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Mercuration of Some Aliphatic Aldehydes. The Crystal Structure of 2,2-Bis(chloromercuri)butyraldehyde*

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Tris(chloromercuri)acetaldehyde (*I*), 2,2-bis(chloromercuri)propionaldehyde (*II*) and 2,2-bis(chloromercuri)butyraldehyde (*III*) were obtained by mercuration of the corresponding aldehyde in an aqueous mercury(II) chloride solution containing sodium acetate. The mercurated aldehydes (*II*) and (*III*) are described for the first time. The crystal structure of (*III*) was determined by means of Patterson and Fourier syntheses based on threedimensional X-ray diffractometer intensity data and refined by the full-matrix least-squares method to an *R* value of 0.049. Crystals are orthorhombic, space group $Pna2_1$ with $z = 4$ formula units in the unit cell of the dimensions: $a = 1114.6(6)$, $b = 1121.3(5)$, $c = 657.3(3)$ pm, $D_{\mathrm{obs}} = 4.51$ and $D_{\mathrm{calc}} = 4.38$ Mg m^{-3}. The structure consists of discrete molecules of 2,2-bis(chloromercuri)butyraldehyde. The Hg—C bond lengths are 216(2) and 209(2) pm. The Hg—C—Hg bond angle is 103(1)°, and the C—Hg—Cl bond angles are 173(2)° and 172(2)°, respectively.

INTRODUCTION

Tris(chloromercuri)acetaldehyde (*I*) was formerly described and identified as the product obtained by passing acetylene through an aqueous mercury(II) chloride solution.[1] It was found recently[2,3] that (*I*) is also obtained by boiling an ethanolic solution of mercury(II) chloride with sodium acetate. Acetaldehyde, when mercurated in aqueous mercury(II) nitrate solution, also gives a trimercurated derivative.[4] Since the mercurated homologoues of acetaldehyde have not yet been described, the aim of our study has been (i) to elaborate a simple method of mercuration applicable to this class of compounds and (ii) to find out the composition of the mercuration product of propionaldehyde and butyraldehyde. By analogy with the acetaldehyde, which is always fully mercurated (only the trimercurated derivative has been obtained in the given conditions), dimercurated derivatives at the α-carbon atom were anticipated.

EXPERIMENTAL

Characterization of the Mercuration Products

Spectral data. — IR spectra in the region of 4000—200 cm^{-1} were recorded on a Perkin-Elmer Model 580 B infrared spectrophotometer using KBr discs.

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

Preparation

Tris(chloromercuri)acetaldehyde(I). — A solution of freshly distilled acetaldehyde (0.27 g) in water (20 cm^3) was added to a solution of mercury(II) chloride (5 g) and sodium acetate trihydrate (6 g) in water (120 cm^3) and the mixture heated on a water bath for three hours. The white crystalline solid was filtered off, washed with water, dried in vacuo and weighed (4.54 g, 99%), dec, at 210 °C. Found: C, 3.30; H, 0.19; Cl, 14.39; Hg, 80.37; $C_2HCl_3Hg_3O$ calcd. C, 3.21; H, 0.14; Cl, 14.20; Hg, 80.33%. For infrared data see reference 2.

2,2-Bis(chloromercuri)propionaldehyde(II). — A solution of propionaldehyde (0.58 g), mercury(II) chloride (5.4 g) and sodium acetate trihydrate (6.5 g) in water (100 cm^3) was heated on a water bath for three hours. The white crystalline precipitate was filtered off, washed with water, dried in vacuo and weighed (4.5 g, 85%), dec. at 218 °C. Found: C, 6.44 H, 1.04; Cl, 13.54; Hg, 75.87; $C_3H_4Cl_2Hg_2O$ calcd. C, 6.82; H, 0.76; Cl, 13.43; Hg, 75.96%. Infrared absorptions: 2945w, 2915w, 2859w, 1630s, 1447m, 1440sh, 1398m, 1182s, 1082m, 1057m, 1009w, 906s, 608m, 572m, 348s and 314s cm^{-1}.

2,2-Bis(chloromercuri)butyraldehyde(III). — A solution of butyraldehyde (0.72 g), mercury (II) chloride (5.4 g) and sodium acetate trihydrate (6.5 g) in water (100 cm^3 was heated on a water bath for two hours. The white crystalline precipitate was filtered off, washed with water, dried and weighed (4.75 g, 88%), dec. at 211 °C. Found: C, 8.92; H, 1.55; Cl, 13.36; Hg, 74.08; $C_4H_6Cl_2Hg_2O$ calcd. C, 8.86; H, 1.12; Cl, 13.08; Hg, 73.99%. Infrared absorptions: 2990w, 2959w, 2870w, 2841w, 2755w, 1620s, 1452w, 1435w, 1396vw, 1378w, 1330vw, 1281vw, 1182s, 1101w, 1078vw, 1011sh, 1002m, 900vw, 878w, 792s, 715vw, 700vw, 630vw, 375w, 325sh and 311m cm^{-1}.

