Глигор Јовановски

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Tetrakis(trifluoroacetoxymercuri)methane and Tetrakis(acetoxymercuri)-methane as the Reaction Products of Hofmann's Base with the Corresponding Acid: *X*-Ray Crystallographic Evidence

By Drago Grdenić,* Boris Kamenar, Branka Korpar-Čolig, Milan Sikirica, and Gligor Jovanovski

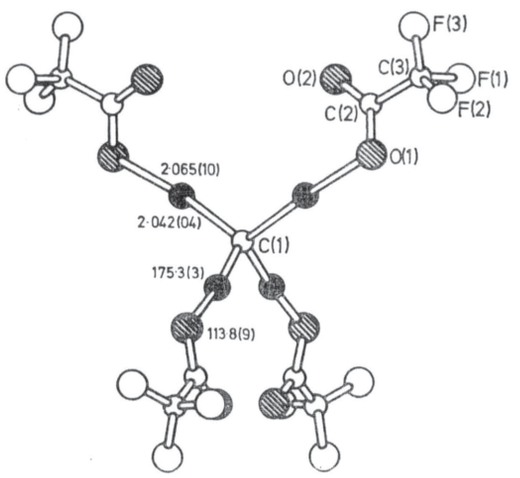
(*Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, 41001 Zagreb, P.O. Box 153, Yugoslavia*)

Summary It has been shown by *X*-ray structure analysis that the crystals obtained from the solution of ethane hexamercarbide (Hofmann's base) in trifluoroacetic or acetic acid are tetrakis(trifluoroacetoxymercuri)methane, $C(HgOCOCF_3)_4$, and tetrakis(acetoxymercuri)methane, $C(HgOCOCH_3)_4$, respectively.

The compound obtained by mercuration of ethanol with mercuric oxide in alkali has been formulated as a derivative of the permercurated ethane, $C_2Hg_6(OH)_2$, and is known as ethane hexamercarbide.[1] With nitric, sulphuric and perchloric acid it forms salts from which the original hexamercarbide is regenerated by alkalis. The anion-exchange properties of ethane hexamercarbide indicated its polymeric structure which also explained its insolubility in all solvents.[2] By analogy with Millon's base[3] we propose the name Hofmann's base for ethane hexamercarbide.[4]

Hofmann's base was found to dissolve completely in aqueous carboxylic acids. The crystalline compounds obtained from the solutions were not the carboxylates of

Hofmann's base but the carboxy-derivatives of permercurated methane $C(HgOCOCF_3)_4$ and $C(HgOCOCH_3)_4$ whose formulae were confirmed by structure analysis. Consequently, Hofmann's base is a methane derivative and can be formulated as the hydroxide of a polymeric oxonium ion containing C–Hg–$(OH)^+$–Hg–C bridges formed by condensation from hydroxide $C(HgOH)_4$, the final mercuration



Figure

product of ethanol. These oxonium bridges are not affected by oxo-acids which give ionic salts (*e.g.*, nitric or perchloric acid) but are split by acids which form covalent salts with mercury (*e.g.*, carboxylic acids). From carboxy-derivatives Hofmann's base is also regenerated by alkalis. Our study of Hofmann's base and its salts will be published shortly elsewhere.

Crystal data: Tetrakis(trifluoroacetoxymercuri)methane, $C(HgOCOCF_3)_4$, tetragonal crystals, space group $P4_2/n$, $a = 12{\cdot}866(4)$, $c = 6{\cdot}111(2)$ Å, $V = 1011{\cdot}6$ Å^3, $D_m = 4{\cdot}06$ g cm^{-3}, $Z = 2$, $D_c = 4{\cdot}15$ g cm^{-3}, $\mu = 309{\cdot}7$ cm^{-1}. 888 non-zero independent reflections were collected on Philips PW 1100 diffractometer using Mo-K_α radiation. The structure was solved by conventional heavy atom methods and refined anisotropically to $R = 0{\cdot}028$ (Figure).

The crystals consist of discrete $C(HgOCOCF_3)_4$ molecules with symmetry as shown in the Figure. The carbon atom C(1) is bonded to four mercury atoms in an almost regular tetrahedron, the tetrahedral angles being 112·36(2) and 108·36(2)°, respectively. The bond lengths are given in the Figure. Each mercury atom is linked to one carboxyl-oxygen atom at 2·065(10) Å while the second oxygen atom from the same carboxyl group is 2·984(12) Å away from mercury, as found in other organomercurials.[5] The geometry of the trifluoroacetoxy group agrees with the known data.

Tetrakis(acetoxymercuri)methane, $C(HgOCOCH_3)_4$, needle-shaped monoclinic crystals, space group $P2_1/c$, $a = 7{\cdot}262(7)$, $b = 21{\cdot}816(12)$, $c = 12{\cdot}003(8)$ Å, $\beta = 98{\cdot}8(8)°$, $V = 1899{\cdot}2$ Å^3, $D_m = 3{\cdot}70$ gcm^{-3}, $Z = 4$, $D_c = 3{\cdot}71$ g cm^{-3}, $\mu = 618{\cdot}7$ cm^{-1}. Diffraction data were collected on an integrating Weissenberg camera (multiple-film technique) using Cu-K_α radiation. 1830 Independent reflections were measured by means of a microdensitometer. The structure was solved by the Patterson and Fourier method and refined by least-squares procedure assuming anisotropic temperature factor for mercury and isotropic temperature factor for all other non-hydrogen atoms to a current R value of 0·114.

The molecular geometry of $C(HgOCOCH_3)_4$ is very similar to that found for the trifluoroacetoxy compound. At the present stage of the analysis the C–Hg bond lengths are from 2·03 to 2·07 Å and the tetrahedral angles from 106 to 112°. The bonds at the mercury atom are nearly collinear, with Hg–O bond lengths from 2·02 to 2·18 Å.

The physical properties and chemical reactions of the crystals correspond to those of tetrakis(acetoxymercuri)-methane obtained previously by a completely different method.[6]

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