Mercuration of n-butyric, n-valeric and isovaleric acid. The crystal structure of $C_2H_5C(HgCl)_2COOH \cdot DMSO$

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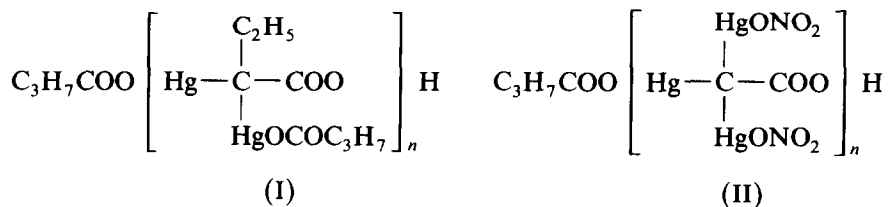
Abstract

n-Butyric acid has been shown to react with mercuric n-butyrate in n-butyric anhydride to give the condensation oligomer 2,2-bis(n-butyryloxymercurio)-n-butyric acid, $C_3H_7COO[HgC(C_2H_5)(HgOCOC_3H_7)COO]_nH$, with $n \cong 4$. Hydrolysis of this with dilute hydrochloric acid gives 2,2-bis(chloromercurio)-n-butyric acid, which crystallizes from dimethylsulfoxide as the solvate $C_2H_5C(HgCl)_2COOH \cdot DMSO$, the crystal structure of which has been determined by X-ray diffraction. Each dimercurated acid molecule is linked through its carboxyl groups to a DMSO molecule by a short hydrogen bond of length 2.617(30) Å. The Hg–Cl bond lengths are 2.329(8) and 2.329(10) Å respectively, and mean value of Hg–C bond length is 2.093(31) Å. The corresponding 2,2-bis(chloromercurio)-acids have been obtained from the mercuration products of n-valeric and isovaleric acid.

Introduction

Mercuration of acetic acid gives mono- or tri-mercurated acetic acid depending upon the mercuration agent and the conditions used. For example, mercuric acetate reacts with boiling glacial acetic acid to give the monomercurated but with boiling acetic anhydride to give the trimercurated derivative, both of them products are condensation polymers, namely $CH_3OCO[HgCH_2COO]_nH$ and mercuretin, $CH_3OCO[Hg(CH_3OCOHg)_2CCOO]_nH$ [1,2]. Mercuretin is obtained when molten mercuric acetate is used as has been confirmed by crystal structure determinations of $(ClHg)_3CCOOH \cdot DMSO$ [2], $[Hg(H_2OHg)(NO_3Hg)CCOO]NO_3$ and $2(NO_3Hg)_3CCOOH \cdot HNO_3$ [3], its acid hydrolysis products. When mercuric nitrate monohydrate and boiling glacial acetic acid are used an analogue of mercuretin is obtained [4]. Little is known about the mercuration of the acetic acid homologues, but mercury di-2-propionic acid has been described [5]. Mercuric propionate and n-butyrate when boiled in corresponding acid give α-monomercurated products in form of polymers analogous to those of monomercurated acetic acid [6]. In this paper the mercuration products of n-butyric, n-valeric and iso-valeric acid and the crystal structure of 2,2-bis(chloromercurio)-n-butyric acid DMSO-solvate are reported. Attempts to mercurate propionic, iso-butyric and trimethylacetic acid by analogous procedures were unsuccessful.

