

On the Structures of the Hydrolysis Complexes of Mercury(II) in Solution

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Possible structures are derived for the hydrolysis complexes of mercury(II) in solution. The conclusions are based on previously reported X-ray scattering measurements on hydrolyzed and non-hydrolyzed mercury(II) perchlorate solutions,¹ on equilibrium measurements by Ahlberg² and others,³ and on crystal structure determinations of basic mercury(II) perchlorates.⁴⁻⁶

The hydrolysis reactions of the mercury(II) ion have been extensively studied. Hayek^{7,8} showed that large amounts of HgO can be dissolved in an aqueous solution of mercury(II) perchlorate. He explained this by assuming the formation of polynuclear complexes $\text{Hg}(\text{HgO})_n^{2+}$. Hietanen and Sillén⁹ made accurate measurements of the hydrogen ion concentration in hydrolyzed solutions in an 0.5 M (Na)ClO₄ medium. For the mercury(II) concentrations used (10^{-3} – 10^{-2} M), they found no evidence for polynuclear complexes, but could explain their data by assuming the formation of HgOH^+ and $\text{Hg}(\text{OH})_2$. They also found that the second acidity constant of Hg^{2+} is larger than the first. The same result was reached by Anderegg *et al.*¹⁰ from measurements in nitrate solutions. Ahlberg² extended the measurements of Hietanen and Sillén⁹ to more concentrated solutions (0.0025–1.3 M), using different ionic media (3 M (Na)ClO₄, 3 M (Mg)ClO₄, and 3 M (Ca)ClO₄). In addition to the previously found mononuclear complexes HgOH^+ and $\text{Hg}(\text{OH})_2$, she also found the polynuclear $\text{Hg}_2\text{OH}^{3+}$ and $\text{Hg}_2(\text{OH})_2^{2+}$. In the more concentrated solutions there were indications of a complex of higher nuclearity, probably $\text{Hg}_4(\text{OH})_3^{5+}$. Arnek and Kakolowicz¹¹ measured ΔH for the hydrolysis reactions, and suggested that the unexpected ratio of the first and second acidity constants may be explained by assuming that the mononuclear complexes are HgOH^+ and HgO .

An X-ray investigation of mercury(II) perchlorate solutions, reported in a previous paper,¹ has shown that hydrolysis of the Hg^{2+} ion leads to a change in its primary coordination sphere and to the formation of polynuclear com-

plexes with Hg–Hg distances of 3.64 Å. In the present paper, these results will be discussed in relation to information from the equilibrium measurements by Ahlberg² and from crystal structure determinations of basic mercury (II) perchlorates,^{4–6} and structures for the hydrolysis complexes, consistent with these experimental data, will be derived.

EQUILIBRIUM DATA

On the assumption that the stability constants derived by Ahlberg² are valid for the more concentrated solutions (3.5 M and 4.6 M in Hg(II)) used for the X-ray scattering measurements,¹ the expected concentrations of the different complexes have been calculated for these solutions. In Fig. 1, the percentage of mercury bonded in the different complexes is given as a function of the degree of hydrolysis, expressed as the total hydrogen ion excess (H) or as the average number of H⁺ split off from each hydrated Hg²⁺ ion (n_{OH}).

The concentrations of the mononuclear complexes in these solutions are negligible. The dominating complex is $Hg_4(OH)_3^{5+}$, which in the solutions investigated by Ahlberg² formed only a minor part of the hydrolysis products, and, therefore, probably is less well founded than the dinuclear complexes. For comparison, therefore, expected concentrations of the hydrolysis complexes, assuming the tetra-nuclear complex not to occur, have also been calculated, and are given in Fig. 1.

The average number of other Hg atoms bonded to each Hg in the solution, if only dinuclear complexes occur, has been calculated from the results