X-Ray Diffraction Experiment

Needle-shaped transparent crystals of *(III)*, suitable for X-ray structure analysis, were obtained by prolonged standing of the filtrate left over after the first crop of the microcrystalline product had been filtered off.

Crystal data were determined with a Philips PW 1100 computer controlled diffractometer (graphite monochromatized Mo—Kα radiation, $\lambda = 71.07$ pm).

Single crystal data. — $C_4H_6Hg_2Cl_2O$, mol. wt. 542.177, orthorhombic, $a = 1114.6(6)$, $b = 1121.3(5)$, $c = 657.3(3)$ pm, $V = 0.8215$ nm^3, $D_{obs} = 4.51$ Mg m^{-3}, $D_{calc} = 4.38$ Mg m^{-3} $Z = 4$, space group $Pna2_1$ (No. 33), F(000) = 928, Mo—Kα radiation ($\lambda = 71.01$ pm), μ (Mo—Kα) = 386.8 cm^{-1} crystal dimensions (mm from centroid) (100)0.176, ($\bar{1}$00)0.176, (010)0.060, (0$\bar{1}$0)0.60, (001)0.260, (00$\bar{1}$)0.260, maximum, minimum transmission coefficients 0.710, 0.311.

Intensity measurements. — The lattice parameters and orientation matrix were obtained by the least-squares method from 18 reflections. The integrated intensities of 866 independent reflections with $I > 3\sigma(I)$ were collected within the interval of $3° < \Theta < 30°$ using $\omega — 2\Theta$ scan technique, with scan range 1.0° and scan rate 0.025° s^{-1}. Three standard reflections (0$\bar{4}$1, $\bar{3}$01, $\bar{2}\bar{3}$0), monitored every 120 minutes, had weakened by a factor of 1.19 by the end of the measurement. Each set of data collected within the given time interval was corrected by a decay factor obtained for the standard reflections over this period.

Determination and refinement of the structure. — 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 the full-matrix least-squares method. Weights of $1/(\sigma I)$ were alloted to all reflections. Corrections for the absorption,[5] Lorentz and polarization effects were applied. The atomic scattering factors were those of Cromer and Mann[6] with corrections for the real and imaginary parts of the anomalous dispersion.[7] The atomic parameters were refined with isotropic temperature factors to R = 0.145. When anisotropic temperature factors were assigned to the mercury and chlorine atoms, further refinement lowered the R value to 0.050. At this stage by the difference synthesis was permited the location of only one methyl H atom H(41). The other ones were given calculated positions and thermal parameters 10% greater than those of bonded atoms. The refinement with anisotropic temperature factors for all nonhydrogen atoms, except the C(2) atom, converged at $R = 0.049$ and $R_w = 0.058$. Still at this stage of the analysis a satisfactory location of the atoms has not been achieved due to high anisotropy of the atomic thermal parameters. For the Hg and Cl atoms they are

TABLE I

Atomic Coordinates and Thermal Parameters ($pm^2 \times 10^4$)*

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	.2767(1)	.1213(1)	.5000(0)	.0222(4)	.0268(5)	.0671(8)	—.0036(3)	.0013(33)	.0063(25)
Hg(2)	.3489(1)	.4094(1)	.4968(14)	.0264(4)	.0258(4)	.0540(7)	.0015(3)	—.0007(30)	.0055(26)
Cl(1)	.1232(6)	—.0203(6)	.4961(54)	.0343(29)	.0312(28)	.0660(70)	—.0079(22)	.0060(104)	—.0179(105)
Cl(2)	.2649(6)	.5995(6)	.5036(63)	.0387(29)	.0354(30)	.0613(53)	.0111(25)	—.0031(168)	.0137(148)
C(1)	.490(4)	.232(4)	.743(7)	.43(18)	.21(15)	.040(23)	.013(13)	—.013(18)	—.021(16)
C(2)	.427(2)	.241(2)	.534(6)	.033(6)					
C(3)	.499(3)	.214(4)	.347(6)	.021(14)	.033(20)	.041(27)	—.003(13)	—.003(15)	.017(16)
C(4)	.540(4)	.102(3)	.234(6)	.063(24)	.058(21)	.038(21)	.012(18)	.016(19)	.002(18)
O	.610(2)	.199(2)	.660(6)	.036(11)	.033(11)	.114(26)	—.001(9)	—.007(15)	—.010(14)
H(11)	.455	.244	.902						
H(31)	.447	.263	.229						
H(32)	.581	.264	.374						
H(41)	.118	.395	.169						
H(42)	.611	.102	.120						
H(43)	.539	.014	.306						

* Anisotropic thermal parameters in the form exp $|-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)|$

about three times and for the O atom four times larger along the *c* than along the *a* or *b* axis direction. Besides, the diffraction effect originated from the layer parallel to (100) which contain all mercury and chlorine atoms, i. e., the majority of the scattering matter in the structure, lowered the reliability of the coordinates of the light atoms particularly those of the O, C(1) and the C(2) atoms.

