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Crystal Structure of the First Polymeric Tetramercurated Methane Derivative of Hofmann's Base*

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Abstract. By dissolving Hofmann's base, $[CHg_4O(OH_2)](OH)_2$ – a polymeric organomercury compound, in trifluoromethanesulfonic acid, crystals of $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$ were obtained and characterized by X-ray diffraction. It is the first polymeric tetramercurated methane derivative of Hofmann's base. The asymmetric unit of the monoclinic $P2_1/n$ space group consists of a monomeric unit of the polymeric cation $[CHg_4(OH)(OH_2)_2]_n^{3n+}$, three trifluoromethanesulfonate anions and two crystallization water molecules. In the polymeric chains two neighbouring tetramercurated methane moieties are interconnected through an OH group – a dimercurated oxonium ion, $–Hg–(OH)^+–Hg–$. H_2O molecules are bound to two mercury atoms that do not take part in the bridging and represent monomercurated oxonium ions $-HgOH_2^+$. The polymeric chains are arranged in parallel puckered layers and are interlinked by an extensive three-dimensional hydrogen-bonding network. The characteristic coordination of mercury atoms is linear, while the effective coordination is 2+3.

Keywords: organomercury, tetramercurated methane; Hofmann's base, X-ray crystal structure

INTRODUCTION

Tetramercurated methane derivatives are interesting organometallic compounds that contain four mercury atoms tetrahedrally bound to a carbon atom. A number of tetrakis(anionomercurio)methane compounds of the general formula $C(HgX)_4$ have been synthesized. Matteson and coworkers during their research on tetrametallomethanes obtained tetrakis(acetoxymercurio)methane, $C(HgOCOCH_3)_4$, as the reaction product of tetrakis-(dimethoxyboryl)methane, $C[B(OMe)_2]_4$, and mercuric acetate.[1] They also isolated some derivatives of permercurated methane by a metathesis reaction, namely $C(HgBr)_4$, $C(HgI)_4$, and the nitrato derivative, but due to their insolubility they characterized them only by chemical analysis. At the same time, Grdenić and coworkers had their attention focused on an organomercury compound which Hofmann obtained by mercuration of ethanol with mercuric oxide in alkali. Hofmann was convinced that the compound was permercurated ethane and named it ethane hexamercarbide, $C_2Hg_6O_2(OH)_2$.[2] Grdenić later named this compound Hofmann's base and suggested for it a polymeric structure with tetramercurated methane moieties.[3] The formula $[CHg_4O(OH)_2OH_2]$, proposed by Grdenić,[7] stems from its chemical analysis and is supported by its properties, however the structure is still not known. In the reaction of Hofmann's base with acids two main types are obtained: salts of the base, $[CHg_4O(OH_2)]X$ (X = halide, NO_3^-), or derivatives of tetramercurated methane. Grdenić and his co-workers were the first to determine the crystal and molecular structure of a tetramercurated derivative of Hofmann's base, $C(HgOCOCF_3)_4$[3,4] and later of a series of derivatives, $C(HgCN)_4 \cdot H_2O$,[5] $C(HgOCOCH_3)_4 \cdot 2H_2O$,[2,6] $C(HgNO_3)_4 \cdot H_2O$,[7] and $C(HgSO_4)_2(HgOH_2)_2$.[7] The structure of the chloro derivative $C(HgCl)_4 \cdot DMSO$ was reported by Breitinger.[8] Therefore, 5 out of 6 structures of tetramercurated derivatives known so far were determined by Grdenić and his group.

In the literature there are a few more papers dealing with spectroscopic characterization of the derivatives of permercurated methane: CHg_4S_2 and $C(HgX)_4$ ($X = SCH_3$),[9] and X = F, Cl, Br, I,[10] X = CN, OOCH, $OCOCH_3$, $OCOCF_3$.[11]

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* Dedicated to Professor Emeritus Drago Grdenić, Fellow of the Croatian Academy of Sciences and Arts, on the occasion of his 90th birthday.

