The Crystal Structure of Hexaaquamercury(II) Perchlorate, $[Hg(H_2O)_6](ClO_4)_2$

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The crystal structure of the hexahydrate of mercury-(II) perchlorate has been determined from three-dimensional single-crystal X-ray diffraction data collected at room temperature on an automatic Syntex $P2_1$ four-circle diffractometer. The unit cell, which is trigonal with $a = b = 8.005(4)$ Å and $c = 5.344(2)$ Å, contains one formula unit. The space group is No. 164: $P\bar{3}m1$. The structure, refined to a final conventional R value of 0.035, is built-up from discrete octahedral $Hg(H_2O)_6^{2+}$ units and perchlorate ions. The six $Hg-O$ bonds are equivalent with bond lengths of 2.341(6) Å. The complexes are held together by weak hydrogen bonds.

Mercury(II) frequently forms an irregular octahedral coordination with two short collinear bonds. Only for the compound $[Hg(C_6H_5NO)_6](ClO_4)_2$ has a regular octahedral oxygen coordination been reported with an $Hg-O$ bond length of 2.35(2) Å.[1] Measurements of X-ray scattering and Raman spectra from aqueous[2,3] and dimethyl sulfoxide[3] (DMSO) solutions of mercury(II) perchlorate have been found to be consistent with a regular octahedral coordination around the mercury(II) ion, with the lengths of the $Hg-O$ bonds close to 2.40 Å. In view of these results it seemed of interest to determine the crystal structures of the corresponding solid solvates for a comparison of the coordination around the mercury(II) ion with that found in solution.

The present paper reports the crystal structure of $[Hg(H_2O)_6](ClO_4)_2$. The crystal structures of $[Hg(DMSO)_6](ClO_4)_2$ and $Hg(ClO_4)_2.4DMSO$ will be reported in separate papers.[4,5]

EXPERIMENTAL

Preparation of crystals. Yellow mercury(II) oxide was dissolved in sufficient perchloric acid to avoid the formation of basic salts. Solutions with mol ratios $HClO_4 - HgO \geq 2$ were used. On slow evaporation over sulfuric acid in a desiccator, large, prismatic, colourless crystals of the hexahydrate were formed. They were found to be extremely soluble and were not stable outside the mother liquor.

Analyses. For the analyses excess solvent was centrifuged off and the crystals were quickly dissolved in water and weighed. Mercury was determined by a complexometric titration procedure using EDTA.[6] Perchlorate was determined by ion exchange on an H^+ saturated Dowex 50 cation exchange resin.

Values found were: 40.7 % Hg, 40.3 % ClO_4 and, by difference, 19.0 % H_2O. Calculated values for $Hg(ClO_4)_2.6H_2O$ are: 39.5 % Hg, 39.2 % ClO_4 and 21.3 % H_2O.

X-Ray data. A crystal, enclosed in a capillary and having the shape of a slightly elongated ellipsoid with a maximum dimension of about 0.2 mm, was used for the collection of the diffraction data.

The unit cell parameters were determined by the standard procedure on the computer controlled Syntex $P2_1$ four-circle diffractometer.[4] The angular coordinates of 15 centred reflections were used in a least-squares refinement of the lattice constants. The dimensions found for the trigonal unit cell were $a = b = 8.005(4)$, $c = 5.344(2)$ Å. The previously reported density[7] $D_m = 2.791$ g cm^{-3} gave $Z = 1$ and $D_x = 2.84$ g cm^{-3}.

The ω scan technique with different scan speeds from 0.5° min^{-1} upwards was used. Four check reflections were measured regularly at intervals of 50 reflections. All 442 hkl and $hk\bar{l}$ reflections up to $2\theta = 50°$ were measured (Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å). In addition, $h\bar{k}l$ and $h\bar{k}\bar{l}$ reflections were recorded,

but during this collection the intensities of the two strong low-angle check reflections $1\bar{1}0$ and $1\bar{2}0$, which had been slowly and continuously increasing, started to decrease rapidly. Therefore, only the first 265 of these reflections were used in the following data treatment. The maximum intensity variation for these two low-angle check reflections were within $\pm 16\%$ for the data range used. The other two, $3\bar{2}1$ and $2\bar{2}2$ at medium angles, remained fairly constant during the data collection.

