Reflections $hkl$ with $h = 2n + 1$ are markedly weaker than those with $h = 2n$.

The positions of the Hg atoms were derived from the Patterson projections $P(pwz)$ and $P(wpz)$ and the parameter values were refined in a number of least squares cycles using about 1250 reflections ($0kl, 1kl, 2kl,$ and $4kl$) visually estimated from Weissenberg photographs. CuKα radiation was used and no absorption corrections were applied. The final $R$ factor was 0.17 and the final parameter values for the 5 Hg atoms in the unit cell (space group $P1$) are:

$2 \text{Hg}_1$ in $2(i)$ with $x = 0.8077$ (15), $y = 0.1767$ (6), $z = 0.3001$ (4), $(B = 1.1)$

$2 \text{Hg}_2$ in $2(i)$ with $x = 0.3100$ (15), $y = 0.1793$ (6), $z = 0.2995$ (4), $(B = 1.1)$

$1 \text{Hg}_3$ in $1(a)$ with $x = 0$, $y = 0$, $z = 0$, $(B = 1.7)$

An electron density map and a difference map calculated with the same limited set of intensity data confirmed the positions and showed that no other Hg atoms were present in the unit cell. The two highest peaks in the difference map (about one tenth of the height of the Hg peaks) occurred at the positions 0.03, 0.28, 0.63 and 0.39, 0.73, 0.03 and probably correspond to the chlorine atoms of the perchlorate groups.

A projection of the structure along the b axis showing the Hg positions, is given in Fig. 1. The shortest Hg–Hg distances are:

Hg$_1$–Hg$_2$, 3.59 (2) Å and 3.61 (2) Å; Hg$_1$–Hg$_3$, 3.44 (2) Å; Hg$_1$–Hg$_5$, 3.47 (2) Å

Other Hg–Hg distances are longer than 5 Å. Thus the structure is built up from infinite one-dimensional complexes running along the a axis of the unit cell.

A comparison with other basic salts of mercury(II) makes it likely that the positions of the bridging oxygens are those marked in Fig. 1, with an oxygen (O$_1$) at the center of the triangle formed by the three Hg atoms Hg$_1$, Hg$_2$, and Hg$_3$, and a hydroxo group, O$_2$, joining the two Hg atoms Hg$_3$ and Hg$_5$. This assumption is supported by the presence of peaks at those positions (O$_1$: 0.04, 0.19, 0.19) and (O$_2$: 0.45, 0.82, 0.60) in the difference map.

This arrangement also leads to the expected digonal coordination of the Hg atoms with two linear Hg–O bonds of lengths about 2.0 Å.

The infinite one-dimensional complexes can thus be described as built up from two infinite $-O–\text{Hg}–O–$ chains of the type found in several other structures, joined by additional Hg atoms (Hg$_4$), or as built up from Hg$_2$O$_4$ groups joined by OH bridges (O$_3$). Alternatively, the complexes can be described as consisting of hexagons with common O–Hg–O edges (Fig. 1). The correct formula should then be Hg$_5$O$_6$(OH)$_4$(ClO$_4$)$_2$(H$_2$O)$_4$.

Although only the Hg positions have been directly determined in the structure analysis the type of complexes in the crystals seems to be uniquely defined and the structure determination will not be continued further. The structure derived is closely related to those of the other basic perchlorates, which will be reported in separate papers.

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New Cyclotridecane Peroxides

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Very few cyclotridecane derivatives are described in the literature, and as far as the present authors are aware, no peroxides are among these. By treating cyclotridecanone, 2-hydroxycyclotridecanone, and cyclotridecane-1,2-dione

with 34 % hydrogen peroxide as previously described, we obtained five different peroxides. Three peroxides, I, II, and III, were isolated from cycloctridecanone. Peroxide I liberates iodine from a solution of sodium iodide in acetonitrile with simultaneous evolution of oxygen. Peroxide II liberates iodine without oxygen evolution, while peroxide III reacts with acidified iodide solution only. Based on chemical tests, spectra and elemental analysis (given in the experimental part) the following structures are proposed for the three peroxides:

![Structures I, II, and III](image)

By treating 2-hydroxycycloctridecanone or cycloctridecane-1,2-dione with excess hydrogen peroxide a peroxide, IV, was isolated. This reacted slowly and incompletely with neutral as well as with acidic iodide solutions. Another peroxide, V, was obtained by treating 2-hydroxy-cycloctridecanone with equimolecular amounts of hydrogen peroxide in acetonitrile with a few drops of perchloric acid added. V was less soluble than IV, especially in hydrophobic solvents. It reacted only slowly and incompletely with neutral iodide solutions, more completely, however, in acidic solutions. Iodine was also liberated by grinding the peroxide with dry potassium iodide, which was not the case with peroxide IV. The structures of peroxides IV and V are uncertain. However, the following, which seem in accordance with elemental analysis and spectra, may be proposed:

![Structures IV and V](image)

The low reactivity towards—and incomplete reaction with—iodide indicate sterically shielded hydroperoxy groups and/or tendency to competing rearrangement reactions.

