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Monomercurated acetic acid. The crystal structure of NO_3HgCH_2COOH

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Abstract

Mercuration of acetic acid with mercuric acetate gives a condensation polymer of monomercurated acetic acid, $CH_3COO[HgCH_2COO]_nH$, with $n \cong 10$, which is soluble in alkali. The hydroxymercurioacetic acid polymer, $OH[HgCH_2COO]_nH \cdot H_2O$, with $n \cong 10$, separates when the alkaline solution is treated with carbon dioxide, and treatment of this with hydrochloric and nitric acid gives $ClHgCH_2COOH$ and NO_3HgCH_2COOH, respectively.

An X-ray diffraction study of NO_3HgCH_2COOH shows it to consist of dimers in which the molecules are linked through their pairs over carboxyl groups by centrosymmetric hydrogen bonds 2.67(2) Å long. The Hg–C and Hg–O bond distances are 2.08(2) and 2.10(2) Å, respectively.

Introduction

Mercuration of acetic acid gives polymeric monomercurated [1] or trimercurated [2] acetic acid, depending upon the conditions and on the mercurating agent used. The only monomeric monomercurated acetic acid previously known was chloromercurioacetic acid, accessible through the ketene synthesis [3]. We have now prepared it by the action of hydrochloric acid on the hydroxymercurioacetic acid polymer obtained from the corresponding acetoxy-derivative [2]. Nitratomercurioacetic acid has also been prepared in the similar way, and its crystal structure determined by X-ray diffraction.

Results and discussion

The acetoxymercurioacetic acid polymer is conveniently prepared by boiling glacial acetic acid with mercuric acetate. It is formulated as $CH_3COO[HgCH_2COO]_nH$, with $n \cong 10$ as indicated by the mercury content. When its solution in aqueous alkali is treated with carbon dioxide a white crystalline solid separates, and this is formulated as the hydroxymercurioacetic acid polymer, $HO[HgCH_2COO]_nH \cdot H_2O$, where $n \cong 10$ as indicated by the mercury content. When its suspension in methanol is treated with dilute aqueous hydrochloric acid it gives chloro-

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mercurioacetic acid, $ClHgCH_2COOH$, as a crystalline precipitate, identical with that obtained by Tilander [3]. Our attempts to mercurate acetic acid directly to $ClHgCH_2COOH$, by using mercuric chloride as the mercuration agent, were unsuccessful, although acetaldehyde, propionaldehyde and butyraldehyde are readily mercurated by that reagent [4].

From a solution of hydroxymercurioacetic acid in the concentrated nitric acid good crystals of nitratomercurioacetic acid, NO_3HgCH_2COOH, were obtained. Nitratomercurioacetic acid cannot be prepared from acetic acid by direct mercuration with mercuric nitrate since the trimercurated derivative is formed, CH_3COO-$[HgC(HgNO_3)_2COO]_2H$, (see Experimental). This gives mercuretin, the well defined condensation polymer [2] when boiled with glacial acetic acid. When acetic anhydride is used instead of glacial acetic acid, trimercurated derivatives are obtained [5,6]. In the cold, acetic anhydride is not mercurated with mercuric nitrate monohydrate but gives the double salt, $Hg(OCOCH_3)NO_3 \cdot Hg(OCOCH_3)_2$ [7]. Mercuration of the acetic acid homologues also gives oligomers in the case of dimercurated n-butyric, n-valeric, and isovaleric acid [8], as does that of monomercurated propionic and butyric acid [9].

X-Ray structure of NO_3HgCH_2COOH

The crystal structure of nitratomercurioacetic acid consists of NO_3HgCH_2COOH molecules associated in pairs by centrosymmetric hydrogen bonds O(1) ··· O(2)^{i} of 2.67(2) Å. The packing is shown in Fig. 1. The interatomic distances and angles, shown in Table 1, have normal values [10]. The coordination of mercury is digonal, the C–Hg–O angle being 176.2(6)°. Mercury is bonded to the carbon atom of the acetic acid with a Hg–C(1) distance of 2.08(2) Å and to the nitrate with a Hg–O(3) distance of 2.10(2) Å. The Hg–C bond length is similar to those in other mercurated aliphatic compounds [11]. The Hg–O bond length and also the lengthening of the N–O(3) bond are comparable with those in nitrates of trimercurated acetic acid, i.e. $[Hg(H_2OHg)(NO_3Hg)CCOO]NO_3$ and $2(NO_3Hg)_3CCOOH \cdot HNO_3$ [6]. There is one intramolecular contact, Hg ··· O(4), of 2.78(1) Å which is below the sum of the van der Waals radii (2.94 Å) and is therefore within the range for possible coordination to mercury [10,12].

