

## On the Crystal Structure of a Basic Mercury(II) Perchlorate

GEORG JOHANSSON

*Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden*

A series of basic mercury(II) perchlorates  $\text{Hg}(\text{ClO}_4)_2 \cdot x\text{HgO} \cdot y\text{H}_2\text{O}$  with values of  $x$  between 1.5 and 3 has been prepared from solutions obtained by dissolving an excess of mercury(II) oxide in perchloric acid. The crystal structures of these salts have been investigated in order to get information on the types of complexes occurring in the crystals and on how these complexes change with changing  $x$ . This information is of interest for the interpretation of measurements of X-ray scattering by hydrolyzed mercury(II) perchlorate solutions.<sup>1</sup> The structure of the least basic of the salts  $\text{Hg}(\text{ClO}_4)_2 \cdot 1.5\text{HgO} \cdot y\text{H}_2\text{O}$  ( $y \approx 2.5$ ) is discussed in the present paper.

Large, plate-like crystals can be obtained from a solution which is 4.6 M in  $\text{Hg}^{2+}$  and 7.4 M in  $\text{ClO}_4^-$ . The crystals are

colourless but easily become slightly yellow. They are unstable in air and decompose to  $\text{HgO}$  on contact with water. An analysis of the amount of mercury and perchlorate gave the results: 68.8 %  $\text{HgO}$ , 24.6 %  $\text{Cl}_2\text{O}_7$ , and, by difference, 6.6 %  $\text{H}_2\text{O}$ . Calculated values for the composition  $2.5\text{HgO} \cdot \text{Cl}_2\text{O}_7 \cdot 2.5\text{H}_2\text{O}$  are 70.4 %  $\text{HgO}$ , 23.8 %  $\text{Cl}_2\text{O}_7$ , and 5.9 %  $\text{H}_2\text{O}$ . The accuracy of the analysis was affected by the difficulty of obtaining the crystals free from other basic salts and from the mother liquor. The number of  $\text{H}_2\text{O}$  molecules found was confirmed by a Karl Fischer titration taking into account contributions from basic oxygens. The density was found to be 5.14  $\text{g/cm}^3$  compared with a calculated value of 5.19 assuming two formula weights in the unit cell.

For the X-ray exposures the crystals were sealed into capillaries in order to prevent decomposition. Weissenberg photographs taken along the  $a$  axis and the  $b$  axis and corresponding precession photographs indicated a triclinic symmetry and the following unit cell was chosen:

$$\begin{aligned} a &= 7.20 \text{ \AA} & b &= 7.56 \text{ \AA} & c &= 10.08 \text{ \AA} \\ \alpha &= 105.1^\circ & \beta &= 88.2^\circ & \gamma &= 111.8^\circ \\ V &= 492.3 \text{ \AA}^3 \end{aligned}$$

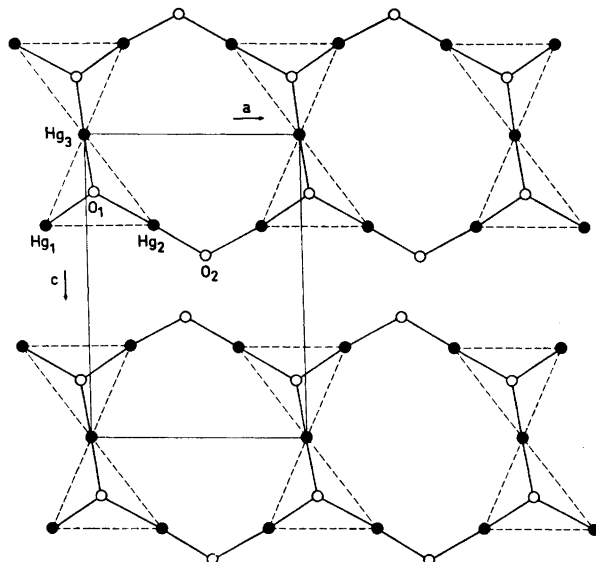


Fig. 1. Projection of the structure along the  $b$  axis, showing the Hg positions, and the postulated O positions.

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  $P(pvw)$  and  $P(uvp)$  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.  $\text{CuK}\alpha$  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  $P\bar{1}$ ) are:

$$\begin{array}{l} 2 \text{ Hg}_1 \text{ in } 2(i) \text{ with } x = 0.8077 \text{ (15),} \\ y = 0.1767 \text{ (6), } z = 0.3001 \text{ (4), } (B = 1.1) \\ 2 \text{ Hg}_2 \text{ in } 2(i) \text{ with } x = 0.3100 \text{ (15),} \\ y = 0.1793 \text{ (6), } z = 0.2995 \text{ (4), } (B = 1.1) \\ 1 \text{ Hg}_3 \text{ in } 1(a) \text{ with } x = 0, \\ y = 0, \quad z = 0, \quad (B = 1.7) \end{array}$$

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:

$\text{Hg}_1 - \text{Hg}_2$ , 3.59 (2) Å and 3.61 (2) Å;  
 $\text{Hg}_1 - \text{Hg}_3$ , 3.44 (2) Å;  $\text{Hg}_2 - \text{Hg}_3$ , 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 ( $\text{O}_1$ ) at the center of the triangle formed by the three Hg atoms  $\text{Hg}_1$ ,  $\text{Hg}_2$ , and  $\text{Hg}_3$  and a hydroxo group,  $\text{O}_2$ , joining the two Hg atoms  $\text{Hg}_1$  and  $\text{Hg}_2$ . This assumption is supported by the presence of peaks at these positions ( $\text{O}_1$ : 0.04, 0.19, 0.19) and ( $\text{O}_2$ : 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  $-\text{O}-\text{Hg}-\text{O}-$  chains of the type found in several other structures,<sup>2,3</sup> joined by additional Hg atoms ( $\text{Hg}_3$ ), or as built up from  $\text{Hg}_3\text{O}_3$  groups joined by OH bridges ( $\text{O}_2$ ). Alternatively, the complexes can be described as consisting of hexagons with common O-Hg-O edges (Fig. 1). The correct formula should then be  $\text{Hg}_5\text{O}_8(\text{OH})_2(\text{ClO}_4)_4(\text{H}_2\text{O})_2$ .

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.

The work has been supported by *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council). Computer time has been made available by the *Computer Division of the National Swedish Office for Administrative Rationalization and Economy*.

My thanks are due to Ernst Hansen for technical assistance and to Dr. Derek Lewis for linguistic corrections.

1. Johansson, G. *Acta Chem. Scand.* **25** (1971). *In press*.
2. Grdenic, D. *Quart. Rev. Chem. Soc.* **19** (1965) 303.
3. Aurivillius, K. *Arkiv Kemi* **24** (1965) 151.

Received May 25, 1971.

## New Cyclotridecane Peroxides

T. DÅSNES and T. LEDAAL

*Universitetets Kjemiske institutt, Blindern, Oslo 3, Norway*

Very few cyclotridecane derivatives are described in the literature,<sup>1-4</sup> and as far as the present authors are aware, no peroxides are among these. By treating cyclotridecanone, 2-hydroxycyclotridecanone, and cyclotridecane-1,2-dione