**Experimental.** I. 0.98 g cycloctridecanone was dissolved in 5 ml cold formic acid, and 0.5 ml 34 % hydrogen peroxide was slowly added to the stirred and ice cooled solution. Stirring was continued for 20 min after completed addition. A colorless solid was isolated, washed with sodium hydrogen carbonate/ice water and dried in vacuo. I, 1.0 g, m.p. 50°—58°. After several washings with pentane was obtained 0.32 g, m.p. 100°—105°. Recrystallization from benzene gave fine needle shaped crystals, m.p. 103°—118° (decomp.). (Found: C 63.5; H 10.4. Calc. for C_{11}H_{16}O_{4}: C 63.4; H 10.6). IR: absorptions at 3200, 1100, 925, and 845 cm⁻¹. NMR: δ ca. 540, 91, and 83 Hz, (ratio 1:2:10).

II. To 0.98 g cycloctridecanone dissolved in 15 ml formic acid was slowly added 1.0 ml hydrogen peroxide. Ca. 0.1 g colorless peroxide, m.p. 128°—129° was isolated. (Found: C 67.3; H 10.6. Calc. for C_{11}H_{16}O_{4}: C 68.1; H 11.0). IR: absorptions at 3360, 1105, 1007, 940, 923, 865, and 817 cm⁻¹. NMR: δ ca. 610, 97, and 84 Hz (1:4:20).

III. 1.96 g cycloctridecanone, 1.0 ml 34 % hydrogen peroxide, 2 drops of 70 % perchloric acid and 10 ml acetonitrile were left open to the atmosphere for 24 h in a fume hood. The residue formed was washed with ice water and dried in vacuo. It was then dissolved in propionic acid to which 2 drops of perchloric acid had been added, and the mixture was stirred for 40 min at 0°. A white solid was

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Properties and Reactions of 1,3-Oxathianes

III. A Novel Route to Alkylated 1,3-Oxathianes

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Only a few reports have been published that deal with 1,3-oxathianes, the cyclic acetals of 1,3-hydroxythiols. In part I of this series, we reported the preparation of several 2- and 6-alkyl-1,3-oxathianes. In this paper the syntheses of fifteen 1,3-oxathianes methylated at the 2, 4, 5, and 6 position are described.

The synthesis of 1,3-oxathianes has been mostly limited by the shortage of suitable initial reactants. Secondary halides and neopentyl-type halides do not react with thiourea to form products that yield thiols on hydrolysis. 3-Mercapto-2,2-dimethyl-1-propanol can, however, be prepared from 3,3-dimethylxetane and thiourea by the method of Rondeelveld. It has been shown previously that thiaoacetic acid adds smoothly to olefins, but that the products formed in the presence of peroxide are “abnormal in character” with respect to Markovnikoff’s rule. For this reason, we conducted this addition reaction with the unsaturated alcohols crotyl alcohol, 2-methyl-3-buten-2-ol, 3-methyl-3-buten-2-ol, and a mixture of cis- and trans-3-penten-2-ols.

Crotly alcohol(I) has been reported to react with thiaoacetic acid to form 3-acetylthio-1-butanol (II) and the corresponding acetate (III), although the disulphide (VI) is also formed (see scheme (1)). However, crotyl alcohol is a “symmetrically” substituted olefin and hence the addition of the two fragments produced on scission of the S–H bond should not take place exclusively at one or the other of the double bond carbons. Consequently, crotyl alcohol should yield a mixture of 1,3- and 1,2-substituted isomers in contrast to the results of Brown et al.

Actually, a 2:3 mixture of 3-mercapto-1-butanol and 2-mercapto-1-butanol was obtained after hydrolysis as concluded from the results of gas chromatographic analyses of the product ratios after acetalization. The mixture of cis- and trans-3-penten-2-