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Soon after the first structure was published it was suggested that such compounds can be useful as polymetallic reagents for labelling sulphur in nucleic acids.[12] Later, indeed, tetrakis(acetoxymercurio)methane (TAMM) was used for mercuration on the 5' extensions of cDNA oligomers containing thiolated bases, and used for site targeting in the crystal structure of the small ribosomal subunit.[13]

In order to put some more insight into the most probable structure of Hofmann's base, we undertook this research on its tetramercurated methane derivative with trifluoromethanesulfonic acid. In all reported structures till now the reaction of Hofmann's base with the corresponding acid gave monomeric derivatives. The structure reported in this paper describes an exciting new structure – the first polymeric derivative of Hofmann's base, $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$.

EXPERIMENTAL SECTION

Synthesis

Purification of Hofmann's Base

Very pure Hofmann's base was obtained by alternating acid and alkali digestion of the crude base as previously described.[2,7] The base is a lemon-yellow powder.

Synthesis of $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$

$[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$ was prepared by dissolving Hofmann's base (0.5 g) in trifluoromethanesulfonic acid (2 mL). This solution was kept in dark and after two weeks needle-shaped, transparent yellowish crystals appeared. The crystals were unstable if left in air and decomposed in a few days.

Methods

IR Spectra

The IR spectra in the region 4000–450 cm^{-1} were recorded on Perkin-Elmer FTIR spectrometer model 1600, using KBr discs.

X-ray Structural Analysis

The X-ray diffraction intensities were collected on a crystal mounted on a glass fiber and protected by silicon oil (apiezon) at 200 K on a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å, crystal-detector distance of 40 mm, 383 frames measured, scan width of 1.5°, 125 s per frame, omega scans up to 2θ of 55°). The data were reduced using the DENZO program.[14] Absorption correction was done by evaluation of partial multiscans. The crystal structure was solved by the Patterson method using the SHELXS97 program.[15] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations based on F^2 against all reflections with the SHELXL97 program[16] implemented in the WinGX package.[17] Hydrogen atoms (except two, one on each H_2O molecule) were found in the difference Fourier map. For the H_2O molecules the other hydrogen atom was calculated using CALC-OH[18] and was included in the refinement with restrained geometry, O–H distance of 0.86(2) Å (using the DFIX command) and H–O–H angle of 106.9° (using the DANG command). These values were obtained by analysis of H_2O molecule geometry from the *Cambridge Structural Database*[19] taking into account only structures with R < 0.05 and without disorder. The O–H distance for the bridging OH group was given the same distance restraints. The displacement parameters were taken as 1.5 times of their parent oxygen atoms. Geometry calculations were done using PLATON[20] and the structure drawings were prepared using PLATON and DIAMOND[21] programs. Crystal data and refinement details are listed in Table 1.

Table 1. Crystal data, data collection and structure refinement

Empirical formula	$C_4H_9F_9Hg_4O_{14}S_3$
Relative molecular mass	1350.65
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	7.6843(10)
b / Å	24.737(3)
c / Å	12.502(2)
α / °	90
β / °	95.305(6)
γ / °	90
V / Å^3	2366.3(6)
Z	4
T / K	200(2)
$D_{\rm calc}$ / g cm^{-3}	3.791
μ(MoK_α) / mm^{-1}	26.263
F (000)	2376
θ range for data collection / °	2.32–28.30
Ranges of h, k, l	–10 to 10, –32 to 32, –16 to 14
Reflections collected	33377
$R_{\rm int}$	0.056
Data/restrains/parameters	5774 / 13 / 334
$R^{(a)}$, $wR^{(b)}$ ($I > 2\sigma(I)$)	0.031, 0.067
R, wR (all data)	0.039, 0.070
g_1, g_2 in $w^{(c)}$	0.0329, 4.1815
Goodness of fit on F^2, $S^{(d)}$	1.079
Largest diff. peak$^{(e)}$ & hole/(e Å^{-3})	1.601, –1.179

