Mercuration Products of Some Aliphatic Carboxylic Acids: Preparation and Spectral Properties. Crystal Structure of the Bipyridyl Complex of the Nitrate of Monomercurated Propionic Acid

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Summary: When propionic acid is heated with mercuric propionate the condensation polymer of the α-monomercurated propionic acid is obtained along with traces of the dimercurated acid. When n-butyric acid is heated with mercuric n-butyrate the condensation polymer of the α-monomercurated n-butyric acid is obtained together with about a 20% yield of the dimercurated one. In contrast, n-valeric and isovaleric acids are mainly dimercurated. The site of mercuration, established by ^1H and ^{13}C NMR spectroscopy, was confirmed by an X-ray crystal structure analysis of the 2,2′-bipyridyl complex of 2-(nitratomercurio)propionic acid. The NMR spectra showed a number of long range $^{199}Hg-^1H$ (up to five bonds) and $^{199}Hg-^{13}C$ (up to four bonds) spin-spin couplings and the relation of three-bond $^{199}Hg-^{13}C$ couplings to molecular conformation. In the crystal structure of $[CH_3CH(Hg(C_{10}H_8N_2))COOH]NO_3$ mercury is bonded to the α-carbon atom of the propionic acid at a distance of 2.11(1) Å and to the nitrogen atoms of the bipyridyl ligand at 2.226(9) and 2.423(7) Å.

Direct mercuration of an aliphatic carboxylic acid leads to mono-, di-, and trimercurated products depending upon the mercuration agent and the conditions under which mercuration is carried out.[1-5]

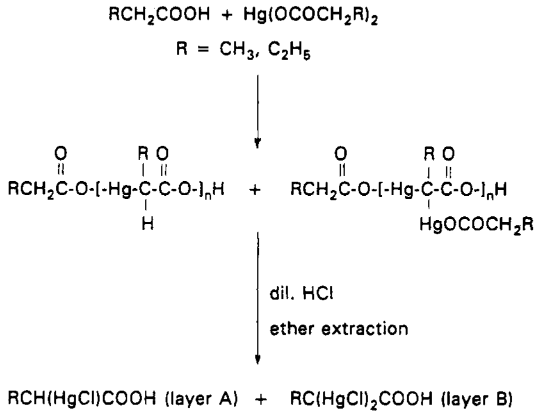
Preparation of monomercurated propionic, *n*-butyric, *n*-valeric, and isovaleric acid, the ^1H and ^{13}C NMR spectral characterization of the 2-chloromercurio derivatives of propionic, *n*-butyric, *n*-valeric, and isovaleric acid, and the crystal structure of 2-propionic acid-(2,2′-bipyridyl)-mercury(II) nitrate is reported in this paper.

Results and Discussion

Synthesis. The product of the direct mercuration of propionic acid by mercuric propionate is the condensation polymer of monomercurated propionic acid formulated as $CH_3CH_2COO[HgC(CH_3)(H)COO]_nH$, with $n \cong 8$, as indicated by the mercury content, with dimercurated acid in traces, as shown in Scheme I. The oligomer of the 2-((propionyloxy)mercurio)propionic acid undergoes hydrolysis with dilute hydrochloric acid leading to 2-(chloromercurio)propionic acid, $CH_3CH(HgCl)COOH$ (**1**). The traces of 2,2-bis(chloromercurio)propionic acid, $CH_3C(HgCl)_2COOH$ (**1a**) can be easily removed by extraction with diethyl ether. **1** was found to be very soluble in dimethyl sulfoxide (DMSO), soluble in common organic solvents (alcohols, ethers), and sparingly soluble in water. Our attempts to obtain crystals of monomercurated propionic acid from DMSO suitable for X-ray investigation were unsuccessful, but good quality crystals of dimercurated propionic acid were obtained as a monosolvate of DMSO, as confirmed by X-ray diffractometry.[6]

On heating *n*-butyric acid and mercuric *n*-butyrate, the condensation polymer of monomercurated *n*-butyric acid is obtained as expected. It is formulated as $C_2H_5CH_2COO[HgC(C_2H_5)(H)COO]_nH$, with $n \cong 8$, as indicated by the mercury content. However, about 20% of dimercurated acid is also formed, formulated as an oligomer of 2,2-bis((*n*-butyryloxy)mercurio)-*n*-butyric acid, $C_2H_5CH_2COO[HgC(C_2H_5)(HgOCOCH_2C_2H_5)COO]_nH$, with $n \cong 4$,

