H multiplet pattern, while the SH proton doublet is centered at 2.86 ppm. These assignments were supported by COSY and long-range (delayed) COSY as well as NOESY spectra.

Only five signals are present in the ^1H NMR spectrum of **2** since the proton of the SH group is replaced by mercury. In addition, the signals of all

TABLE IV

^{1}H NMR chemical shifts (δ/ppm),[a] H–H coupling constants (J/Hz)[b] and binding shifts ($\Delta\delta$/ppm)[c] in **1** and its complexes **2** and **3**[d]

Molecule		**1**	**2**	**3**
CH	δ	3.54 (m)	4.05(q)	4.08(q)
	J_{HH}	–	6.9	6.0
	$\Delta\delta$		0.51	0.54
SH	δ	2.86(d)	–	–
	J_{HH}	5.0	–	–
CH_2	δ	3.81(d); 3.73(d)	3.83(d); 3.75(d)	3.85(d); 3.75(d)
	J_{HH}	5.9; 17.7	5.8; 18.4	6.2; 17.7
	$\Delta\delta$	–	0.02; 0.02	0.04; 0.02
CH_3	δ	1.36(d)	1.44(d)	1.44(d)
	J_{HH}	6.9	6.9	6.4
	$\Delta\delta$	–	0.08	0.08
CONH[e]	δ	8.31(t)	8.54(t)	8.55(t)
	J_{HH}	5.5	5.6	5.6
	$\Delta\delta$	–	0.23	0.24
COOH[f]	δ	12.56	12.66	–
	$\Delta\delta$	–	0.10	–

[a] Referred to TMS in DMSO solutions; (d) doublet, (t) triplet, (q) quartet.

[b] Digital resolution ±0.3 Hz.

[c] Binding shifts are defined as the difference of proton chemical shifts in the mercury complex and the parent molecule.

[d] The chemical shifts of γ-pic moiety are: H-2,6 = 8.42 ppm, ^3J = 5.0 Hz; H-3,5 = 7.21 ppm, ^3J = 5.0 Hz; CH_3 = 2.32 ppm.

[e] The amide proton signal appears as a triplet at the magnetic field of 7.05 T.

[f] Signal is very broadened.

protons are more or less shifted downfield relatively to the corresponding ones in **1**, due to the electron withdrawing effect of mercury. The greatest change of the ^{1}H chemical shift in **2**, as compared to the parent compound, was observed for the CH proton. The binding shift ($\Delta\delta$) of the CH proton, which is three bonds away from mercury, amounts to 0.51 ppm, *i.e.* 153 Hz (digital resolution ± 0.3 Hz). The NH proton shows *ca.* two times greater $\Delta\delta$ (0.23 ppm = 69 Hz) than the CH_3 protons (0.08 ppm = 24 Hz), though the former is five, while the latter four bonds away from mercury. One can con-

TABLE V

^{13}C NMR chemical shifts (δ/ppm),[a] C–H coupling constants (J/Hz)[b] and binding shifts ($\Delta\delta$/ppm)[c] in **1** and its complexes **2** and **3**[d]

Molecule		**1**	**2**	**3**
CH	δ	36.02 (d)	39.78 (d)	39.62 (d)
	J_{CH}	143.2 (1)	141.2 (1)	141.4 (1)
	$\Delta\delta$	–	3.76	3.60
CH_2	δ	40.92 (t)	41.42 (t)	41.06 (t)
	J_{CH}	138.0 (1)	139.0 (1)	138.9 (1)
	$\Delta\delta$	–	0.50	0.14
CH_3	δ	22.14 (q)	25.92 (q)	26.24 (q)
	J_{CH}	129.9 (1)	128.7 (1)	128.9 (1)
	$\Delta\delta$	–	3.78	4.10
CONH	δ	173.36 (m)	177.18 (m)	177.48 (m)
	J_{CH}	–	–	–
	$\Delta\delta$	–	3.82	4.12
COOH	δ	171.47 (t)	171.57 (t)	171.36 (t)
	J_{CH}	5.9 (2)	5.9 (2)	5.9 (2)
	$\Delta\delta$	–	0.10	–0.11

[a] Referred to TMS in DMSO solutions; (d) doublet, (t) triplet, (q) quartet and (m) complex multiplet.