The final values of the atomic coordinates and thermal parameters with e.s.d.'s are listed in Table I. Calculations were carried out on the UNIVAC 1110 of the SRCE, University Computing Centre, Zagreb, using the XRAY System.[8]

RESULTS AND DISCUSSION

At the beginning of our study, when mercury(II) acetate was used as the mercuration reagent, badly defined products were obtained. The AcOHg-derivative hydrolized in the aqueous medium to an HOHg-derivative which polymerized over the Hg—O—Hg bridges as assumed for Hofmann's base.[9] Using a mixture of mercury(II) chloride and sodium acetate in the aqueous solution as the mercuration reagent we succeeded in preparations chloromercurated derivatives. The aldehyde carbonyl group was not affected by the mercuration reagent as evidenced by the characteristic absorption band at about 1620 cm^{-1} in the IR spectra of all three mercurated products. The substitution of both hydrogen atoms at the α-carbon atom by the ClHg group was proved by X-ray structure analysis of the mercurated butyraldehyde (*III*).

The mercurated aldehydes reported are almost insoluble in water and in common organic solvents and cannot be recrystallized.

Description of the Structure. The crystal structure of 2,2-bis(chloromercuri)butyraldehyde projected on (001) is shown in Figure 1. The interatomic distances and bond angles are given in Table II.

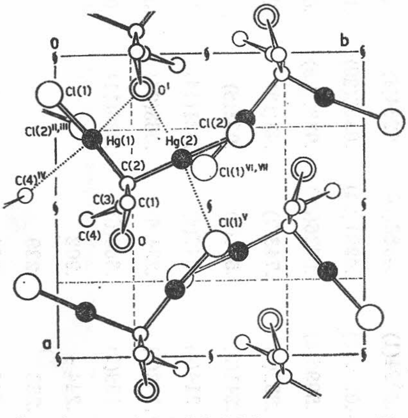

Figure. The structure of 2,2-bis(chloromercuri)butyraldehyde, $C_2H_5C(HgCl)_2CHO$, viewed along the *c*-axis direction

The crystal structure consists of discrete molecules whose ClHg and CO groups have the preponderant influence on the mutual arrangement of the molecules. Each molecule is actually a substituted C(2) tetrahedron, $(ClHg)_2 \cdot C(C_2H_5)CHO$, and the best packing conditions are achieved when the tetrahedra approach with their CHg_2 and $(C_2H_5)CHO$ edges perpendicularly to each other. Such a packing is corroborated by the polar Hg . . . O and Hg . . . Cl interactions. In the layers formed at $z = 1/4, 3/4$, with the atoms related by diagonal

TABLE II

*Interatomic Distances (pm) and Bond Angles (°), with Standard Deviations in Parantheses**

(a) *Distances*

C(2) — Hg(1)	216(2)	Hg(1) . . . O^{i}	294(3)
C(2) — Hg(2)	209(2)	Hg(1) . . . Cl(2)^{ii}	330(4)
Hg(1) — Cl(1)	233(1)	Hg(1) . . . Cl(2)^{iii}	335(4)
Hg(2) — Cl(2)	233(1)	Hg(1) . . . C(4)^{iv}	358(4)
C(1) — C(2)	157(6)	Hg(2) . . . O^{i}	312(3)
C(1) — O	148(5)	Hg(2) . . . Cl(1)^{v}	330(4)
C(2) — C(3)	150(5)	Hg(2) . . . Cl(1)^{vi}	339(4)
C(3) — C(4)	153(6)	Hg(2) . . . Cl(1)^{vii}	340(4)
		C(4) . . . C(4)^{iv}	410(5)