Scheme I



R	compound	R	compound
CH_3	1	CH_3	1a (in traces)
C_2H_5	2 (~80%)	C_2H_5	2a (up to ~20%)

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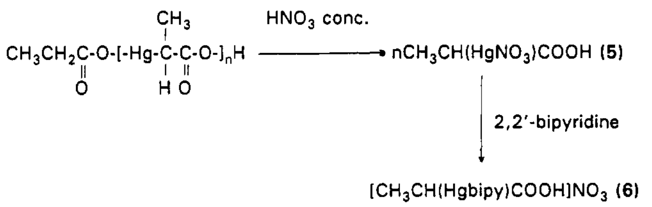
Scheme II



based on the mercury content. The separation of 2-(chloromercurio)-*n*-butyric acid, $CH_3CH_2CH(HgCl)COOH$ (**2**), from 2,2-bis(chloromercurio)-*n*-butyric acid, $CH_3CH_2C(HgCl)_2COOH$ (**2a**), after hydrochloric acid hydrolysis of the crude mercuration product was effected in the same way as described for mercurated propionic acid. Dimercurated *n*-butryic acid, confirmed by X-ray diffractometry as reported earlier,[5] was obtained by heating mercuric *n*-butyrate in butyric anhydride as the only mercuration product.

Treatment of *n*-valeric acid with mercuric *n*-valerate as well as isovaleric acid with mercuric oxide gives a dimercurated *n*-valeric and isovaleric acid oligomer[5] with corresponding monomercurated acids in traces. 2-(Chloromercurio)-*n*-valeric acid, $C_3H_7CH(HgCl)COOH$ (**3**), and 2-(chloromercurio)isovaleric acid, $(CH_3)_2CHCH(HgCl)COOH$ (**4**), although obtained in very low yield, were characterized by ^1H and ^{13}C NMR spectroscopy.

2-(Nitratomercurio)propionic acid, $CH_3CH(HgNO_3)COOH$ (**5**), is obtained from a solution of the oligomer of 2-((propionyloxy)mercurio)propionic acid in concentrated nitric acid (Scheme II), **5** is a microcrystalline product, slightly soluble in methanol, acetone, and DMSO. With 2,2′-bipyridine it forms a one-to-one complex, $[CH_3CH(Hg(C_{10}H_8N_2))COOH]NO_3$ (**6**), as confirmed by X-ray diffractometry. In its IR spectrum the "ring breathing" absorption is shifted to higher frequency (1021 cm^{-1}) due to chelation. The presence of a strong absorption band at 1378 cm^{-1} and the absence of absorption in the regions of 1540–1480 and 1290–1250 cm^{-1} indicate the presence of the free nitrate anion in the complex.

NMR Spectra. The most prominent feature of the NMR spectra is a series of ^{199}Hg–^1H and ^{199}Hg–^{13}C (Hg–H and Hg–C) coupling constants determined from ^1H and ^{13}C signal satellites. However all possible couplings could not be determined because of broadening and overlapping of signals or complex multiplicities.

The data from ^1H NMR are collected in Table I. We have remeasured the ^1H spectra of (chloromercurio)acetic acid and found the value $^2J(Hg,H) = 309.1$ Hz, which is in a good agreement with the published value,[7,8] while in **1**–**3** this coupling is 40–50 Hz greater. The greatest value, 453 Hz, was observed for (chloromercurio)isovaleric acid. The increase of magnitude of this coupling is due to steric hindrance and electronic effects caused by increased alkyl substitution at the carbon atom in coupling. In **1**, **3**, and **4**, $^3J(Hg,H)$ were observed ranging from 226.2 Hz at CH_2 in **3** to 252.4 Hz at CH_3 in **1**. The corresponding coupling in **2** could not be completely resolved due to broadening and overlapping of signals (in Table I this coupling was denoted as not observed, n.o.). For **4** proton chemical shifts of two CH_3 groups differ slightly (0.91 and 0.82 ppm) but their $^4J(Hg,H)$ are the same (125.1 Hz). It means that the substitution of H by HgCl breaks down the chemical shift equivalency of CH_3 groups which exists in isovaleric acid (CH_3 chemical shift is 0.90 ppm). The four-bond coupling in **2** at CH_3 and in **3** at C-γ could not be resolved due to partial overlapping of signals. The observation of this coupling in **3** was additionally impossible due to the complex H–H spin–spin coupling multiplet pattern. In **3** the five-bond Hg–H coupling at CH_3 was observed, amounting to 125.10 Hz. This large coupling constant may arise predominantly from the through-space interaction between Hg and H since in **3** CH_3 and HgCl groups may be spatially closer than in **4**.