[b] Digital resolution ±0.7 Hz. In brackets is the number of intervening bonds between C and H in coupling.

[c] Binding shifts are defined as the difference of carbon chemical shifts in the mercury complex and in the parent molecule.

[d] The chemical shifts of γ-pic moiety are: C-2,6 = 149.60 ppm; C-3,5 = 124.80 ppm; C-4 = 146.91 ppm and CH_3 = 20.36 ppm.

nect this with closer spatial proximity of NH than CH_3 protons to the mercury. Such situation was found in the related complex **3** by X-analysis. The COOH proton in **2** is broadened as in **1**, but slightly shifted downfield. Due to binding with mercury, the H–H spin-spin coupling multiplet pattern of some protons is also changed. Thus, methine proton in **2,** which in **1** shows complex H–H multiplet because of interactions with CH_3 and SH protons, is resolved as a quartet due to coupling with methyl group only (SH proton is replaced with Hg in **2**). The complex methylene coupling pattern in **1** is perturbed in **2** (see Table IV and proton part of top and middle spectra in Figure 2.) due to slight changes in chemical shifts of non-equivalent methylene protons after mercury binding. Since these protons are as many as six bonds

away from the mercury binding site, chemical shift changes probably arise from the small difference in spatial orientation of methylene protons in the glycine moiety of **1** and **2**.

The ^{1}H spectrum of **3** displays seven signals, out of the expected eight (COOH signal is missing). Four signals belong to the Hg[SCH(CH_3)-$CONHCH_2COOH]_2$ moiety, while three to the C_6H_7N (γ-pic) moiety. The chemical shifts of protons in **3** are only slightly changed as compared to those in **2**. However, the lack of carboxyl proton signal in **3** in comparison with its existence in **2** and the difference of methylene coupling patterns in **3** and **2** are in agreement with the H-bonding between glycine COOH proton and N-atom of γ-pic in **3**. Due to the existence of H-bond, the COOH proton disappears in the spectrum of **3** since it rapidly exchanges between O- and N-atoms. At the same time, H-bonding induces slight spatial reorientation of glycine methylene protons, altering their chemical shift non-equivalency and changing their coupling pattern in **3** (see bottom spectrum in Figure 2.) The existence of H-bonding in **3** was established by X-ray analysis and IR spectra in the solid state.

The ^{13}C NMR data confirmed the structure of **1**, **2** and **3**. In **1** methylene carbon is more deshielded than the methine carbon, since the former is bonded to the nitrogen atom and the carboxyl group, while the latter to the mercapto and carbonyl groups. This assignment was substantiated by C–H coupling pattern and HETCOR spectra (Figure 2.). On the other hand, the amide carbonyl carbon is more deshielded than the carboxylic carbon. This was determined on the basis of long-range C–H couplings. The CONH displays a complex multiplet, while COOH a well resolved triplet (Table V). In addition, partial deuteration of exchangable protons was performed. The deuterium isotope effect on ^{13}C chemical shift of CONH (–100.7 ppb) is of opposite sign and greater in magnitude than that of COOH (64.9 ppb). The signs and the magnitudes of these deuterium effects are in agreement with literature data.[23] A very large deuterium isotope effect was also observed at methylene carbon, amounting to 119.3 ppb.