Results and discussion

n-Butyric acid is mercurated to give dimercurated n-butyric acid by treatment with mercuric n-butyrate in n-butyric anhydride. The mercuration product is an oligomer (I) with n ≅ 4, as indicated its mercury content. When acetic anhydride is used, exchange occurs and polymeric trimercurated acetic acid is the main product. When mercuric nitrate monohydrate is used the n-butyric acid undergoes carbon-carbon bond cleavage to give trimercurated acetic acid which is isolated in the form of a condensation oligomer, 2,2-bis(nitratomercurio)-2-n-butyryloxymercurioacetic acid (II).

$$C_3H_7COO \left[Hg - \overset{\displaystyle C_2H_5}{\underset{\displaystyle HgOCOC_3H_7}{\vert\ \ C\ \ \vert}} - COO \right]_n H \qquad C_3H_7COO \left[Hg - \overset{\displaystyle HgONO_2}{\underset{\displaystyle HgONO_2}{\vert\ \ C\ \ \vert}} - COO \right]_n H$$

$$\text{(I)} \qquad\qquad\qquad\qquad \text{(II)}$$

Hydrolysis of oligomer (I) with dilute hydrochloric acid gives 2,2-bis(chloromercurio)-n-butyric acid. This crystallizes from dimethylsulfoxide (DMSO) as a one-to-one solvate. Its crystal structure, as revealed by X-ray diffractometry, is made up of 2,2-bis(chloromercurio)-n-butyric acid and DMSO molecules, and thus the mercuration product is an oligomer of 2,2-bis(n-butyryloxymercurio)-n-butyric acid.

Treatment of n-valeric acid with mercuric n-valerate in n-valeric acid gives a dimercurated n-valeric acid oligomer analogous to I, namely $C_4H_9COO[HgC(C_3H_7)(HgOCOC_4H_9)COO]_nH$, predominantly as the dimer, since the mercury content corresponds to value of n of ca. 2. In the case of the 2,2-bis(chloromercurio)-product, obtained by hydrochloric acid hydrolysis of the dimer, no crystals suitable for X-ray structure analysis could be obtained; the product is not soluble in common solvents or in DMSO or DMF.

Isovaleric acid is converted into the dimercurated acid by mercuric oxide, and the mercurated product gives 2,2-bis(chloromercurio)-isovaleric acid, $(CH_3)_2CHC(HgCl)_2COOH$, upon hydrolysis by dilute hydrochloric acid, and this product has been isolated as crystals insoluble in common solvents. By analogy with n-butyric acid derivatives, the mercuration products from n-valeric and iso-valeric acid are almost certainly condensation oligomers of 2,2-bis(n-valeryloxymercurio)-n-valeric acid and 2,2-bis(iso-valeryloxymercurio)-isovaleric acid, respectively.

The structure of $C_2H_5C(HgCl)_2COOH \cdot DMSO$

In the crystal each 2,2-bis(chloromercurio)-n-butyric acid molecule is bonded to a DMSO molecule through a short hydrogen bond, 2.617(30) Å. The hydrogen atom is at a distance of 1.19 Å from the carboxyl oxygen with the bond angle at hydrogen of 159(1)°. The mercury-to-carbon distances are 2.097(30) and 2.089(33) Å and the mercury-to-chlorine distances 2.329(8) and 2.329(10) Å, values in very good agreement with the sum of the corresponding covalent radii [7,8]. The coordination at mercury is digonal, as expected, with a bond angle of 178° at both mercury atoms,
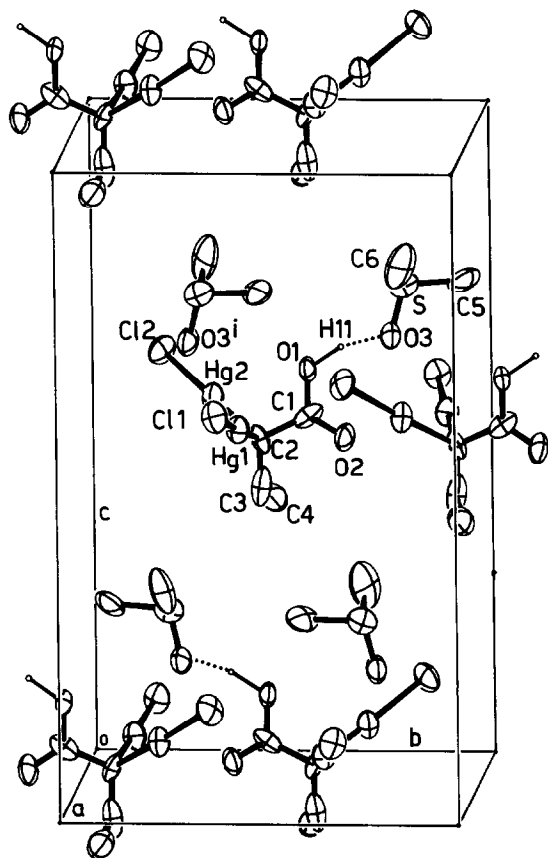
Fig. 1. ORTEP drawing of the structure of $C_2H_5C(HgCl)_2COOH \cdot DMSO$ viewed along the a axis (0 to 0.5 a).