$^{(a)}$ $R = \Sigma||F_0| - |F_c|| / \Sigma|F_0|$

$^{(b)}$ $wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

$^{(c)}$ $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2) / 3$

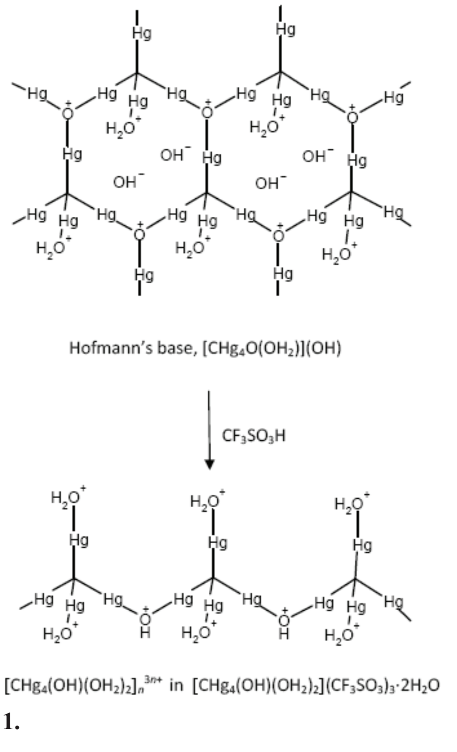
$^{(d)}$ $S = \Sigma[w(F_o^2 - F_c^2)^2 / (N_{\rm obs} - N_{\rm param})]^{1/2}$

$^{(e)}$ 0.94 Å from Hg3

RESULTS AND DISCUSSION

Reactions of Hofmann's base, and Synthesis and Characterization of $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$

Reaction of Hofmann's base with diluted acids gives salts of the base, $[CHg_4O(OH_2)]X_2$ (X = halide, nitrate, perchlorate), or $[CHg_4O(OH_2)]X$ (X = sulfate).[3,7] By this reaction the polymeric cation remains unchanged, and addition of alkalis regenerates the original Hofmann's base.[3] Unfortunately, none of these structures are known. The insolubility of the base in solvents and these anion-exchange properties indicate its polymeric structure. However, Hofmann's base dissolves completely in aqueous carboxylic acids such as acetic, trifluoroacetic;[2–4,7] or lactic acid,[22] giving monomeric derivatives of tetramercurated methane, *i.e.* tetrakis(anionomercurio)methane compounds, $C(HgOCOCH_3)_4 \cdot 2H_2O$,[2,6] $C(HgOCOCF_3)_4$,[3,4] $C(HgOCOCHOHCH_3)_4$,[22] respectively. Hofmann's base also dissolves well in some concentrated acids such as nitric giving $C(HgNO_3)_4 \cdot H_2O$, or sulfuric, resulting in $C(HgSO_4)_2(HgOH_2)_2$.[7] The later one, bis(sulfatomercurio)bis(aquamercurio)methane has an unique structure since two mercury atoms have H_2O molecules as ligands giving thus monomercurated oxonium ions. Another way of obtaining derivatives of tetramercurated methane is by addition of salts or acids to a solution of Hofmann's base in acetic acid. This way $C(HgCN)_4 \cdot H_2O$ monohydrate was obtained by addition of potassium cyanide.[5]



Scheme 1.

In the present reaction Hofmann's base was dissolved in trifluoromethanesulfonic acid (triflic acid) resulting in $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$, a structure quite different from those described above, Scheme 1. An accurate assignment of the vibrational modes of $CF_3SO_3^-$ observed in the IR spectrum was difficult since S–O and C–F vibrations are of the identical symmetry and are therefore found in the same spectral region. However, generally good correspondence between the observed bands and those reported for uncoordinated $CF_3SO_3^-$ ion are found – a broad and very strong absorption band centered at 1252 cm^{-1}, along with the one centered at 1177 cm^{-1}.[23–25] IR bands of weak to medium intensity indicative of strong hydrogen bonding are found between 3000 and 1900 cm^{-1}.[26,27]

Crystal Structure of $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$

The crystal structure represents the first polymeric derivative of Hofmann's base. The structure confirmed that the trifluoromethanesulfonate anions are indeed not bound to mercury atoms. A drawing of the structure is given in Figure 1, and the interatomic distances and angles are given in Tables 2 and 3, respectively. The asymmetric unit consists of a monomeric unit of the polymeric cation $[CHg_4(OH)(OH_2)_2]_n^{3n+}$ (Scheme 1), three $CF_3SO_3^-$ anions and two H_2O molecules. In the tetramercurated methane moiety the Hg–C distances, in the range 2.040(7) to 2.088(6) Å, correspond to the sum of covalent radii of carbon and digonally coordinated mercury atom (*r*(Hg) = 1.30 Å). This value is in agreement with distances found in other structures containing the CHg_4 moiety (2.04–2.11 Å).[4–8] The tetrahedron is slightly distorted with Hg–C–Hg angles ranging from 105.0(3) to 112.7(3)°. Similar Hg–C distances and