The binding of mercury to sulfur induces the greatest changes of ^{13}C chemical shift for carbon-atoms in close vicinity to the binding site, *i.e.* for CH, CH_3 and CONH carbons (see Table V). Although the methine carbon is two bonds away, while methyl and amide carbons are three bonds away from the bound mercury, their $\Delta\delta$ are very similar in **2**, but somewhat greater in **3** for remoter methyl and amide carbons. Contrary to that, $\Delta\delta$ at methylene and COOH carbons in **3** are of lower magnitude and even of opposite sign (for COOH) than in **2**. These small differences between $\Delta\delta$ in **2** and **3** could be connected with the existence of H-bonding to γ-pic in **3**. The differences in magnitude of C–H spin-spin coupling upon binding to

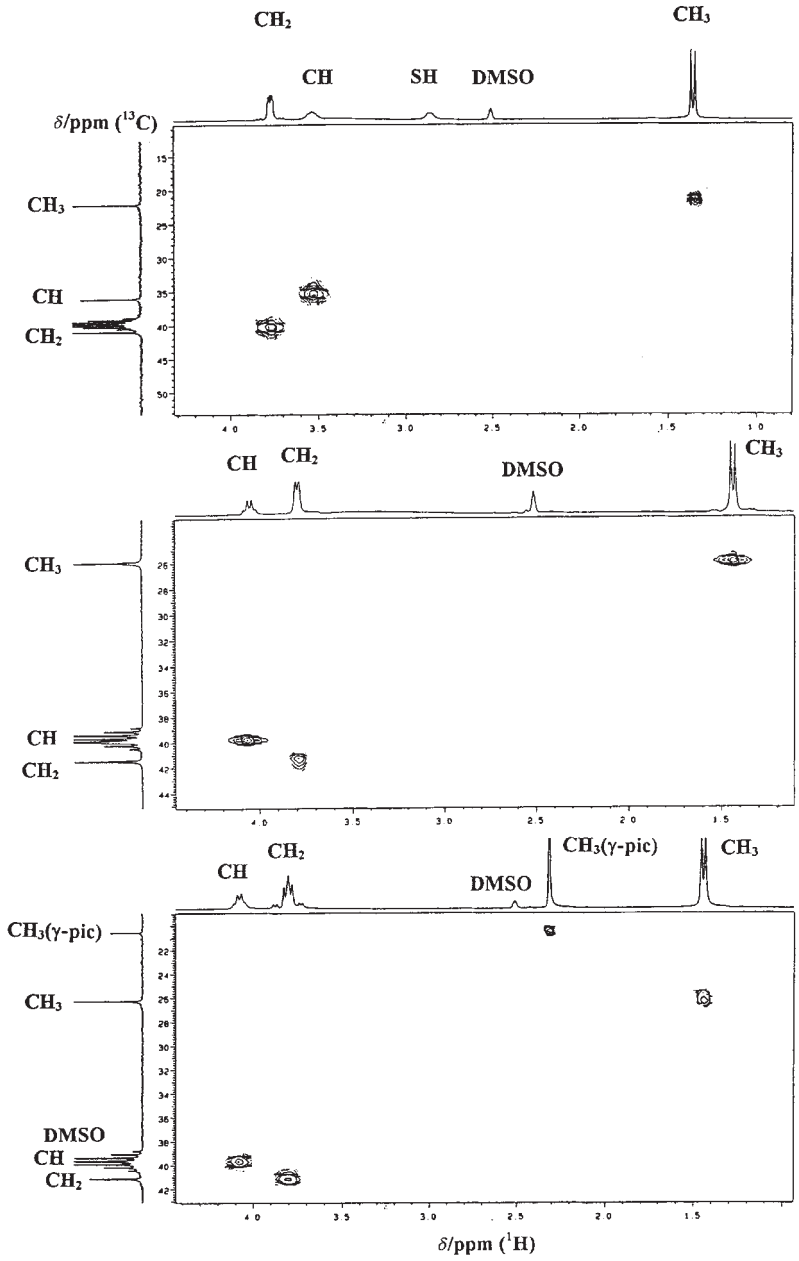

Figure 2. The HETCOR spectra (^{1}H-^{13}C correlation) of parent molecule **1** (top) and its complexes **2** (middle) and **3** (bottom). Changes of ^{1}H and ^{13}C chemical shifts and H–H spin-spin coupling multiplicities due to the binding to mercury can be seen in **2** and **3**.