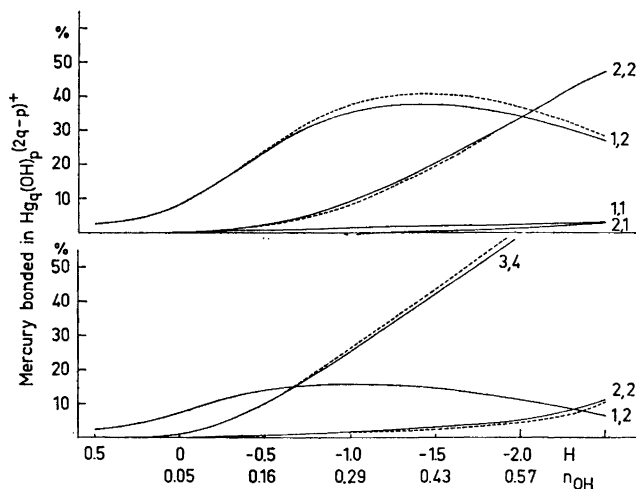


Fig. 1. Percentage of mercury bonded in the different hydrolysis complexes $Hg_q(OH)_p^{(2q-p)+}$ (identified by the values p, q in the drawing), calculated for a 3.5 M solution with the use of the stability constants given by Ahlberg.² Dashed lines represent corresponding concentrations in a 4.5 M solution. The upper drawing gives the concentrations when the four-nuclear complex $Hg_4(OH)_3^{5+}$ is not included in the calculations.

in Fig. 1, and is given in Fig. 2 as a function of the degree of hydrolysis. The same calculations have been made for the complex concentrations calculated with $\text{Hg}_4(\text{OH})_3^{5+}$ included, assuming two limiting cases, two and three, for the average number of Hg atoms bonded to each Hg in the tetra-nuclear complex. The experimentally determined values from the solution X-ray measurements are also shown in Fig. 2, with their estimated standard devia-

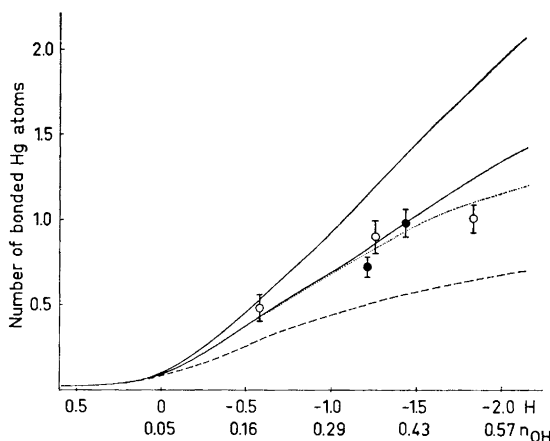


Fig. 2. Average number of Hg neighbors at 3.64 Å around each Hg atom in a solution as a function of the analytical hydrogen ion excess (referred to a 3.5 M solution). Observed values are indicated by open circles (3.5 M solutions) or filled circles (4.6 M solutions). The standard deviations from the least squares refinement,¹ are given for each point. The dotted line connects the experimental points. The two full-drawn lines represent the number of neighbors calculated with the use of the stability constants given by Ahlberg,² and assuming three (upper line) or two (lower line) Hg atoms bonded to each Hg in the $\text{Hg}_4(\text{OH})_3^{5+}$ complex. The dashed line is calculated, assuming only dinuclear complexes to occur.

tions. The experimental values are thus larger than expected for only dinuclear complexes in the solution, but are in good agreement with the curve calculated for two Hg atoms bonded to each Hg in the complex, which according to the emf measurements, should be $\text{Hg}_4(\text{OH})_3^{5+}$. The X-ray measurements thus support the conclusions by Ahlberg, that complexes of a higher nuclearity than two are formed.

THE CRYSTAL STRUCTURES OF BASIC MERCURY(II) PERCHLORATES

Three different basic mercury(II) perchlorates were obtained in crystallized form from the solutions used for the X-ray measurements. The least basic,⁴ $\text{Hg}_5\text{O}_2(\text{OH})_2(\text{ClO}_4)_4(\text{H}_2\text{O})_x$, is triclinic with n_{OH} — representing the average number of protons removed from a hydrated Hg^{2+} ion — equal to 1.20. The next,⁵ $\text{Hg}_7\text{O}_4(\text{OH})_2(\text{ClO}_4)_4$, is orthorhombic, with $n_{\text{OH}} = 1.43$, and the most basic,⁶ $\text{Hg}_2\text{O}(\text{OH})\text{ClO}_4$, is monoclinic, with $n_{\text{OH}} = 1.50$.

In all of the crystals, the characteristic formation of two short (1.9–2.1 Å), linear covalent Hg–O bonds, found in several other structures,^{12–14} is observed. Other Hg–O contacts, usually four or five, are larger than about 2.7 Å. The covalently bonded oxygen atoms can act as bridges between the Hg atoms, with the resulting Hg–Hg distances ranging from 3.38 to 3.62 Å (average value 3.50 Å). The value 3.64 Å found for the Hg–Hg distances in the polynuclear complexes in solution is close to these values, indicating the same type of bridging in the hydrolyzed solutions as in the crystals.