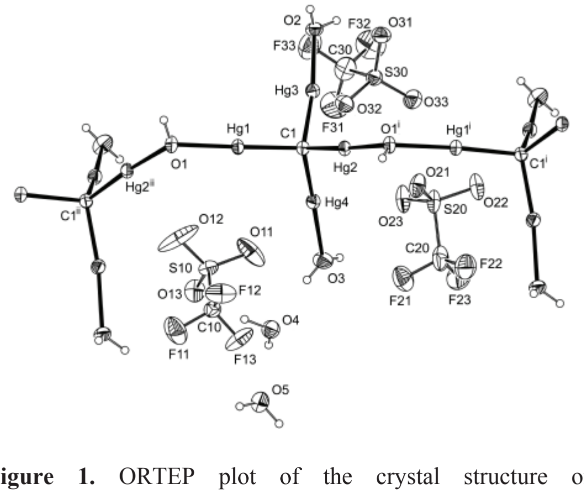


Figure 1. ORTEP plot of the crystal structure of $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level. Hydrogen atoms are shown as spheres of the arbitrary size. Symmetry transformations used to generate equivalent atoms: (i) $x - 0.5, 0.5 - y, z - 0.5$; (ii) $x + 0.5, 0.5 - y, z + 0.5$.

Table 2. Selected interatomic distances / Å

Hg1–C1	2.088(6)	Hg3–C1	2.059(7)
Hg1–O1	2.090(4)	Hg3–O2	2.100(5)
Hg2–C1	2.066(6)	Hg4–C1	2.040(7)
Hg2-O1$^{\rm i}$	2.080(5)	Hg4–O3	2.087(5)
Hg1···Hg2	3.4590(6)	Hg2···O21	2.779(6)
Hg1···Hg3	3.2895(5)	Hg2···O12$^{\rm iv}$	2.820(9)
Hg1···Hg4	3.3524(5)	Hg2···O22$^{\rm ii}$	2.857(6)
Hg2···Hg3	3.3215(5)	Hg3···O32$^{\rm v}$	2.859(6)
Hg2···Hg4	3.3713(6)	Hg3···O33	2.974(6)
Hg3···Hg4	3.4122(5)	Hg3···O13$^{\rm iv}$	3.122(6)
Hg1···O23$^{\rm ii}$	2.834(6)	Hg4···O11	2.771(10)
Hg1···O21$^{\rm iii}$	2.820(6)	Hg4···O22$^{\rm iii}$	2.808(6)
Hg1···O33	2.923(7)	Hg4···O23	2.861(6)

Symmetry transformations used to generate equivalent atoms: (i) $x - 0.5, 0.5 - y, z - 0.5$; (ii) $1 + x, y, z$; (iii) $0.5 + x, 0.5 - y, 0.5 + z$; (iv) $x - 0.5, 0.5 - y, z - 0.5$; (v) $x - 0.5, 0.5 - y, z - 0.5$

angles are found also in other highly mercurated aliphatic compounds, such as trimercurated acetic acid,[28,29] or trimercurated acetaldehyde.[30–33] The coordination of mercury atom is digonal (linear) with the greatest deviation of the C–Hg–O angle from collinearity of 8°. In the polymeric chains two neighbouring tetramercurated methane moieties are interconnected through an OH group (Hg1–O1 2.090(4), Hg2–O1[$x - 0.5, 0.5 - y, z - 0.5$] 2.080(5) Å), which can also be described as a dimercurated oxonium ion, –Hg–(OH)$^+$–Hg–, Figure 1. Such bridging oxonium ions are found also in the structure of trimercurated acetaldehyde, $[\mathrm{HOHg_2(NO_3Hg)CCHO]NO_3}$,[31] which also consists of polymeric chains. H_2O molecules are bound to two mercury atoms that are not part of the bridging oxonium ion. These H_2O molecules are monomercurated oxonium ions, $-\mathrm{HgOH_2^+}$, at distances Hg3–O2 2.100(5) and Hg4–O3 2.087(5) Å. Such oxonium ions are found in the structure of $\mathrm{C(HgSO_4)_2(HgOH_2)_2}$ (Hg–O 2.131(5) Å),[7] or in the structure of trimercurated acetaldehyde, $\mathrm{[Hg(H_2OHg)(NO_3Hg)CCHO]NO_3}$, which is polymeric (Hg–O 2.17(3) Å).[28] Hg–O distances in the monomercurated oxonium are always among the longer ones in the mercurated oxonium species. In the present structure such connectivity results in infinite $\mathrm{[CHg_4(OH)(OH_2)_2]_n^{3n+}}$ chains along $[\bar{1}01]$, Figure 2. The chains are situated in puckered layers parallel to (010), while between these layers there are trifluoromethanesulfonate anions and crystallization water molecules (Figure 3).