and the Hg(1)–C(2)–Hg(2) angle is 103(1)°. The interatomic distances and bond angles are listed in Table 1.

Experimental

Spectral data: The IR spectra in the region of 4000–450 cm^{-1} were recorded on a Perkin–Elmer FT–IR Spectrophotometer Model 1600.

Preparation of 2,2-bis(n-butyryloxymercurio)-n-butyric acid

A mixture of mercuric n-butyrate (3.5 g) in n-butyric anhydride (30 mL, freshly redistilled) was heated and stirred at 90–95° C until the Hg^{2+} ions had disappeared (about 10 h). The excess of butyric anhydride was removed by distillation under reduced pressure and the remaining solution of dimercurated butyric acid was allowed to cool. The crystals that separated were filtered off, washed with diethyl ether, and dried. Yield: 2.6 g (65%). Anal. Found: C, 18.36; H, 2.72; Hg, 67.31. $C_4H_8O_2$ $(C_8H_{12}Hg_2)_4$ calcd.: C, 18.15; H, 2.37; Hg, 67.38%. IR ν(CO): 1584 cm^{-1}.

Table 1

Interatomic distances (Å) and angles (°) with esd's in parentheses [a]

C₂H₅C(HgCl)₂COOH molecule			
Hg1–Cl1	2.329(8)	C2–Hg1–Cl1	178(1)
Hg2–Cl2	2.329(10)	C2–Hg2–Cl2	178(1)
Hg1–C2	2.097(30)	Hg1–C2–Hg2	103(1)
Hg2–C2	2.089(33)	O1–C1–O2	121(3)
C1–O1	1.330(38)	O1–C1–C2	115(3)
C1–O2	1.217(46)	O2–C1–C2	124(3)
C1–C2	1.503(53)	C1–C2–C3	114(3)
C2–C3	1.428(59)	C2–C3–C4	119(3)
C3–C4	1.425(46)		
O1–H11	1.19		
DMSO molecule			
S–O3	1.513(25)	O3–S–C5	108(2)
S–C5	1.726(45)	O3–S–C6	106(2)
S–C6	1.689(54)	C5–S–C6	95(2)
Hydrogen bond			
O1 · · · O3	2.617(31)		
H11 · · · O3	1.47	O1–H11 · · · O3	159
Van der Waals contacts less then 3.00			
Hg1 · · · O3ⁱ	2.922(23)		
Hg2 · · · O3ⁱ	2.960(22)		

[a] Symmetry code: (*i*) $1/2 - x$, $y - 1/2$, z.

2,2-bis(chloromercurio)-n-butyric acid DMSO-solvate

A cooled suspension of the oligomer of 2,2-bis(n-butyryloxymercurio)-n-butyric acid (0.33 g) in dilute hydrochloric acid (3.5 mL 0.1 M, was stirred for 0.5 h and the liquid was decanted off and the procedure was repeated twice with 3.5 ml portions of the acid. The solid was filtered off, washed with water and ethanol, and dried. Yield: 0.22 g (71%). Crude dimercurated n-butyric acid was freed from decomposition products (mainly mercurous chloride) by dissolving it in DMSO. The crystalline product was pure DMSO 1 : 1 solvate of 2,2-bis(chloromercurio)-n-butyric acid. Anal. Found: C, 11.97; H, 1.97; Cl, 10.87; Hg, 63.33. $C_6H_{12}Cl_2Hg_2O_3S$ calcd.: C, 11.32; H, 1.90; Cl, 11.40; Hg, 63.05%. IR ν(CO): 1556 cm⁻¹.