The ^{13}C data are shown in Table II. The $^1J(Hg,C)$ are in the range 1638–1680 Hz. These larger than usual values are due to the electronegativity of the COOH group.[9] The same effect was also found for $^2J(Hg,C)$ at carboxyl C atoms. For $^2J(Hg,C)$ at aliphatic carbons it is obvious that the increasing C substitution on the carbon involved in two-bond coupling decreases its magnitude. The $^3J(Hg,C)$ values are greater than $^2J(Hg,C)$, the former ranging from 108.3 to 188.1 Hz. In ^{13}C NMR spectra of **4**, as in ^1H NMR spectra, two different signals for the methyl carbons, 23.55 and 25.93 ppm, were observed. The signal with lower three-bond Hg–C coupling (108.3 Hz) is more deshielded than the signal with greater three-bond coupling (180.0 Hz). Since rotation around the C–C bond is possible, a distribution of different conformer (rotamer) populations exists. Three distinct arrangements of CH_3 groups toward the HgCl group in **4** may be recognized in Figure 1: (I) and (III) represent a combination of *gauche* (60°) and *anti* (180°) arrangements of CH_3 groups with respect to the HgCl group, while (II) represents a *gauche* arrangement of both CH_3 groups. It has been reported[10] that vicinal Hg–C couplings are strongly dihedral angle dependent, showing the Karplus type relationship. In cyclohexylmercurio derivatives three-bond Hg–C couplings amount up to 275 Hz for equatorial HgX groups, i.e. *anti* arrangement, and from ca. 70 Hz up for axial HgX groups, i.e. *gauche* arrangement. These values change with substituents which cause different bond angle deformations. The three-bond coupling at C3 in (2-methoxycyclohexyl)mercury chloride[10] with an axial HgCl group (*gauche*) was found to be 102 Hz, which is very close to the value observed for the less shielded methyl group in **4** (108.3 Hz). The value determined in the mentioned cyclohexyl derivative with an equatorial HgCl group (*anti*) was 184 Hz, which is similar to the three-bond coupling observed at the more shielded CH_3 signal in **4** (180.0 Hz). On the basis of these data one can assume that the lower $^3J(Hg,C)$ in **4** might correspond to the lower dihedral angle (θ) between CH_3 and HgCl groups, which could be *gauche* or close to a *gauche* arrangement, while greater $^3J(Hg,C)$ might correspond to greater θ, which could be *anti* or close to an *anti* arrangement. Therefore one can anticipate that conformations I and III in **4** are more populated than conformation II. It is also reasonable to assume that (I) is less populated than (III) since in the former one CH_3 group is placed between the HgCl and COOH groups which is a less sterically favorable situation than that in (III). However one has to emphasize that at room temperature measured couplings are in fact averaged values of cou-

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Table I. ^{1}H NMR Data for Chloromercurio Aliphatic Acids RCH(HgCl)COOH with Chemical Shifts (δ/ppm) and Hg–H and H–H Spin–Spin Coupling Constants (J/Hz)

			1	2	3		4	
H atom		R = H	R = CH_3	R = CH_2CH_3	R = $CH_2(\beta)CH_2(\gamma)CH_3$		R = $CH(\beta)(CH_3)_2$	
COOH	δ	11.08	11.42	11.60	11.59		11.50	
	J_{Hg-H}	n.o.[a]	n.o.	n.o.	n.o.		n.o.	
	J_{H-H}	n.o.	n.o.	n.o.	n.o.		n.o.	
							(α)	(β)[e]
CH	δ	–[b]	2.89	2.83	2.88		2.74	2.22
	J_{Hg-H}	–	366.7 (2)[c]	349.6 (2)	351.0 (2)		453 (2)	229 (3)
	J_{H-H}	–	6.84 (q)[d]	7.32 (t)	7.53 (t)		7.6 (d)	m[f]
					(β)[g]	(γ)[g]		
CH_2	δ	2.27	–	1.87	1.82	1.32	–	
	J_{Hg-H}	309.1 (2)	–	n.o.	226.2 (3)	n.o.	–	
	J_{H-H}	n.o.	–	7.32 (qn)	7.32 (sx)	m[f]	–	
CH_3	δ	–	1.38	0.91	0.86		0.91,[h] 0.82	
	J_{Hg-H}	–	252.4 (3)	n.o.	124.9 (5)		125.1 (4), 125.1 (4)	
	J_{H-H}	–	6.84 (d)	7.32 (t)	7.32 (t)		6.5 (d), 6.5 (d)	