Table 3. Selected interatomic angles / °

C1–Hg1–O1	175.8(2)	Hg1–C1–Hg4	108.6(3)
C1–Hg2–O1$^{\rm i}$	175.4(2)	Hg2–C1–Hg3	107.3(3)
C1–Hg3–O2	172.0(2)	Hg2–C1–Hg4	110.4(3)
C1–Hg4–O3	172.9(3)	Hg3–C1–Hg4	112.7(3)
Hg1–C1–Hg2	112.8(3)	H1–O1–Hg2$^{\rm ii}$	120.1(2)
Hg1–C1–Hg3	105.0(3)		

Symmetry transformations used to generate equivalent atoms: (i) $x - 0.5, 0.5 - y, z - 0.5$; (ii) $0.5 + x, 0.5 - y, 0.5 + z$

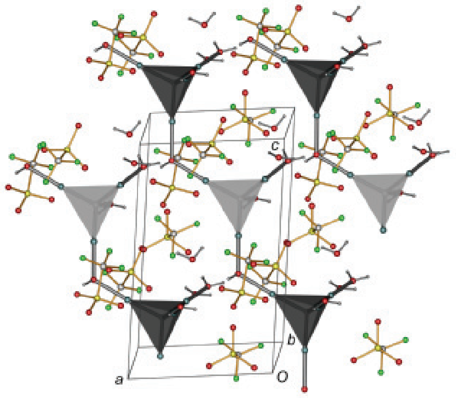


Figure 2. The infinite $\mathrm{[CHg_4(OH)(OH_2)_2]_n^{3n+}}$, chains along the $[\bar{1}01]$, direction in the crystal structure of $\mathrm{[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O}$. Tetramercurated methane ($\mathrm{CHg_4}$) moieties are depicted as grey tetrahedra. Colour code: Hg, blue-grey; C, grey; O, red; F, green; S, yellow.

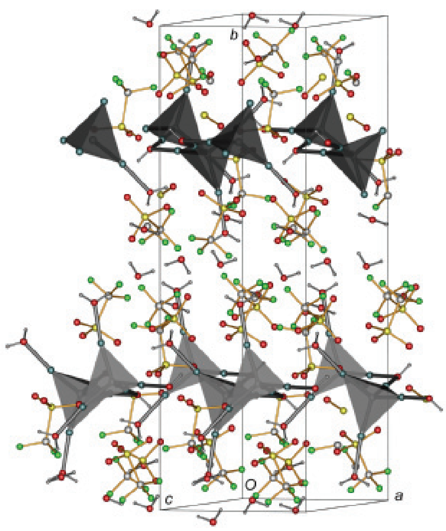


Figure 3. The $\mathrm{[CHg_4(OH)(OH_2)_2]_n^{3n+}}$, chains are arranged in the layers parallel to the (010) plane and sandwich the layers of $\mathrm{CF_3SO_3^-}$ anions and H_2O molecules. Tetramercurated methane ($\mathrm{CHg_4}$) moieties are represented as grey tetrahedra. Colour code: Hg, blue-grey; C, grey; O, red; F, green; S, yellow.

Effective Coordination of Hg

When considering the coordination of mercury atom, the interactions with atoms within the coordination sphere that are longer than covalent but shorter than the