Table 1

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

Hg–C(1)	2.08(2)	C(1)–Hg–O(3)	176.2(6)
Hg–O(3)	2.10(2)	Hg–C(1)–C(2)	110(1)
C(1)–C(2)	1.52(2)	C(1)–C(2)–O(1)	124(2)
C(2)–O(1)	1.22(2)	C(1)–C(2)–O(2)	113(1)
C(2)–O(2)	1.32(2)	O(1)–C(2)–O(2)	123(2)
N–O(3)	1.29(2)	Hg–O(3)–N	111(1)
N–O(4)	1.24(2)	O(3)–N–O(4)	118(2)
N–O(5)	1.23(2)	O(3)–N–O(5)	118(2)
		O(4)–N–O(5)	124(2)
O(1) ··· O(2)^{i}	2.67(2)		
Hg ··· O(3)^{ii}	2.94(2)		
Hg ··· O(4)	2.78(1)		
Hg ··· O(4)^{iii}	2.94(1)		

[a] Transformation of the asymmetric unit (x, y, z); (i) $-x, -1-y, 1-z$; (ii) $0.5-x, y-0.5, 1.5-z$; (iii) $x, y, 1+z$.

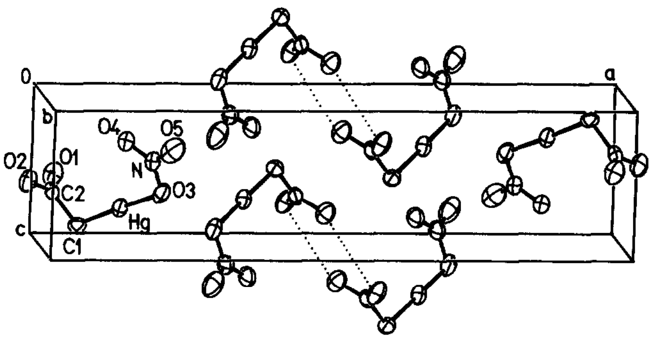

Fig. 1. A view of the molecular packing in the unit cell. Hydrogen bonds are shown by dotted lines.

Experimental

Preparation and characterization of the mercuration products

Spectral data. The IR spectra in the region of 4000–180 cm^{-1} were recorded on a Perkin–Elmer spectrophotometer Model 580 D with KBr discs.

Acetoxymercurioacetic acid polymer

Glacial acetic acid (50 mL) was boiled with mercuric acetate (10 g) until a sample did not turn yellow on treatment with aqueous sodium hydroxide (about 9 h). Most of the acetic acid (about 3/4) was distilled off, and the mixture left for several hours at room temperature. The solid was filtered off, washed with dilute acetic acid (2%) and ethanol, and dried over NaOH pellets to constant weight. Yield: 7.7 g (92.7%). Anal. Found: C, 10.11; H, 1.24; Hg, 75.68. $C_2H_4O_2(C_2H_2O_2Hg)_{10}$ calcd.: C, 9.99; H, 0.91; Hg, 75.80%. IR max (cm^{-1}) 3400mbr, 2960vw, 1675m, 1575s, 1535s, 1425s, 1366vs, 1215sh, 1140vw, 1100vw, 1082vs, 1022w, 945m, 795w, 785w, 680m, 665sh and 650vw.

Hydroxymercurioacetic acid polymer

A solution of acetoxymercurioacetic acid (6 g) in aqueous sodium hydroxide (10%, 30 mL) was diluted with water (150 mL) and then a carbon dioxide stream was passed through the solution until no further precipitate appeared (about 1 h, pH 7.5). The precipitate was filtered off, washed with water and ethanol, and dried over $CaCl_2$. Yield: 4.9 g (83%). Anal. Found: C, 9.36; H, 1.20; Hg, 76.17. $HO[HgCH_2COO]_nH \cdot H_2O$ for $n = 10$, calcd.: C, 9.16; H, 0.92; Hg, 76.49%. IR max. (cm^{-1}) 3455mbr, 2953w, 2928vs, 2922vs, 2904w, 2878vw, 2691w, 1656w, 1590vs, 1500w, 1423m, 1309s, 1109m, 1087m, 946w, 808w, 704w, 588w, 526w, 461w.