TABLE VI

Selected bond lengths and angles for $Hg(mpgH)_2 \cdot 2\gamma$-pic

Bond lengths / Å	
Hg–S	2.3414(18)
S–C2	1.842(3)
C1–C2	1.520(5)
C2–C3	1.520(4)
C3–O3	1.237(4)
C3–N1	1.334(4)
N1–C4	1.444(5)
C4–C5	1.507(5)
C5–O1	1.295(5)
C5–O2	1.181(5)
Bond angles / °	
S–Hg–S^{i}	180.0
C2–S–Hg	101.35(11)
C1–C2–C3	112.0(3)
C1–C2–S	108.6(2)
C3–C2–S	108.0(2)
O3–C3–N1	122.1(3)
O3–C3–C2	122.0(3)
N1–C3–C2	115.9(3)
C3–N1–C4	121.3(3)
N1–C4–C5	112.4(3)
O2–C5–O1	124.1(4)
O2–C5–C4	123.5(3)
O1–C5–C4	112.4(3)

Symmetry transformation used to generate equivalent atoms: (i) *-x,-y,-z*.

mercury are much smaller here than those in chemical shifts. However, the slight decrease (*ca.* 2.0 Hz) of $^{1}J_{CH}$ in **2** and **3,** as compared to **1,** is observed at methine carbon (Table V). The assignments of carbons were confirmed by HETCOR measurements. Figure 2. demonstrates the part of HETCOR spectra of **1**, **2** and **3**, displaying the change of the ^{1}H and ^{13}C chemical shifts and H–H coupling multiplicities upon binding to mercury.

Mercury(II) ion is bound firmly to the sulfhydryl group from $mpgH_2$ as a mercaptide, which is consistent with the results of Stricks and Kolthoff[8] and Rabenstein.[24] The crystal structure of $Hg(mpgH)_2 \cdot 2\gamma$-pic is

built up of $Hg(mpgH)_2$ and γ-picoline molecules. Selected bond lengths and angles are given in Table VI. Mercury atom is bonded centrosymmetrically to two sulfur atoms from two $mpgH^-$ ligands at the Hg–S distance of 2.341(2) Å. Since mercury is in the center of symmetry, the angle S–Hg–S is 180°. The Hg–S distance agrees well with the sum of covalent radii of Hg (1.30 Å)[25,26] and S (1.04 Å)[27]. There are two additional centrosymmetrical contacts Hg···O3 of 2.896(4) Å, which are shorter than the sum of the van der Waals radii of Hg (1.54 Å)[26] and O (1.54 Å)[28]. In the structure of bis(*N*-(1-pyrolidinyl-thiocarbonyl)-benzamidato)mercury(II),[29] there is a similar coordination around Hg with two Hg–S bonds of 2.341(6) and 2.356(5) Å and two Hg···O contacts of 2.51(1) and 2.52(1) Å. These contacts Hg···O are shorter thn the ones in the present structure. In $Hg(mpgH)_2$ atom O3 is also involved in hydrogen bonding. A closer approach to mercury would probably weaken or prevent hydrogen bond formation and is not favourable. Each $Hg(mpgH)_2$ molecule forms two pairs of centrosymmetrically related hydrogen bonds N1–H···O3 of 2.922(5) Å, having two peptide nitrogen donors and two carbonyl oxygen acceptors. These hydrogen bonds connect the molecules into chains along [100]. Each molecule also forms two hydrogen bonds O1–H···N2 of 2.612(6) Å, involving the hydrogen atom from the carboxylic group and the nitrogen atom from the solvent γ-picoline molecule. The crystal packing, hydrogen bonds and Hg···O contacts are shown in Figure 3, and the hydrogen bonding geometry is given in Table VII.