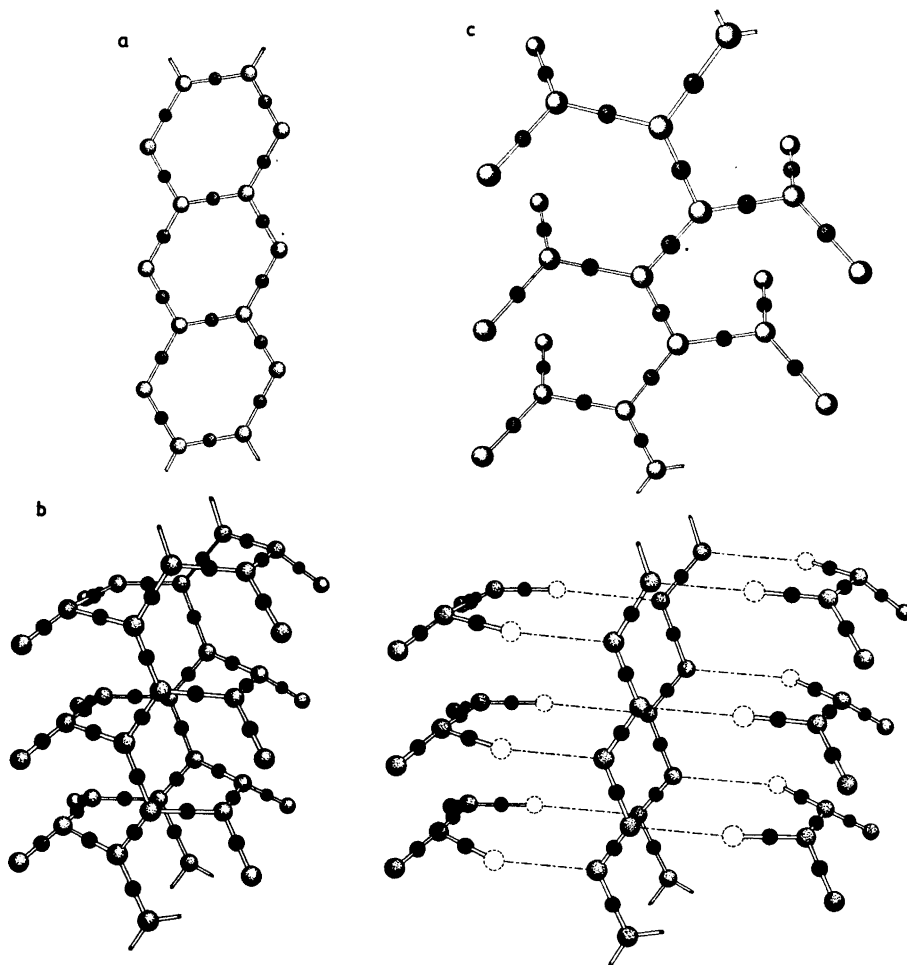


Fig. 3. Part of the infinite onedimensional complexes in the basic mercury(II) perchlorates. The smaller, darker circles indicate Hg atoms. Only mercury atoms and covalently bonded oxygens are shown. a. The triclinic $\text{Hg}_5\text{O}_2(\text{OH})_2(\text{ClO}_4)_4(\text{H}_2\text{O})_2$ (only the positions of the mercury atoms were determined in the structure analysis). b. The orthorhombic $\text{Hg}_7\text{O}_4(\text{OH})_2(\text{ClO}_4)_4$. To the right, some characteristic structural elements in the complex are separately drawn in order to give a more clear view of the structure. c. The monoclinic $\text{Hg}_2\text{O}(\text{OH})\text{ClO}_4$.

All the three different structures are built up from infinite one-dimensional mercury-oxygen complexes. They are illustrated in Fig. 3, which shows the mercury atoms and the covalently bonded oxygen atoms. Although the positions of the hydrogen atoms could not be directly determined in the structure analyses, reasonable assignments are obtained by assuming oxygens, bonded to one or two mercury atoms, to be hydroxo groups, and oxygens bonded to three mercury atoms not to be associated with hydrogen atoms.