A semi-empirical absorption correction, obtained by measuring intensity variations for selected reflections when rotating around the diffraction vector, was applied to the data.[8,4] The largest relative reduction in intensity measured for any of the reflections was from 1 to 0.36. The linear absorption coefficient is $\mu(\text{Mo}K\alpha) = 138 \text{ cm}^{-1}$.

Equivalent reflections were averaged giving a total number of 223 independent reflections, none of which had an observed intensity $< 7\sigma(I)$.

The data were corrected for Lorentz and polarization effects and approximate values for the temperature and scale factors were obtained by Wilson's method. All calculations were carried out by means of the *Syntex* XTL Crystallographic Program System.[9]

STRUCTURE DETERMINATION AND REFINEMENT

Space-group determination. The diffraction symmetry indicated the Laue group to be $\bar{3}m$. Since no systematic absences were observed, six space groups are possible, *viz.* $P312$, $P321$, $P3m1$, $P31m$, $P\bar{3}1m$, and $P\bar{3}m1$.[10]

With only one formula weight in the unit cell the single Hg atom and the two Cl atoms must occupy special positions on three-fold axes according to any of these symmetries. Some of the possible space groups would not lead to reasonable arrangements of oxygen atoms around the Hg and Cl atoms and

could be eliminated on that ground. A three-dimensional Patterson function was consistent with a centrosymmetric structure having atomic positions according to the space group of highest symmetry, $P\bar{3}m1$ (No. 164), which, therefore, was assumed to be the correct one.

Least-squares refinements. With the atomic positions derived from the Patterson function as the starting point a full-matrix least-squares refinement was carried out. The function minimized was $\Sigma w \|F_o| - |F_c\|^2$ with the weighting function $w = 1/\{\sigma^2(F_o) + (0.04F_o)^2\}$ which, according to a statistical analysis of the error distribution, leads to a satisfactory weighting scheme.

The scattering factors used were calculated from analytical expressions for the neutral atoms.[10] Anomalous dispersion corrections were included for Hg and Cl.[10]

With isotropic temperature factors for all atoms, the final conventional R value $(R = \Sigma \|F_o| - |F_c\|/\Sigma|F_o|)$ was 0.082 and $R_w = (\Sigma w \|F_o| - |F_c\|^2/\Sigma w |F_o|^2)^{\frac{1}{2}}$ was 0.133. With anisotropic temperature factors for Hg only, the values were $R = 0.045$ and $R_w = 0.055$. In the final refinement anisotropic temperature factors were introduced for all atoms and a total of 20 parameters were refined, giving $R = 0.035$ $(R_w = 0.045)$.

A similar refinement using data to which absorption corrections had not been applied, resulted in final R values about twice as large as those obtained for the corrected data.

The parameter shifts in the final refinement cycle were all less than 1% of the corresponding standard deviation. A difference map calculated from the final parameter values showed some spurious peaks, the highest of which was 0.58 e/Å^3. None of these peaks seemed possible to relate to hydrogen atom positions.

The final parameter values are given in Tables 1 and 2.

Table 1. Final fractional atomic positional parameters. For the independently refined parameters estimated standard deviations are given in parenthesis.

Atom	Position	x	y	z
Hg	1(a)	0	0	0
Cl	2(d)	1/3	2/3	0.2043(7)
O1	6(i)	0.1327(5)	−0.1327	−0.2711(14)
O2	6(i)	0.4291(9)	−0.4291	0.2827(30)
O3	2(d)	1/3	2/3	−0.0715(44)

Table 2. Final anisotropic thermal parameters in $Å^2$ with estimated standard deviations within parenthesis. The temperature factor expression used is $\exp[-1/4(B_{11}h^2a^{*2}+\cdots+2B_{12}hka^*b^*+\cdots)]$.