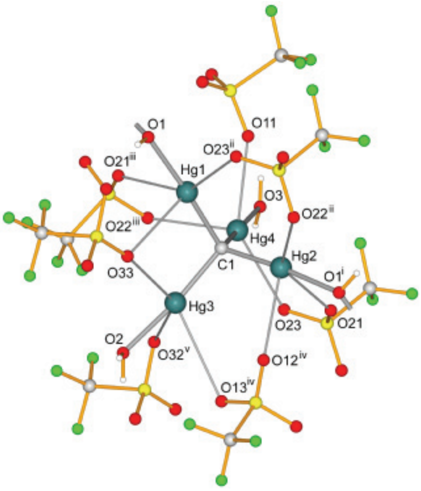


Figure 4. Each mercury atom has the linear characteristic coordination (indicated by the thicker grey bonds) and the effective coordination of 2+3. Symmetry transformations used to generate equivalent atoms: (i) $x - 0.5, 0.5 - y, z - 0.5$; (ii) $1 + x, y, z$; (iii) $0.5 + x, 0.5 - y, 0.5 + z$; (iv) $x - 0.5, 0.5 - y, z - 0.5$; (v) $x - 0.5, 0.5 - y, z - 0.5$. Colour code: Hg, blue-grey; C, grey; O, red; F, green; S, yellow.

sum of the van der Waals radii also have to be taken into account. According to Grdenić, covalently bonded atoms are within the effective coordination sphere; however, when considering the characteristic coordination sphere, atoms at distances shorter than the sum of the van der Waals radii also have to be added.[34,35] To be able to calculate which atoms are within the characteristic coordination, the van der Waals radius of the mercury atom (R_w(Hg)) has to be defined. Grdenić suggested 1.50 Å for R_w(Hg) from the structure of metallic mercury,[34] Bondi suggested 1.55 Å,[36] a value of 1.73 Å was given by Canty and Deacon who suggested that the range $1.70 \leq R_w(\text{Hg}) \leq 2.00$ Å can also be considered.[37] Later, Grdenić took into account new structures that were solved, and he recalculated the value suggesting R_w(Hg) = 1.54 Å, but also the possible range $1.50 \leq R_w(\text{Hg}) \leq 1.60$ Å. Finally, Matković-Čalogović made an analysis of interactions of mercury atom with surrounding atoms taking into account all structures from the *Cambridge Structural Database*, and also anisotropy of the van der Waals radius of the coordinating atoms,[38] and obtained the range $1.55 \leq R_w(\text{Hg}) \leq 1.65$ Å.[39] Using these values, the coordination of mercury atoms in the present structure is obtained. Each mercury atom is coordinated digonally by a carbon and an oxygen atom which define the digonal characteristic coordination described above, and also by three oxygen atoms from the three trifluoromethanesulfonate anions with Hg···O distances in the range 2.771(10)–3.122(6) Å, resulting in the effective coordination of 2+3, Table 2, Figure 4. These contacts cause deformation from the ideal linear characteristic coordination.

The bonds and angles in the trifluoromethanesulfonate anions do not differ significantly from those in structures where it is not coordinated to a metal atom.[40]

Hydrogen Bonding

In the crystal structure of $[\text{CHg}_4(\text{OH})(\text{OH}_2)_2](\text{CF}_3\text{SO}_3)_3 \cdot 2\text{H}_2\text{O}$, the polymeric $[\text{CHg}_4(\text{OH})(\text{OH}_2)_2]_n^{3n+}$, chains are interlinked by an extensive three-dimensional hydrogen-bonding network (Table 4; Figures 5 and 6). All potential hydrogen-bond donors participate in the hydrogen bonding. While the mercury-coordinating H_2O molecules serve only as donors in the hydrogen-bonding interactions, the OH group of the bridging oxonium ion (O1–H1) acts both as a donor and an acceptor (Figure 5). The crystallization water molecules maximally utilize their hydrogen-bond donor/

Table 4. Hydrogen bonds

D–H···A	*d*(D–H) / Å	*d*(H···A) / Å	*d*(D···A) / Å	∠ (DHA) / °
O1–H1···O32	0.85	1.99	2.771(7)	151
O2–H21···O31^{i}	0.86	2.06	2.831(7)	150
O2–H21···F13^{ii}	0.86	2.39	2.958(7)	124
O2–H22···O5^{ii}	0.85	1.82	2.669(8)	173
O3–H31···O1^{i}	0.86	2.50	3.088(7)	127
O3–H31···O12^{i}	0.86	1.93	2.689(11)	147
O3–H32···O4	0.85	1.81	2.662(8)	179
O4–H41···O13	0.86	2.03	2.868(8)	166
O4–H42···O5^{iii}	0.86	2.13	2.928(8)	155
O5–H51···F13	0.86	2.53	3.177(8)	133
O5–H51···O4	0.86	2.20	2.862(8)	134
O5–H52···O31^{iv}	0.86	2.59	3.202(8)	130