Chloromercurioacetic acid

Hydrochloric acid 0.1 *M* (190 mL) was added in small portions to a gently-heated and shaken methanolic suspension of finely-ground hydroxymercurioacetic acid (5 g in 125 mL) until the mixture was neutral. The solution was then evaporated to a half its volume then set aside for several hours in the cold. The crystalline precipitate formed was filtered off, washed with water, and dried over $CaCl_2$. Yield: 4.3 g (76.4%), m.p. 193 °C. The product was recrystallised from hot methanol. Anal. Found: C, 8.12; H 1.15; Cl, 11.67; Hg, 67.88. $C_2H_3ClHgO_2$ calcd.: C, 8.14; H, 1.03;

Cl, 12.01; Hg, 67.98%. IR max (cm^{-1}) 3415mbr, 3020w, 2958vw, 2900m, 2805vw, 2625m, 2500w, 1685vs, 1615s, 1530vw, 1415s, 1385w, 1275vs, 1118s, 1075vs, 928m, 885mbr, 786m, 765vw, 642s, 495vw, 432m, 335vw and 315m.

Nitratomercurioacetic acid

Finely-ground hydroxymercurioacetic acid (2 g) was added in small portions to concentrated nitric acid (5.5 mL) with gentle heating (40 ° C) and the clear solution was left to stand overnight. The crystalline product was filtered off, washed with absolute ethanol, and dried over NaOH. Yield: 1.5 g (61.3%). Anal. Found: C, 7.59; H, 1.20; N, 3.96; Hg, 62.39; $C_2H_3NHgO_5$ calcd.: C, 7.47; H, 0.94; N, 4.35; Hg, 62.37%. IR max (cm^{-1}) 3500wbr, 3040w, 2965w, 2890vw, 2785vw, 2645m, 2527vw, 1842w, 1770w, 1667vs, 1514s, 1498s, 1428vs, 1385sh, 1363vs, 1265vs, 1120s, 1095s, 1078m, 988vs, 935vw, 921m, 890w, 837m, 815w, 802m, 758m, 710w, 657s, 502w, 455m, 310m.

Tris(acetoxymercurio)acetic acid–mercuretin

Mercuric nitrate monohydrate (2 g) was heated and stirred in boiling glacial acetic acid (6 mL) until Hg^{2+} ions had disappeared from the solution (3 h). The crystalline product, consisting of the dimer of 2-acetoxymercurio-2,2-bis(nitratomercurio)acetic acid, was filtered off, washed with absolute ethanol, and dried. Yield: 1.54 g (91.7%). Anal. Found: Hg, 73.74; N, 4.01. $C_2H_4O_2(C_2N_2O_8Hg_3)_2$ calcd.: Hg, 74.13; N, 3.45%. IR max (cm^{-1}) 3441wbr, 2931s, 2924s, 2917s, 1684m, 1654s, 1636s, 1508vs, 1458m, 1380sh, 1360vs, 1320sh, 1274vs, 1093m, 988m, 817m, 802w, 743m, 692w, 637w, 615w, 540m, 522m, 508m and 458m.

Finely-ground dimeric 2-acetoxymercurio-2,2-bis(nitratomercurio)acetic acid ('nitrato–mercuretin') (1 g) was heated with glacial acetic acid (8 mL) for a few minutes (5–10 min) to give pure mercuretin, which was filtered off, washed with ether, and dried. Yield: 0.8 g (81%). Anal. Found: Hg, 74.68. $C_2H_4O_2(C_6H_6O_6Hg_3)_2$ calcd.: Hg, 74.67%. The IR spectrum was identical with that of mercuretin, as well as the parameters of the unit cell of the $(ClHg)_3CCOOH \cdot DMSO$ crystals obtained from the product [2].

Crystal structure determination

Crystal data. $C_2H_3HgNO_5$, $M = 321.64$, monoclinic, space group $P2_1/n$, $a = 20.267(4)$, $b = 5.424(2)$, $c = 5.226(1)$ Å, $\beta = 90.34(2)°$, $V = 574.5(3)$ Å^3, $Z = 4$, $D_c = 3.719$ g cm^{-3}, $F(000) = 568$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 267.3$ cm^{-1}, crystal dimensions (mm from centroid): $(\bar{1}00)$ 0.057; (001) 0.051; $(30\bar{1})$ 0.018; $(\bar{5}03)$ 0.017; $(1\bar{5}1)$, $(\bar{1}5\bar{1})$ 0.272; minimum, maximum transmission coefficients 0.061, 0.449, $R = 0.059$, $R_w = 0.076$.