Atom	$B_{11}=B_{22}$	B_{33}	B_{12}	$B_{13}=-B_{23}$
Hg	4.53(4)	2.97(4)	$=\frac{1}{2}B_{11}$	0
Cl	3.25(8)	4.07(15)	$=\frac{1}{2}B_{11}$	0
O1	5.6(3)	4.5(3)	3.7(3)	0.33(1)
O2	9.7(6)	10.9(8)	7.1(7)	−0.67(26)
O3	9.9(10)	6.7(11)	$=\frac{1}{2}B_{11}$	0

Table 3. Interatomic distances (Å) and angles (°) with estimated standard deviations in parenthesis. Assigned H bonds are denoted by dots.

Within an $Hg(H_2O)_6^{2+}$ octahedron

Hg−O1	2.341(6)	O1−Hg−O1	85.81(18)
O1−O1	3.188(6)		94.19(18)
	3.430(9)		

Within a ClO_4^- tetrahedron

Cl−O2	1.394(9)	O2−Cl−O2	111.4(6)
Cl−O3	1.472(24)	O2−Cl−O3	107.5(7)
O2−O2	2.302(6)		
O2−O3	2.311(24)		

Remaining distances < 3.6 Å and bond angles

O1···O1	3.059(9)	Hg−O1···O3	120.9(3)
O1−O2	3.073(6)	Hg−O1···O1	104.9(2)
	3.390(14)	Cl−O3···O1	110.9(7)
O1···O3	2.981(10)	O1···O3···O1	108.0(4)
O2−O2	3.041(18)	O3···O1···O1	124.5(3)
O2−O3	3.483(11)		

DISCUSSION OF THE STRUCTURE

General. The atomic arrangement is illustrated in Figs. 1 and 2. Some interatomic distances and angles are given in Table 3.

The structure is built up of discrete HgO_6 octahedra and ClO_4 tetrahedra having no oxygen atoms in common. Both the mercury atom and the two chlorine atoms in the unit cell occupy positions on the three-fold axes.

The $Hg(H_2O)_6^{2+}$ complex ion. The $Hg(H_2O)_6$ octahedra are stacked on top of each other along the three-fold inversion axis with triangular faces
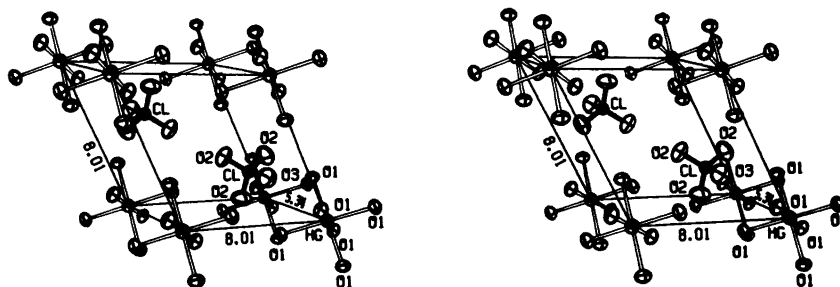

Fig. 1. A stereoscopic view of the trigonal unit cell. The lengths of the unit cell edges are given in Å. The *a* edge is horizontal in the picture. The ellipsoids are drawn to enclose 30 % probability.

Fig. 2. A stereoscopic view showing a string of $Hg(H_2O)_6^{2+}$ octahedra along the z axis (vertical in the picture). Two of the six surrounding parallel columns of perchlorate ions are also shown. The assigned H bonds are illustrated by the unfilled bonds. The six equivalent H bond directions possible between the O1 water molecules in two adjacent $Hg(H_2O)_6^{2+}$ octahedra (see text) are indicated. Distances are given in Å. The thermal ellipsoids enclose 30 % probability.

parallel (Fig. 2). A string of octahedra of O1 atoms along the z axis is thus formed, every second of which contains an Hg atom. The distances between oxygen atoms in the triangular faces perpendicular to the three-fold axis are 3.19 Å. Since the z parameter of the O1 atom is slightly larger than 1/4 (Table 1), the octahedra containing the Hg atoms are slightly elongated along the z axis, resulting in a longer distance, 3.43 Å, for the remaining O1 – O1 distances within the HgO$_6$ octahedron. The empty octahedra are correspondingly compressed, leading to O1 – O1 distances of 3.06 Å, which are therefore the shortest distances between water molecules belonging to different $Hg(H_2O)_6$ octahedra. This deviation from a regular octahedral coordination around the Hg atom is the only one allowed by the space group symmetry. All the Hg – O1 bond lengths will still be equal and are found to be 2.341(6) Å which, for a regular octahedron, would correspond to an O – O distance of 3.31 Å.