[a] Not observed (n.o.) due to the signal broadening and/or overlapping. [b] Not applicable (–). [c] In parentheses is the number of intervening bonds between nuclei in coupling. [d] The multiplicity of H–H coupling: doublet (d), triplet (t), quartet (q), quintet (qn), sextet (sx). [e] CH group at the β-position to the COOH group, two bonds away from the HgCl group. [f] Complex multiplet (m). [g] CH_2 group at the β-position i.e. γ-position to COOH. [h] The values in the first column are assigned to the *gauche* while in the second column to the *anti* arrangement of CH_3 and HgCl groups.

Table II. ^{13}C NMR Data for Chloromercurio Aliphatic Acids RCH(HgCl)COOH with Chemical Shifts (δ/ppm), Hg–C Spin–Spin Coupling Constants (J/Hz), and Substituent Effects of ^{199}Hg on ^{13}C Chemical Shifts ($\Delta\delta$/ppm)[a]

			1	2	3		4	
C atom		R = H	R = CH_3	R = CH_2CH_3	R = $CH_2(\beta)CH_2(\gamma)CH_3$		R = $CH(\beta)(CH_3)_2$	
COOH	δ	174.03	175.93	174.92	175.44		174.67	
	J_{Hg-C}	121.4 (2)	117.9 (2)	119.7 (2)	121.8 (2)		121.2 (2)	
	$\Delta\delta$	–0.72	–0.96	–0.29	1.09		1.22	
							(α)	(β)[c]
CH	δ	–[b]	40.31	49.86	47.81		59.08	28.99
	J_{Hg-C}	–	1680.4 (1)	1659.9 (1)	1659.8 (1)		1670.6 (1)	91.4 (2)
	$\Delta\delta$	–	12.75	13.76	14.55		15.80	3.84
					(β)[d]	(γ)[d]		
CH_2	δ	29.50	–	22.41	31.34	23.91		
	J_{Hg-C}	1637.7 (1)	–	100.9 (2)	103.2 (2)	177.0 (3)	–	
	$\Delta\delta$	8.19	–	3.81	4.70	2.26	–	
CH_3	δ	–	14.84	15.53	13.71		25.93, 23.55[e]	
	J_{Hg-C}	–	109.4 (2)	188.1 (3)	33.5 (4)		108.3 (3), 180.0 (3)	
	$\Delta\delta$	–	5.45	1.71	0.36		4.07, 1.74	

[a] $\Delta\delta$ defined as the difference between the chemical shifts of the chloromercurio and parent acid molecule; + sign denotes deshielding. [b] Not applicable (–). [c] CH group at the β-position to the COOH group. [d] CH_2 group at the β-position i.e. γ-position to COOH. [e] The values in the first column are assigned to the *gauche* while in the second column to the *anti* arrangement of CH_3 and HgCl groups.

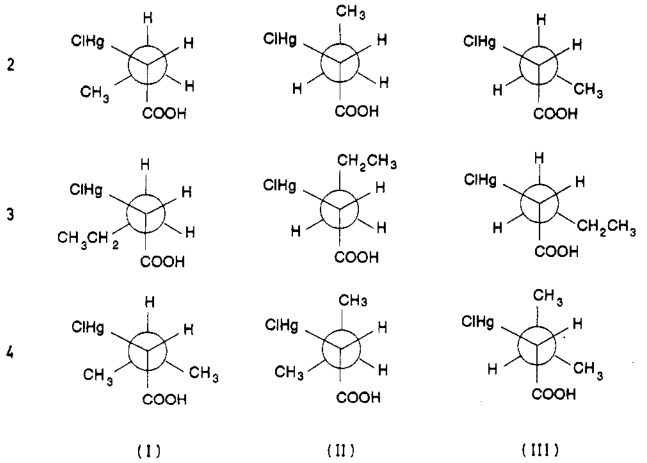

Figure 1. Energetically favorable conformations of 2–4.

plings. This is determined by distribution of different rotamer populations, with some populations having a greater weighting factor, as it is here most probably the population of conformer III. This conclusion based on three-bond Hg–C couplings in 4 is consistent with ^{199}Hg effects on ^{13}C chemical shifts in 4, i.e. greater deshielding for the *gauche* than for the *anti* arrangement, which is also found in cyclohexylmercurio derivatives (e.g. in C_6H_{11}-$HgOCOCH_3$ *gauche* 52.28 ppm while *anti* 47.80 ppm[10]).