Hg-O-Hg chains of the types occurring in other structures¹²⁻¹⁴ can also be recognized in the basic perchlorates, although they are usually condensed further by a covalent bond from the bridging oxygen to a third mercury atom (Fig. 3). Only in the least basic of the salts are bridging oxygens present which are bonded to only two mercury atoms (Fig. 3a). Therefore, the structures are perhaps best described as being built up from planar or pyramidal OHg_3 -groups, joined by common corners. Similar OHg_3 groups have been found in several other basic salts,¹²⁻¹⁴ the most characteristic being the discrete $\text{OHg}_3\text{Cl}_3^+$ ions in the compound Hg_3OCl_4 . Here the coordination about oxygen is a very flat pyramid, with the oxygen atom about 0.3 Å above the plane through the three Hg atoms. The two bonds formed by each Hg atom are approximately linear, the Hg-O bond lengths are 2.05 Å, and the Hg-Hg distances are 3.53₂ Å.¹²

The average numbers of Hg atoms bonded to each Hg in the complexes in the basic perchlorates are 3.20, 3.43, and 3.00, in order of increasing basicity of the crystals, which can be compared with the value of about two, found for the complexes with more than two Hg atoms in the solutions (Fig. 2). The hydroxo groups, which are bonded to only one Hg atom in the complexes in the crystals (Fig. 3), are usually also in contact with an Hg atom from another complex, but the corresponding Hg-O distances are much longer (> 2.7 Å) and do not correspond to covalent bonds.

THE STRUCTURES OF THE HYDROLYSIS COMPLEXES IN SOLUTION

According to the solution X-ray measurements, no diaquo ions seem to occur in an acidic mercury(II) perchlorate solution. In the hydrolyzed solutions, however, some of the Hg-O bonds, roughly corresponding to two bonds per Hg atom in the hydrolysis complexes, are shortened to about 2.0-2.1 Å. It seems reasonable to relate this change to the formation of two linear covalent bonds of the kind observed in the basic perchlorates. It seems likely that this shortening occurs when the first proton is dissociated from the hydrated mercury ion (Fig. 4). This could explain the observation³ that in the formation of the mononuclear complexes, HgOH^+ and $\text{Hg}(\text{OH})_2$, the second proton is more easily dissociated than the first, which would seem less likely, if no changes occurred in the bonding situation around the mercury ion between the two steps. This is not, however, directly proved by the scattering data, since the concentrations of the mononuclear complexes in the solutions investigated are too low to have any noticeable effect on the scattering curves.

The derivation of the structures of the polynuclear complexes in solution has to be based on the results, obtained from the scattering measurements, that the primary building elements are linear O-Hg-O groups, that the

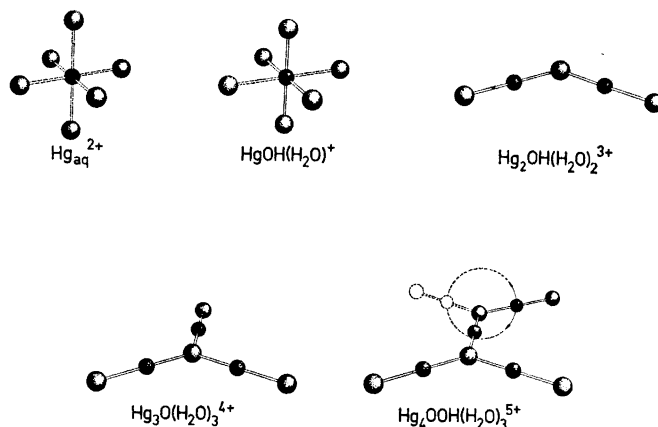


Fig. 4. Possible structures of the hydrolysis complexes of mercury(II) in solution.

bridging between the Hg atoms is of the same type as in the solid basic perchlorates, that each Hg atom in the complexes with more than two metal atoms is bonded to an average of about two other Hg atoms, and that longer Hg–Hg distances than 3.64 Å do not occur or at least have considerably lower frequencies than the primary distance. Structures, which, if dominating in the solutions, would be consistent with these assumptions, are shown in Fig. 4.