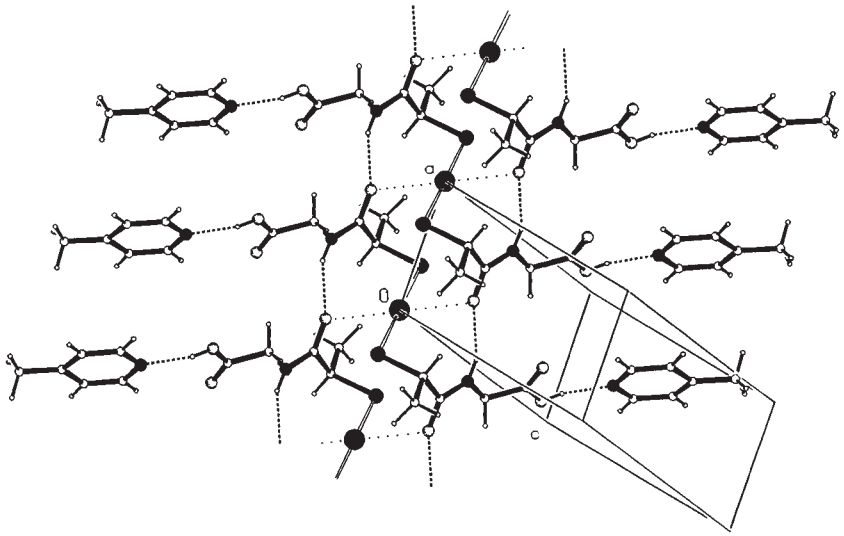

Figure 3. Packing of $Hg(mpgH)_2$ and γ-picoline molecules in the unit cell. Contents of three unit cells are shown. Hydrogen bonds are drawn by dashed lines and Hg···O contacts by dotted lines.

TABLE VII

Interatomic contacts and hydrogen bonding geometry / (Å, deg) for $Hg(mpgH)_2 \cdot 2\gamma$-pic

Interatomic contact				
Hg···O3^{i} 2.896(4)				
Hydrogen bonds				
Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
N1–HN1···O3	0.86(5)	2.12(5)	2.922(5)	156(4)
O1–HO1···N2	0.78(10)	1.85(10)	2.612(6)	168(10)

Symmetry transformation used to generate equivalent atoms: (i) 1-*x*,-*y*,-*z*.

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Supplementary Material. – Crystallographic data for the $Hg(mpgH)_2 \cdot 2\gamma$-pic structure reported in this paper have been deposited (no. 103210) with the Cambridge Crystallographic Data Centre (excluding structure factors, which are available from the authors). Deposited data can be obtained from the CCDC Technical Editors by e-mail request at deposit@ccdc.cam.ac.uk.

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SAŽETAK

Vezanje žive(II) s pomoću *N*-(2-merkaptopropionil)glicina. Priprava, IR i NMR karakterizacija. Kristalna struktura 1:2 solvata bis[*N*-propionil-2-tiolato)glicin]žive(II) s 4-metilpiridinom

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Bis[*N*-propionil-2-tiolato)glicin]živa(II), $Hg[SCH(CH_3)CONHCH_2COOH]_2$, dobivena je reakcijom vodenih otopina *N*-(2-merkaptopropionil)glicina i živina(II) acetata. Iz 4-metilpiridinske (γ-pikolinske) otopine ona kristalizira kao 1:2 solvat, $Hg[SCH(CH_3)CONHCH_2COOH]_2 \cdot 2C_6H_7N$, u triklinskom sustavu, prostornoj grupi $P\bar{1}$ s parametrima jedinične ćelije a = 4,810(5) Å, b = 9,711(4) Å, c = 15,615(8) Å, α = 105,76(4)°, β = 103,44(4)°, γ = 94,01(4)°, Z = 1, R = 0,027. Dvije *N*-(propionil-2-tiolato)glicinske molekule vezane su na živu preko sumporovih atoma poput merkaptida na udaljenosti od 2,341(2) Å. Molekule $Hg(mpgH)_2$ centrosimetrično su povezane vodikovim

vezama N1–H···O3, duljine 2,922(5) Å, u lance uzduž [100]. Svaka molekula takoder gradi i dvije vodikove veze tipa O1–H···N2 od 2,612(6) Å s dvjema molekulama γ-pikolina. Strukture spojeva i vezanje preko sumpora određeni su iz ^{1}H i ^{13}C NMR spektara, na osnovi živom induciranih kemijskih pomaka, konstanata sprege H–H i C–H, te povezanosti u dvodimenzijskim homo- i heteronuklearnim korelacijskim spektrima.