For 4 greater deshielding of *gauche* CH_3 than of *anti* CH_3 may be explained by balancing the steric effect of mercury with the electron-withdrawal effect of mercury d orbitals and steric and electronic influences of the COOH group. In 2 only one CH_3 group exists and it can be also *gauche* or *anti*, Figure 1. On the basis of the magnitudes of the three-bond Hg–C coupling (188.1 Hz) and of the deshielding effect (1.71 ppm) on the chemical shift one may again assume that the population of rotamers with *anti* or close to *anti* arrangement of CH_3 toward HgCl has a high weighting factor. This may be also true for 3 with CH_3-CH_2 (Figure 1) where the three-bond coupling is 177.0 Hz and the deshielding effect is 2.26 ppm. Such an assumption can be rationalized by the greater steric requirements of HgCl than of the COOH group, since mercury has a huge number of electrons. It is well-known that the stereochemistry of mercury is peculiar; e.g. cyclohexylmercurio derivatives exist preferentially in the axial form. In alkylmercury chlorides of the type R–CH_2–CH_2–HgCl three-bond Hg–C couplings were found[10] to be as follows: R = CH_3, 190 Hz; R = CH_3CH_2, 183 Hz; R = *i*-Pr, 212 Hz; R = *t*-Bu, 227 Hz. The first two values are very close to values found in 2 (CH_3, 188.1 Hz) and 3 (CH_3CH_2, 177.0 Hz). Anet et al. argued if these values in alkylmercury chlorides indicate the presence of substantial proportions of *gauche* forms. They concluded that the population of

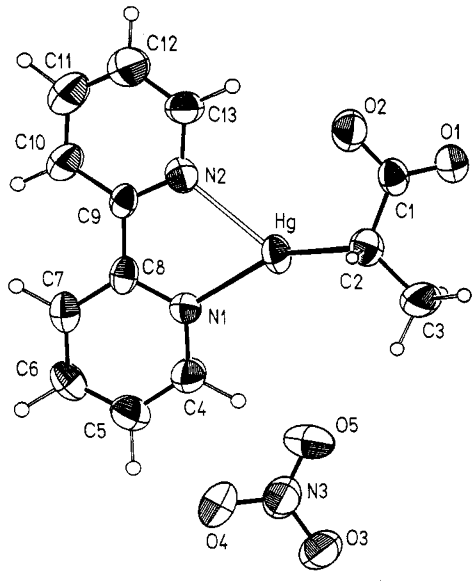

Figure 2. ORTEP drawing of 6 with thermal ellipsoids at the 50% probability level.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for 6

Hg–N1	2.226(9)	N2–Hg–C2	131.7(4)
Hg–N2	2.423(7)	N1–Hg–C2	153.5(4)
Hg–C2	2.11(1)	N1–Hg–N2	71.5(3)

gauche forms in the aliphatic compounds is probably not as great as might be anticipated from the axial preference of different mercurio groups on cyclohexane, since there are substantial differences in the two systems. From three-bond Hg–C coupling data and known dihedral angles in 2-norbornylmercury acetates and mercury chlorides[10] we tried to estimate averaged dihedral angles in **2**–**4** from measured ^3J (as mentioned rotationally averaged values). The estimated averaged dihedral angles are 30–50° for *gauche* in **4** and 130–150° for *anti* forms in **2**–**4**. Although these angles are lower than *gauche* (60°) and *anti* (180°) angles, it is expected since one is dealing with the distribution of different rotamer populations. This result also corroborates our assumptions that *anti, gauche* forms in **4** and *anti* forms in **2** and **3** are highly populated. The Hg–C coupling of greatest extent was found to be ^4J(Hg,C) in **3**, amounting to 33.5 Hz.

The attempt to provide more data by performing measurements at different temperatures failed. Because of solubility problems, low temperature measurements of monomercurated acids were unsuccessful. Dimercurated acids were practically insoluble and ^{13}C measurements were unsuccessful, even at high temperatures. The additional problem was the instability at high temperatures as well.