The only possible dinuclear complex consists of two linear O–Hg–O groups, having an oxygen in common. For dominating complexes with three or more mercury atoms chains are less likely, since longer Hg–Hg distances are not clearly indicated in the radial distribution curves. A dominating trinuclear complex would be expected to have the structure shown in Fig. 4, which is closely related to the structural elements found in the solid state. With Hg–Hg distances of 3.64 Å, as determined from the scattering data, this would lead to Hg–O distances of 2.10 Å, if the oxygen in the center of the triangle were in the same plane as the Hg atoms, or 2.12 Å, if it were about 0.3 Å above this plane, as it is in the basic perchlorates. In the crystals, the corresponding Hg–O distances vary between 2.02 Å and 2.07 Å (average value 2.05 Å), but the non-bridging covalently bonded oxygens are more closely bonded with Hg–O distances ranging from 1.93 Å to 1.98 Å (average value 1.96 Å). If the same shortening of the covalent Hg–O bonds for the non-bridging oxygens occurs in solution, the observed average bond length of 2.0–2.1 Å for Hg–O in the hydrolysis complexes in solution are consistent with those expected for a complex of the type shown in Fig. 4.

A dominating tetra-nuclear complex could be tetrahedral, which would result in only one type of Hg–Hg distance and three Hg atoms bonded to each Hg. However, assuming an oxygen at the centre of the tetrahedron, this would lead to Hg–O bond lengths of 2.23 Å, which are much longer than those actually observed in the solutions. Moreover, the scattering data indicate two rather than three Hg atoms bonded to each Hg in the complexes

containing more than two Hg atoms (Fig. 2). The fact, that in the solid state the condensation does not lead to OHg_4 groups, also seems to argue against such an arrangement in solution.

A more likely structure is shown in Fig. 4. The average number of nearest Hg neighbours in this model is two, which is consistent with the scattering data. Two longer distances would occur between $\sqrt{3} \times 3.64 = 6.3 \text{ \AA}$ and $2 \times 3.64 = 7.3 \text{ \AA}$, depending on the orientation of the fourth Hg atom. Because of their low frequencies compared with the primary distance, they might escape detection in the radial distribution curves, particularly if the orientation of the fourth Hg atom is changeable.

Still larger complexes are unlikely to be dominant in the solutions, as longer Hg–Hg distances would then have been clearly indicated in the distribution curves.

CONCLUSIONS

The scheme for the hydrolysis reactions of the Hg^{2+} ion, given in Fig. 4, seems to be consistent with all the experimental data. Any of the polynuclear complexes, if dominant in the solutions, would explain the scattering data. This is also true, if only dinuclear complexes are assumed to occur, as even in the most hydrolyzed of the solutions investigated, the scattering data do not indicate more than an average of one Hg atom bonded to each Hg. If, however, part of the mercury in these solutions is still unhydrolyzed, as is indicated by the stability constants given by Ahlberg, the nuclearity of the hydrolysis complexes must be larger than two. The absence, on the other hand, of clearly marked longer Hg–Hg distances in the radial distribution curves, makes it unlikely that complexes larger than those given in Fig. 4 can be dominant. The scattering data are thus consistent with the conclusions made by Ahlberg from emf measurements. The scattering data alone, however, cannot be used to decide which of the polynuclear complexes given in Fig. 4 are dominating in the solutions. Intuitively, however, one would perhaps expect a trinuclear complex with the "closed" structure given in Fig. 4 to be more stable than the "open-structure" tetra-nuclear complex.

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REFERENCES

1. Johansson, G. *Acta Chem. Scand.* **25** (1971) 2787.
2. Ahlberg, I. *Acta Chem. Scand.* **16** (1962) 887.
3. Sillén, L. G. and Martell, A. E. *Stability Constants*, Spec. Publ. No. 17, The Chemical Society, London 1964.
4. Johansson, G. *Acta Chem. Scand.* **25** (1971) 1905.
5. Johansson, G. and Jelen, A. *To be published*.
6. Johansson, G. and Hansen, E. *To be published*.
7. Hayek, E. *Z. anorg. allgem. Chem.* **223** (1935) 382.
8. Hayek, E. and Schnell, E. *Monatsh.* **85** (1954) 472.

9. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 747.
10. Anderegg, G., Schwarzenbach, G., Padmayo, M. and Borg, O. F. *Helv. Chim. Acta* **41** (1958) 988.
11. Arnek, R. and Kakolowicz, W. *Acta Chem. Scand.* **21** (1967) 1449.
12. Aurivillius, K. *Arkiv Kemi* **24** (1965) 151.
13. Grdenic, D. *Quart. Rev.* **19** (1965) 303.
14. Roberts, H. L. *Advan. Inorg. Chem. Radiochem.* **11** (1968) 309.

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