Symmetry transformations used to generate equivalent atoms: (i) $x - 1, y, z$; (ii) $0.5 - x, 0.5 + y, 0.5 - z$; (iii) $-x, 1 - y, 2 - z$; (iv) $0.5 - x, 0.5 + y, 1.5 - z$

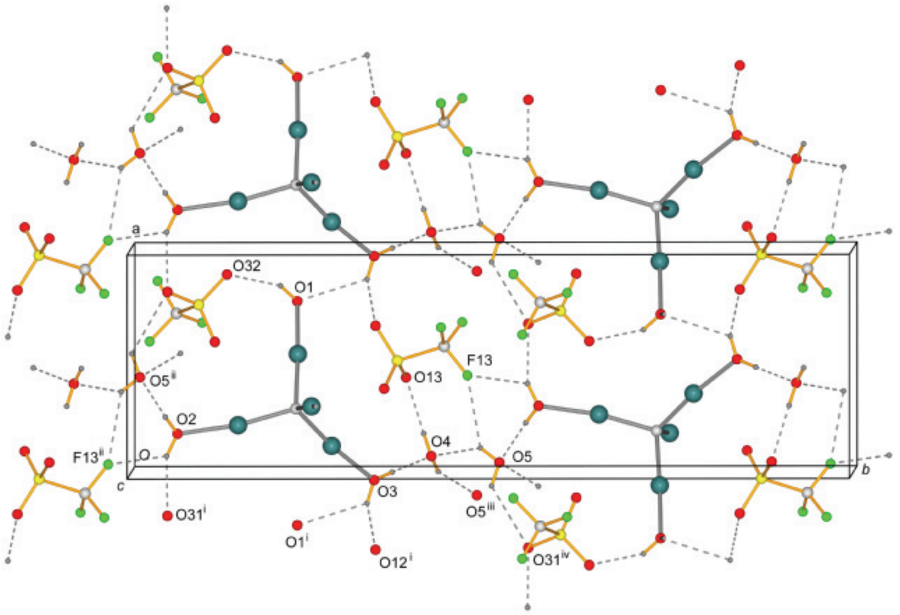


Figure 5. An extensive network of hydrogen bonds (depicted as dashed lines) connects the polymeric $[CHg_4(OH)\ (OH_2)_2]_n^{3n+}$, cations. Symmetry transformations used to gene-rate equivalent atoms: (i) $x - 1, y, z$; (ii) $0.5 - x, y - 0.5, 0.5 - z$; (iii) $-x, 1 - y, 2 - z$; (iv) $0.5 - x, 0.5 + y, 0.5 - z$. Colour code: Hg, blue-grey; C, grey; O, red; F, green; S, yellow

acceptor capabilities (Table 4). By forming centrosymmetric rings of the graph-set notation $R_4^4(8)$, these H_2O molecules are arranged into tetramers (Figure 6). Two adjacent layers, such as the one shown in Figure 5, are connected by O4–H42···O5[$-x$, $1-y$, $2-z$] hydrogen bonds. $CF_3SO_3^-$ anions are involved in hydrogen bonding through their oxygen and/or fluorine atoms (Figure 5). The $CF_3SO_3^-$ oxygen atoms O21, O22, O23 and O33 – each of which bridges two mercury atoms – form no hydrogen bonds. On the contrary, the O31 atom – that does not coordinate any mercury atom – is an acceptor of two hydrogen bonds (Table 4). Each of O12, O13 and O32 atoms coordinate only one mercury atom and forms one hydrogen bond. Even though O11 coordinates only one mercury atom, it is not hydrogen-bonded to any atom.