Crystal Structure of Complex 6. The crystal structure of **6** consists of $[CH_3CH(Hg(bpy))COOH]^+$ cations and NO_3^- anions (bpy = bipyridyl). A drawing of the molecule is shown in Figure 2. The interatomic distances and angles are given in Table III. Mercury is bonded to the α-carbon atom of the propionic acid at a distance of 2.11(1) Å, which is within the usual range of Hg–C bond lengths.[11] The Hg–N bond lengths are 2.226(9) and 2.423(7) Å and the angles N1–Hg–C2 and N2–Hg–C2 are 153.5(4) and 131.7(4)°, respectively. These values are similar to those in (2,2′-bipyridyl)methylmercury(II) nitrate,[12] where the Hg–N distances are 2.24(3) and 2.43(3) Å and the N–Hg–C angles are 164(1) and 126(1)°, and in (bpy)$Hg(NO_3)_2$[13] (Hg–N = 2.222(8) and 2.313(10) Å, N–Hg–O = 162.2(2) and 124.0(2)°). The N1–Hg–N2 chelate bite angle of 71.5(3)° is similar to the bite angles in other bipyridyl complexes[12–14] (69(1)–73.3(3)°). The irregular coordination geometry in **6** can be described as a very deformed digonal coordination with a strong additional Hg···N interaction which causes the large distortion from collinearity. The deviation of the angle from 180° and the Hg–N bond length depends upon additional interactions which are within the effective coordination of mercury.[15] In $[CH_3Hg(C_5H_4N)_2CH_2)]NO_3$[16] (C–Hg–N = 172(1)°, Hg–C = 2.10(2) Å, Hg–N = 2.16(1) Å) there are two additional contacts, Hg···N of 2.75(2) Å and Hg···O from the nitrate ion of 2.76(2) Å. If the additional interaction is shorter, as in **6**, the Hg–N bond is lengthened and the deviation of the N–Hg–C angle from collinearity is larger while there is no influence on the Hg–C bond length. In **6** the nitrate ion does not enter the effective coordination sphere of mercury when 1.60 Å is taken as the van der Waals radius of mercury. There is a Hg···O1 $(1 - x, -y, 1 - z)$ interaction with the carbonyl oxygen of 2.802(9) Å. Since C1–O2 is larger than C1–O1, it is supposed that the hydrogen atom of the propionic acid is on O2 and forms a hydrogen bond with the nitrate ion of O2···O3 $(x, y, z + 1)$ of 2.70(2) Å. The mercury atom is 0.202 Å out of the plane defined by N1, N2, and C2.

Experimental Section

NMR Spectra. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 99.55 MHz for ^{1}H and 25.05 MHz for ^{13}C. A few ^{1}H and ^{13}C measurements were performed on Varian VXR-300 spectrometer (75 MHz for ^{13}C) as well. All spectra were recorded at ambient temperatures in 5-mm tubes. Samples were dissolved in DMSO-d_6 which was also used for an internal lock signal. Typical conditions for ^{13}C measurements were flip angle 20–30°, 7000-Hz spectral width, 2000–5000 transients, 3-s pulse repetition time, and 8K data points with digital resolution ±1.71 Hz. ^{13}C measurements were performed using broad-band proton decoupling and gated decoupling for proton coupled spectra. The identifications and structure determinations have been performed on the basis of ^{1}H and ^{13}C chemical shifts, C–H and H–H spin–spin coupling, and multiplet patterns as well as on the satellite spin–spin couplings of mercury (^{199}Hg) with carbon and hydrogen.

IR Spectra. The IR spectra in the region of 4000–180 cm^{-1} were recorded on Perkin-Elmer spectrophotometer Model 580 D for compounds **1**–**4**, and for **5** and **6** they were recorded in the region 4000–450 cm^{-1} on Perkin-Elmer FT-IR spectrophotometer Model 1600 using KBr disks.

2-(Chloromercurio)propionic Acid (1). Mercuric propionate (5 g, 14.4 mmol, finely ground) was heated in propionic acid (50 mL) at 120 °C until a sample did not turn yellow on treatment with aqueous sodium hydroxide (about 5–6 h). The excess of the propionic acid was removed by distillation under reduced pressure. Acetone then was added very slowly (50 mL) to the concentrated solution. The colorless product was filtered

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Table IV. Crystal Data, Data Collection Parameters, and Refinement Details for 6

empirical formula	$C_{13}H_{13}HgO_5N_3$
fw	491.85
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	7.694(4)
b, Å	10.415(6)
c, Å	10.786(6)
α, deg	112.15(3)
β, deg	102.39(3)
γ, deg	104.69(2)
V, Å^3	726.5(8)
Z	2
density (calc), g cm^{-3}	2.249
$F(000)$	464
face indices; distances from centroid, mm	(2,–1,1), (–2,1,–1); 0.090
	(0,1,0), (0,–1,0); 0.053
	(0,1,–1), (0,–1,1); 0.016
μ, cm^{-1}	106.2
min, max transm coeff	0.286, 0.728
2θ range, deg	4–52
scan type	θ–2θ
no. of reflns collcd	2860
no. of unique reflns with $I > 3\sigma(I)$	1695 (R_{int} = 0.024)
no. of params refined	201
index ranges	$-9 \leq h \leq 9, -13 \leq k \leq 13, 0 \leq l \leq 13$
$R = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$	0.033
$R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$	0.040
weighting scheme	$w = 0.987/(\sigma^2(F) + 0.000704F^2)$
largest final shift/esd	0.001
largest final $\Delta\rho$, e Å^{-3}	1.01 (0.93 Å from Hg)