Diffraction data were collected at room temperature on a Philips PW 1100 computer-controlled diffractometer with graphite monochromated Mo-K_α radiation. The cell dimensions were obtained by the least squares procedure from 18 reflections ($10.8 < 2\theta < 19.5°$). Intensities were measured by the θ–2θ technique with a scan width of 1.6° and scan speed of 0.04 °s^{-1}. 1499 reflections were collected over the range $2 < \theta < 30°$ ($-28 \leqslant h \leqslant 28$, $0 \leqslant k \leqslant 7$, $0 \leqslant l \leqslant 7$). Three standard reflections (411, $\bar{6}00$, $\bar{8}\bar{1}1$) measured every 2 h indicated a decay of 28%. The intensities were corrected for decay and Lorentz, polarization and absorption effects. 1235 unique reflections with $I > 3\sigma(I)$ were used for structure determination.

Table 2

Atomic coordinates and equivalent isotropic thermal parameters (Å^2)

Atom	x	y	z	U_{eq} [a]
Hg	0.1536(1)	0.0204(1)	0.8252(1)	0.0363(1)
C(1)	0.091(1)	−0.237(2)	0.989(3)	0.035(3)
C(2)	0.050(1)	−0.361(2)	0.782(3)	0.034(3)
O(1)	0.059(1)	−0.570(2)	0.705(3)	0.050(3)
O(2)	0.003(1)	−0.217(2)	0.689(2)	0.049(3)
O(3)	0.214(1)	0.299(2)	0.675(2)	0.044(2)
O(4)	0.152(1)	0.234(3)	0.342(2)	0.050(3)
O(5)	0.222(1)	0.538(2)	0.346(3)	0.070(4)
N	0.195(1)	0.360(3)	0.448(2)	0.042(3)

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

The Hg atom was located by the heavy atom method, and the other non-hydrogen atoms were found from a difference Fourier map. All atoms were refined by a full-matrix least squares method using SHELX76 [13]. The final refinement with anisotropic thermal parameters for all atoms converged at $R = 0.059$ and $R_w = 0.076$ ($w = 4.7706/(\sigma^2(F) + 0.000937F^2)$). The highest final shift/esd was 0.001. The hydrogen atoms were not included in the model. Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 14.

The atomic coordinates are given in Table 2. Tables of anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

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References

1 P.R. Wells and W. Kitching, Aust. J. Chem., 16 (1963) 508.
2 D. Grdenić, B. Korpar-Čolig and M. Sikirica, J. Organomet. Chem., 276 (1984) 1.
3 B. Tilander, Ark. Kemi, 25 (1966) 459.
4 B. Korpar-Čolig, Z. Popović and M. Sikirica, Croat. Chem. Acta, 57 (1984) 689.
5 J.E. Marsh and R. de J. Fleming Struthers, J. Chem. Soc., (1927) 2658.
6 D. Grdenić, M. Sikirica and D. Matković-Čalogović, J. Organomet. Chem., 306 (1986) 1.
7 D. Grdenić, M. Sikirica and B. Korpar-Čolig, Croat. Chem. Acta, 62 (1989) 27.
8 B. Korpar-Čolig, Z. Popović, M. Sikirica and D. Grdenić, J. Organomet. Chem., 405 (1991) 59.
9 D. Grdenić, Z. Popović, B. Korpar-Čolig and D. Matković-Čalogović, unpublished results.
10 D. Grdenić, in D. Dodson, J.P. Glusker and D. Sayre (Eds.), Connections in the Crystal Structures of Mercury compounds, Structural Studies of Molecules of Biological Interest, a Volume in Honour of Professor Dorothy Hodgkin, Clarendon Press, Oxford, 1981, p. 207.
11 L.G. Kuz'mina and Yu.T. Struchkov, Croat. Chem. Acta, 57 (1984) 701.
12 D. Grdenić, Quart. Rev., 19 (1965) 303.
13 G.M. Sheldrick, SHELX76. Program for crystal structure determination, Univ. of Cambridge, England, 1976.
14 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.