Possible Structure of Hofmann's Base

Are we any closer to the structure of Hofmann's base? The X-ray powder diffractogram of microcrystalline Hofmann's base gives very broad maxima indicating its partially amorphous structure. A crystallization trial by diffusion of reactants that lasted a few years did not result in a compound of higher crystallinity.[41] Interestingly, the first proposed structure[3] was that of oxonium bridged tetramercurated methane, C–Hg–$(OH)^+$–Hg–C, *i.e.* dimercurated oxonium cations, similar to those found in the present structure. Later,[42] it was suggested that it is made of networks of polymeric trimercurated oxonium ions $[HgCHg_3O]_n^{2n+}$ with OH^- ions and crystallization water molecules in the voids. Polymeric trimercurated oxonium ions, $[OHg_3CCHO]_n^{n+}$, are found in two structures of trimercurated acetaldehyde, one

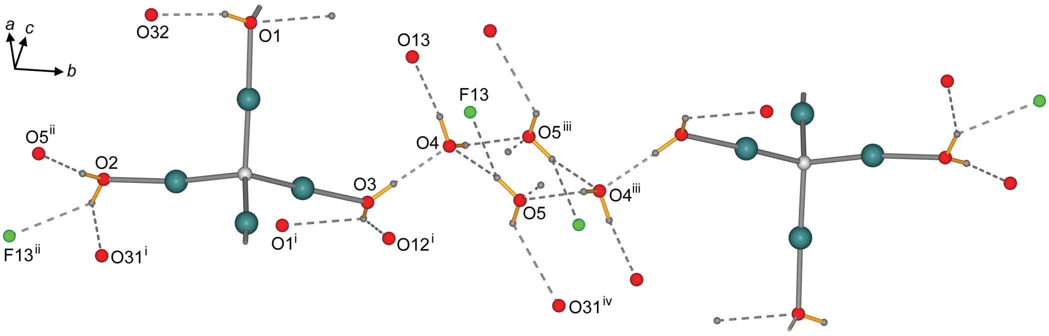


Figure 6. The crystallization water molecules are mutually hydrogen-bonded (dashed lines) in the tetrameric centrosymmetric rings. Symmetry transformations used to generate equivalent atoms: (i) $x - 1, y, z$; (ii) $0.5 - x, y - 0.5, 0.5 - z$; (iii) $-x, 1 - y, 2 - z$; (iv) $0.5 - x, 0.5 + y, 0.5 - z$. Colour code: Hg, blue-grey; C, grey; O, red; F, green; S, yellow.

columnar,[30] and the other made of infinite parallel networks.[31] Formula $[\mathrm{CHg_4O(OH)_2OH_2}]$ was the one proposed last.[7] When the present structure is taken into account, there are now two structures derived from Hofmann's base that contain the monomercurated oxonium ion $-\mathrm{HgOH}_2^+$. It is, therefore, not unreasonable to suppose that such cation can exist also in Hofmann's base. We propose a polymeric structure having both tri- and monomercurated oxonium ions, with $\mathrm{OH^-}$ ions in the voids, $[\mathrm{CHg_4O(OH_2)}](\mathrm{OH})_2$, Scheme 1. This is also consistent with the anion exchange properties of this salt.

Supplementary Materials. – The crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary material with the deposition number: CCDC 704379. Copies of the data can be obtained free of charge *via* http:/www.ccdc.cam.ac.uk/const/retrieving.html.

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SAŽETAK

Kristalna struktura prvog polimernog derivata Hofmannove baze

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Otapanjem Hofmannove baze, $[CHg_4O(OH_2)](OH)_2$ – polimernog organoživinog spoja, u trifluormetansulfonskoj kiselini priređeni su kristali $[CHg_4(OH)(OH_2)_2](CF_3SO_3)_3 \cdot 2H_2O$ i okarakterizirani su difrakcijom rentgenskih zraka. Navedeni spoj sadrži jedinice tetramerkuriranog metana i prvi je polimerni derivat Hofmannove baze. Asimetrična jedinica monoklinske prostorne grupe $P2_1/n$ sadrži jednu monomernu jedinicu polimernog kationa $[CHg_4(OH)(OH_2)_2]_n^{3n+}$, tri trifluormetansulfonatna aniona i dvije molekule kristalizacijske vode. U polimernim su lancima dvije susjedne jedinke tetramerkuriranog metana povezane OH skupinom dajući dimerkurirani oksonijev ion, $–Hg–(OH)^+–Hg–$. Molekule H_2O vezane su na preostala dva atoma žive koji ne sudjeluju u premošćivanju i predstavljaju monomerkurirane oksonijeve ione $–HgOH_2^+$. Polimerni lanci smješteni su u međusobno paralenim slojevima i međusobno su povezani trodimenzijskom mrežom vodikovih veza. Karakteristična koordinacija živinog atoma je digonska, dok je efektivna 2+3.