The perchlorate ion. The tetrahedral ClO_4^- group is slightly elongated along the three-fold rotation axis (Fig. 2). The Cl – O3 bond, 1.472(24) Å, coinciding with this axis, is significantly longer than the three equivalent Cl – O2 bonds of 1.394(9) Å. The average Cl – O bond distance, 1.41$_4$ Å, does not differ significantly from values found for other weakly H bonded perchlorates, *e.g.* 1.42$_6$ Å for $NaClO_4.H_2O$ and $LiClO_4.3H_2O$.[11]

Hydrogen bonds. The distorsion of the $Hg(H_2O)_6^{2+}$ octahedron and the comparatively short O1 – O1

distance, 3.06 Å, between the water molecules in adjacent octahedra, can probably be related to a formation of hydrogen bonds. The arrangement of other oxygens around an O1 atom seems to suggest that one of the protons associated with O1 is involved in a bond of length 3.06 Å to one of the two equidistant O1 atoms belonging to a different $Hg(H_2O)_6$ octahedron.

With the assumed space group symmetry there are two equivalent alternatives for O1 to accept the H-bond. Since the refinement of the structure indicated no deviations from the symmetry $P\bar{3}m1$, a statistical distribution of the proton between the two possible positions seems likely. Of the six equivalent H bond directions between two different $Hg(H_2O)_6^{2+}$ octahedra, which are indicated in Fig. 2, only three would then be occupied simultaneously. Moreover, it seems probable that each O1 water molecule is the acceptor of only one of the H bonds at the same time. A bifurcated H bond seems less probable since this would lead to less favorable acceptor angles[12] than those given in Table 3.

The second proton of the O1 water molecule probably forms an H bond, of length 2.98(1) Å, to the O3 oxygen atom belonging to a perchlorate group. The arrangements around the atoms O1 and O3 are illustrated in Fig. 2, where the H bond lengths are given. Corresponding angles are found in Table 3.

Two more perchlorate oxygens, O2, occur within possible H bonding distances, 3.073(6) Å, from the

O1 water molecule. However, the corresponding angles $(O3-O1-O2$ 70.2(3)°, $O2-O1-O2$ 136.5(3)°, $C1-O2-O1$ 125.8(6)°) deviate considerably from the tetrahedral value, which therefore makes an H bond formation between O1 and O2 less likely.

According to the proposed H bonding scheme, the O1 water molecule thus forms two weak H bonds to surrounding atoms and, on the average, accepts one bond. The O3 atom is the acceptor of three symmetrically arranged H bonds, with almost tetrahedral acceptor angles (Table 3). This assignment of H bonds is supported by the long $Cl-O3$ bond distance, 1.472(24) Å. Similar lengthenings of $Cl-O$ bond distances, where the oxygen atom is engaged in H bonding, have been reported for other perchlorates.[13,14]

CONCLUSIONS

This crystal structure determination confirms the conclusions from previous X-ray scattering measurements on solutions,[2,3] that the mercury(II) ion can be octahedrally coordinated to oxygen atoms, forming six equivalent $Hg-O$ bonds. The $Hg-O$ bond lengths found for the solid compounds $[Hg(H_2O)_6](ClO_4)_2$(2.341(6) Å), and $[Hg(DMSO)_6]$ $(ClO_4)_2$ (2.317(6), 2.320(6) and 2.376(6) Å), are, however, significantly shorter than the corresponding $Hg-O$ bond lengths found for solutions, 2.41(1) Å in aqueous solution[2,3] and 2.393(5) Å in DMSO solution.[3]

The compound $[Cd(H_2O)_6](ClO_4)_2$ seems to be isostructural with $[Hg(H_2O)_6](ClO_4)_2$. A slightly smaller trigonal unit cell with $a=b=7.96, c=5.30$ Å, $D_m=2.368$ g cm^{-3} and $Z=1$ has been reported.[7]

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