out, washed with acetone, and dried. Yield: 3.9 g (96%). The crude product (3 g) was treated with a mixture of 0.1 M hydrochloric acid (107 mL, divided in three equal portions) and diethyl ether (4-fold volume of the acid). The suspension was stirred and kept cool (5–8 °C). After 30 min the ether layer (A), separated from the aqueous layer (B), was dried over sodium sulfate during 1 h. The acid digestion and ether extraction were repeated and the ether solutions combined and allowed to evaporate to dryness. The crystalline product of 1 was kept over NaOH pellets to a constant weight. Yield: 2.5 g (76%). Anal. Calcd for $C_3H_5ClHgO_2$: C, 11.69; H, 1.63; Cl, 11.47; Hg, 64.89. Found: C, 11.78; H, 1.64; Cl, 11.61; Hg, 64.38. IR, ν(CO): 1673 cm^{-1}.

Isolation of 2,2-Bis(chloromercurio)propionic Acid (1a). The insoluble solid isolated from the aqueous (B) layer was treated with DMSO. The decomposition products were separated by filtration, and the filtrate was diluted with acetone. Crystallization in this manner, followed by filtration, afforded crystals which were the pure 1/1 DMSO solvate of 2,2-bis(chloromercurio)propionic acid, as confirmed by X-ray diffractometry.[6] Anal. Calcd for $C_5H_{10}Cl_2Hg_2O_3S$: C, 9.65; H, 1.62; Hg, 64.47. Found: C, 9.70; H, 1.84; Hg, 64.52. IR, ν(CO): 1650 cm^{-1}.

2-(Chloromercurio)-*n*-butyric Acid (2). Mercuric *n*-butyrate (5 g, 13.3 mmol) was heated in *n*-butyric acid (50 mL) at 120–125 °C until a sample did not turn yellow on treatment with aqueous sodium hydroxide (about 5–6 h). The volume of acid was reduced by one-fifth, acetone was added slowly (50 mL), and the solution was left to stand overnight. The crude colorless product was filtered out, washed with acetone, and dried. Yield: 5.5 g (98%). 2 was isolated as pure product by a hydrochloric acid digestion procedure analogous to that described for 1 (1.62 g, 50.5 mL, 0.1 M). Yield: 1.3 g (75%). Anal. Calcd for $C_4H_7ClHgO_2$: C, 14.87; H, 2.18; Cl, 10.97; Hg, 62.07. Found: C, 14.87; H, 2.21; Cl, 10.25; Hg, 62.09. IR, ν(CO): 1680 cm^{-1}.

2,2-Bis(chloromercurio)-*n*-butyric acid (2a) was obtained from the aqueous layer after purification by dissolving in DMSO. The crystalline product was a 1/1 DMSO solvate of $C_2H_5C(HgCl)_2$-COOH. Anal. Calcd for $C_6H_{12}Cl_2Hg_2O_3S$: C, 11.32; H, 1.90; Hg, 63.05. Found: C, 11.78; H, 2.05; Hg, 63.30. The IR spectrum and parameters of the unit cell were identical with those reported.[5]