Preparation of 2,2-bis(n-valeryloxymercurio)-n-valeric acid

A mixture of mercuric n-valerate (4 g) and n-valeric acid (40 mL) was heated at 125–130 ° C until a sample did not turn yellow on treatment with aqueous sodium hydroxide (about 4 h). The excess of the acid was distilled off under reduced pressure and the cooled solution was treated with a mixture of ethanol and water. The crystalline precipitate was filtered off, washed with water, and dried. Yield: 1.8 g (56%). Anal. Found: C, 23.52; H, 3.25; Hg, 61.25. $C_4H_{10}O_2(C_{10}H_{16}O_4Hg_2)_2$ calcd.: C, 23.01; H, 3.24; Hg, 61.48%. IR ν(CO): 1698 cm⁻¹.

2,2-Bis(chloromercurio)-n-valeric acid

The 2,2-bis(n-valeryloxymercurio)-n-valeric acid oligomer (1 g) was treated with dilute hydrochloric acid (40 mL, 0.1 M) in the presence of the four-fold volume of

ether (160 mL). 2,2-Bis(chloromercurio)-n-valeric acid, obtained by the digestion procedure described above, was filtered off, washed with ethanol and dried. Yield: 1 g (57%). Anal. Found: C, 11.10; H, 1.53; Cl, 11.66; Hg, 70.07. $C_5H_8Cl_2Hg_2O_2$ calcd.: C, 10.49; H, 1.41; Cl, 12.39; Hg, 70.11%. IR ν(CO): 1555 cm^{-1}.

2,2-Bis(chloromercurio)-isovaleric acid

Mercuric oxide (5 g) was dissolved in isovaleric acid (50 mL). The water was distilled off and the mixture heated at 110–125°C until mercuric ions had disappeared from the solution (about 4–5 h). The solution was treated with a mixture of dilute hydrochloric acid and diethyl ether. The pale yellow crystalline precipitate was filtered off, washed with water, and dried. Yield: 6 g (91%). Anal. Found: C, 11.10; H, 1.75; Cl, 11.56; Hg, 70.69. $C_5H_8Cl_2Hg_2O_2$ calcd.: C, 10.49; H, 1.41; Cl, 12.39; Hg, 70.11%. IR ν(CO): 1559 cm^{-1}.

X-ray diffraction experiment

Single crystals of the 2,2-bis(chloromercurio)-n-butyric acid DMSO solvate, $C_2H_5(HgCl)_2COOH \cdot DMSO$, were obtained by slow crystallisation from the solution of the 2,2-bis(chloromercurio)-n-butyric acid in dimethylsulfoxide to which acetone had been added.

The X-ray data used for strucrure determination were collected on a Philips PW 1100 diffractometer with Cu-K_α radiation (graphite monochromator, $\lambda = 1.5418$ Å) and θ–2θ scan mode.

Single crystal data: $C_6H_{12}Hg_2Cl_2SO_3$, mol. wt. 636.26, orthorhombic, $a = 12.233(3)$, $b = 11.362(1)$, $c = 18.895(1)$ Å, $V = 2626.2(27)$ Å, $D_{calc} = 3.218$ g cm^{-3}, $D_{obs} = 3.16$ g cm^{-3}, $Z = 8$ formula units, space group *Pbcn* (No. 60), $F(000) = 2256$, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 494.2 cm^{-1}, crystal size (mm from centroid): (1 0 0), (−1 0 0) 0.070, (0 1 0), (0 −1 0) 0.056, (0 0 1) 0.105, (0 −1 −1) 0.075.