(b) *Angles*

C(2) — Hg(1) — Cl(1)	173(1)	Cl(1) — Hg(1) . . . O^{i}	90(1)
C(2) — Hg(2) — Cl(2)	172(2)	Cl(1) — Hg(1) . . . Cl(2)^{ii}	81(1)
Hg(1) — C(2) — Hg(2)	103(1)	Cl(1)— Hg(1) . . . Cl(2)^{iii}	82(1)
C(1) — C(2) — Hg(1)	113(2)	C(2)—Hg(1) . . O^{i}	92(1)
C(1) — C(2) — Hg(2)	111(2)	C(2)— Hg(1) . . Cl(2)^{iii}	93(1)
C(3) — C(2) — Hg(1)	102(2)	Cl(2)^{ii} . . . Hg(1) . . O^{i}	108(1)
C(3) — C(2) — Hg(2)	108(2)	Cl(2)—Hg(2) . . . O^{i}	90(1)
C(3) — C(2) — C(1)	118(3)	Cl(2) — Hg(2) . . . Cl(1)^{vi}	79(1)
C(2) — C(3) — C(4)	136(4)	Cl(2) — Hg(2) . . . Cl(1)^{vii}	81(1)
C(2)— C(1) — O	132(4)	C(2) —Hg(2) . . . O^{i}	88(1)
		C(2) — Hg(2) . . . Cl(1)^{v}	87(1)
		C(2)— Hg(2) . . . Cl(1)^{vi}	93(1)
		Cl(1)^{vi} . . . Hg(2) . . . Cl(1)^{v}	80(1)
		Cl(1)^{v} . . . Hg(2) . . . Cl(1)^{vii}	80(1)
		Cl(1)^{vii} . . . Hg(2) . . . O^{i}	120(1)

* Transformation of the asymmetric unit (x, y, z):

(i) x — ½, ½ — y, z;
(ii) ½ — x, y — ½, z — ½;
(iii) ½ — x, y — ½, z + ½;
(iv) 1 — x, —y, z + ½;
(v) ½ + x, ½ — y, z;
(vi) ½ — x, ½ + y, z + ½;
(vii) ½ — x, ½ + y, z — ½.

glide-plane symmetry, both mercury atoms are in the octahedral effective coordination,[10] but due to the packing demand of the ethyl group the octahedron around the Hg(1) atom differs from that one around the Hg(2) atom. The extend of the octahedral distortion is seen from the values of corresponding angles listed in Table II. The Hg(1)—C(2) bond of 216(2) pm is unexpectedly longer than the Hg(2)—C(2) bond of 209(2) pm, while Hg(1 . . . O contact of 294(3) pm is significantly shorter than the Hg(2) . . . O contact of 312(3) pm. Due to the Hg(1) . . . O contact an elongation of the C(1)—O bond of the carbonyl group is normally expected, but that of 148(5) pm seems to be too large to be ascribed only to this effect and is partly due to the diffraction effect (see Experimental). The mean values of the bond lengths are in agreement with values found in the structure of the analogous compounds.[11–13] The C(4) methyl group is conditionally included into the Hg(1) octahedron. The shortest distance of its H(42) hydrogen atom to the Hg(1) mercury atom of 291(4) pm is larger than the expected sum of the van der Waals radii (~ 275 pm). The cause of such a looseness is to be found in a very close methyl-to-methyl contact, C(4) . . . C(4)^{iv}, of 410(5) pm which fixed their position as evidenced by the low value of their thermal parameters.

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SAŽETAK

Merkuriranje nekih alifatskih aldehida. Kristalna struktura 2,2-bis(kloromerkuri)butiraldehida

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Priređeni su tris(kloromerkuri)acetaldehid (*I*), 2,2-bis(kloromerkuri)propionaldehid (*II*) i 2,2-bis(kloromerkuri)butiraldehid (*III*) merkuriranjem odgovarajućeg aldehida živa(II)-kloridom u vodenoj otopini, uz dodatak natrij-acetata. Merkurirani aldehidi (*II*) i (*III*) priređeni su prvi puta, a 2,2-bis(kloromerkuri)butiraldehidu, (*III*), određena je i kristalna struktura. Struktura je određena na osnovi 866 neovisnih refleksa prikupljenih na automatskomu rendgenskom difraktometru i utočnjena metodom najmanjih kvadrata do faktora $R = 0.049$. Kristali su ortorompski, prostorne grupe $Pna2_1$ i sadržavaju četiri formulske jedinice u jediničnoj ćeliji veličine $a = 1114.6(6)$, $b = 1121.3(5)$, $c = 657,3(3)$ pm. Izmjerena gustoća iznosi $D_m = 4,51$ Mg cm^{-3}, izračunana $D_x = 4,38$ Mg cm^{-3}. Struktura se sastoji od diskretnih molekula 2,2-bis(kloromerkuri)butiraldehida. Duljine veza Hg—C iznose 216(2) i 209(2) pm. Kut između Hg—C—Hg je 103(1)°, a kutevi između atoma C—Hg—Cl iznose 173(2)° i 172(2)°.