Table V. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for 6

	x	y	z	U_{eq}[a]
Hg	0.49792(6)	0.18764(4)	0.35993(5)	0.0491(2)
O1	0.2852(11)	–0.1427(8)	0.4269(8)	0.057(4)
O2	0.2331(11)	0.0683(8)	0.5239(9)	0.065(4)
C1	0.2635(13)	–0.0344(10)	0.4208(11)	0.044(5)
C2	0.2592(14)	–0.0081(11)	0.2924(11)	0.052(5)
C3	0.2510(19)	–0.1361(13)	0.1674(12)	0.075(7)
N1	0.6846(11)	0.3635(8)	0.3258(8)	0.041(4)
N2	0.6452(11)	0.4184(9)	0.5805(9)	0.047(4)
C4	0.6853(16)	0.3310(11)	0.1933(12)	0.056(6)
C5	0.7718(16)	0.4397(12)	0.1597(12)	0.058(6)
C6	0.8637(17)	0.5810(13)	0.2635(13)	0.065(6)
C7	0.8710(15)	0.6155(11)	0.4012(12)	0.054(5)
C8	0.7737(12)	0.5051(10)	0.4310(10)	0.040(5)
C9	0.7612(13)	0.5331(9)	0.5744(10)	0.038(4)
C10	0.8597(15)	0.6717(11)	0.6930(11)	0.053(5)
C11	0.8329(17)	0.6879(13)	0.8208(13)	0.067(7)
C12	0.7135(18)	0.5699(14)	0.8258(13)	0.064(7)
C13	0.6235(15)	0.4360(12)	0.7071(11)	0.052(5)
N3	0.2637(14)	0.0644(11)	–0.1582(11)	0.064(5)
O3	0.2267(12)	–0.0361(9)	–0.2827(9)	0.072(4)
O4	0.2930(18)	0.1921(10)	–0.1406(11)	0.112(7)
O5	0.2601(21)	0.0317(12)	–0.0618(10)	0.125(8)

[a] $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

2-(Chloromercurio)-*n*-valeric acid (3) was obtained as an admixture to 2,2-bis(chloromercurio)-*n*-valeric acid which had been prepared by the procedure described earlier.[5] The monomercurated acid was separated from the dimercurated product by extraction with ether. Anal. Calcd for $C_5H_9ClHgO_2$: C, 17.81; H, 2.69; Hg, 59.49. Found: C, 17.64; H, 3.19; Hg, 59.70.

2-(Chloromercurio)isovaleric acid (4) was separated from 2,2-bis(chloromercurio)isovaleric acid by an extraction procedure analogous to that described for *n*-valeric acid. Anal. Calcd for $C_5H_9ClHgO_2$: C, 17.81; H, 2.69; Hg, 59.49. Found: C, 17.74; H, 2.75; Hg, 59.64.

2-(Nitratomercurio)propionic Acid (5). 2-((Propionyloxy)-mercurio)propionic acid (0.5 g, 0.22 mmol) was dissolved in warm concentrated nitric acid (0.5 mL; 30–40 °C) and left in an ice bath for 1 h. Colorless plates were filtered out, washed with absolute ethanol, and dried. Yield: 0.41 g (69%). Anal. Calcd for $C_3H_5NO_5Hg$: Hg, 59.76; N, 4.17. Found: Hg, 60.11; N, 4.31.

2-(2,2′-Bipyridylmercurio)propionic Acid Nitrate (6). A solution of 2,2′-bipyridine (0.18 g, 1.15 mmol in 10 mL of methanol) was added to an acetone solution of 2-(nitratomercurio)propionic acid (0.33 g, 0.94 mmol in 70 mL). The clear solution was left to stand over 3–4 days to crystallize. Colorless crystals were filtered out, washed with cold acetone, and dried. Yield: 0.41 g (83%). Anal. Calcd for $C_{13}H_{13}N_3O_5Hg$: C, 31.75; H, 2.66; N, 8.54; Hg, 40.78. Found: C, 32.06; H, 2.27; N, 8.92; Hg, 40.65. IR, ν(CO): 1682 cm^{-1}.

Crystal Structure Determination of 6. X-ray diffraction data were collected at room temperature on a Philips PW1100 diffractometer (upgraded by STOE) using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Unit cell dimensions were obtained by least-squares refinement of 22 reflections within the range 18 < 2θ < 26°. The unit cell parameters and details of data collection and refinement are given in Table IV. Standard reflections (–3,1,1; 2,–3,–1; –2,–2,1) monitored every 80 min indicated no significant change in intensities. Intensities were corrected for Lorentz, polarization, and absorption effects. The structure was solved by Patterson and Fourier synthesis. Hydrogen atoms were included in calculated positions (C–H = 1.08 Å) with grouped isotropic thermal parameters. The carbonyl hydrogen atom could not be located and was not included in the calculations. The structure was refined by full-matrix least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms. Atomic scattering factors and anomalous dispersion coefficients were taken from the standard sources.[17] No extinction correction was made, only the low angle reflections

001 and 010 were omitted from calculations in the last cycles. Computing was carried out on an IBM PC/AT-compatible computer using *SHELX-76*.[18] Atomic coordinates are given in Table V.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, the equation of the least-squares plane, and complete interatomic distances and angles and a figure with the packing diagram of **6** (5 pages). Ordering information is given on any current masthead page.

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