Integrated intensities of 1196 unique reflections with $I > 3\sigma(I)$ were collected over the range $3 < \theta < 70°$ by the ω–2θ scan technique, with a scan range of 1.2° and scan rate of 0.04 s^{-1}. Three standard reflections, monitored every two hours, had weakened by a factor of 2.28 by the end of the measurements and each set of data collected within a given time interval was corrected by the appropriate decay factor. Because of the strong secondary extinction the reflections 0 0 2, 1 0 2 and 0 2 0 were excluded from the structure refinement procedure. Corrections for absorption [9], Lorentz and polarization effects were applied. Weights of $1/\sigma(I)$ were alloted to all reflections. Anisotropic temperature factors were assigned to all nonhydrogen atoms.

The structure was solved by means of three-dimensional Fourier synthesis, based upon the mercury atom coordinates obtained from the Patterson synthesis, and then refined by full-matrix least-squares method. The position of the hydrogen atoms were determined from a difference Fourier map and included in the last three cycles of the refinement. The position of the hydrogen atoms were taken from the Fourier map since they could not be refined. The final value of the reliability index was $R = 0.068$ and $R_w = 0.078$. The atomic scattering factors were those of Cromer and Mann [10] with corrections for real and imaginary parts of the anomalous dispersion [11]. The final values of atomic coordinates with esd's are listed in Table 2. List of the thermal parameters and observed and calculated structure factors can be obtained from the authors. Calculations were carried out on the Univac 1110

Table 2

Atomic coordinates and equivalent isotropic thermal parameters ($\mathring{A}^2$) with esd's in parentheses for 2,2-bis(chloromercurio)-n-butyric acid DMSO

Atom	x	y	z	U_{eq} [a]
Hg1	0.3763(1)	0.3973(1)	0.5364(1)	0.0499(3)
Hg2	0.1229(1)	0.3099(1)	0.5562(1)	0.0543(4)
Cl1	0.5534(6)	0.3570(9)	0.5746(5)	0.0608(27)
Cl2	0.0185(7)	0.1717(9)	0.6172(5)	0.0680(23)
S	0.1769(10)	0.7994(11)	0.7368(6)	0.083(4)
O1	0.1884(17)	0.5554(18)	0.6082(11)	0.044(7)
O2	0.1840(19)	0.6462(21)	0.5043(13)	0.058(7)
O3	0.2008(18)	0.7683(20)	0.6605(12)	0.061(6)
C1	0.1965(24)	0.5559(36)	0.5380)17)	0.047(10)
C2	0.2164(24)	0.4377(30)	0.5047(19)	0.044(9)
C3	0.2023(22)	0.4371(31)	0.4297(25)	0.063(13)
C4	0.0960(27)	0.4574(35)	0.4014(19)	0.069(11)
C5	0.1534(31)	0.9489(38)	0.7420(19)	0.086(12)
C6	0.2989(41)	0.8039(41)	0.7786(33)	0.145(22)
H11	0.1980	0.3580	0.1430	
H31	0.2532	0.4996	0.4034	
H32	0.2259	0.3562	0.4078	
H41	0.0843	0.4316	0.3509	
H42	0.0395	0.4166	0.4322	
H43	0.0784	0.5479	0.4022	
H51	0.0990	0.9710	0.7100	
H52	0.1383	0.9782	0.7903	
H53	0.2255	0.9957	0.7234	
H61	0.3200	0.7350	0.7880	
H62	0.2803	0.8409	0.8318	
H63	0.3504	0.8557	0.7567	

[a] $U_{eq} = 1/3[U_{11}(aa^\star)^2 + U_{22}(bb^\star)^2 + U_{33}(cc^\star)^2 + 2U_{12}aba^\star b^\star \cos \gamma + 2U_{13}aca^\star c^\star \cos \beta + 2U_{23}bcb^\star c^\star \cos \alpha]$.

computer of the Zagreb University Computing Center SRCE, with the programmes described in ref. 12.

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