Structure and dynamics of Hg^{2+} in aqueous solution: an Ab Initio QM/MM molecular dynamics study

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Abstract. The human body mostly (more than 80%) consists of liquid, so that the metabolic processes in the human body involve the interaction between solvents and solutes in both ionic and compounds. Metal mercury is a toxic metal, can cause poisoning. The hydration of mercury ions is observed by performing molecular dynamics simulations of molecular mechanics. The base set used is DEF2-ECP for Hg atoms, while for water molecules used dunning DZP base collection. Simulation is done using potential partners and potential 3 bodies. The simulation is done by mixing 1 Hg^{2+} ion mixed with 499 H_{2}O molecules. The simulation results in the form of trajectory data are further processed to determine the structure and dynamics. Based on RDF analysis shows that the average Hg and O (water) atoms are 2.22 Å. Based on CND analysis, it is known that the coordination numbers of hydration of Hg in water are as much as 6 molecules of water. Thus it is known that the hydration of Hg ions in water forms a distorted octahedral molecule structure. Ligand (water) residence time in Hg based on molecular dynamics analysis shows that hydration of Hg with water is stable.

1. Introduction

Chemistry is natural science based on experiments. This is evidenced by the history of chemistry that developed rapidly through experiments. The development of chemistry no longer depends only on experiments in the past two decades. Developments in chemistry today, theoretical predictions of chemical properties can rival the accuracy of the data obtained from experiments [1]. The rapid development of technology and information also influences the development of chemistry. One such development is the use of computers as a means or equipment in chemical laboratory work. The use of computer as a work tool has been developed into an aspect of study called computational chemistry. The rapid development of computational chemistry has changed the description of a chemical system with the inclusion of a new element between experimentation and theory, namely computer experiments. In experiments, the measurement of the system is expressed in numerical form, while in theory uses mathematical equations to model a system generally. So computational chemistry is a bridge that connects experimental results in a laboratory with a theoretical basis. Researchers conducted by previous researchers, can be explained that a metal in the human body has a function, both of which can be beneficial for example in the metabolic process or harmful to the body [2], as antibodies and others. An element that belongs to a group of heavy metals such as cadmium (Cd), arsenic (As), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) are present in the environment both in air, water and food [3-4-5] and can enter the human or animal body. Transition metals included in class IIB such as cadmium (Cd) and mercury (Hg) which are toxic (toxic) [4]. Cadmium and mercury are in nature there are two ways,
naturally and anthropogenic. Mercury metal if it enters the human body can be dangerous and have a high risk of blood vessels and can accumulate in the liver and kidneys causing metabolic disorders [6]. In the human body most (more than 80%) consist of liquid substances, so that the metabolic processes in the human body involve the interaction between solvents and solutes. Interactions that only involve water solvents are called hydration. Because the metabolic processes in the human body are mostly water, of course it involves hydration with solutes. Hydration events involve several shells of solution called dissolution cells. The shell closest to the metal cation is the first (cell) shell, the next shell is called the second shell, and so on until the outer phase. The outer phase is a shell that is not affected by the strength of the cation charge. In this phase only hydration occurs between solvents. The dissolved substance in the first shell has sufficiently strong hydration power. This solute is a ligand that is hydrated with a central ion (cation). Ligands in the first shell can move to the second shell and vice versa. Ligand exchange can affect activity. By using the help of computers and software programs that are increasingly advanced as it is today, it can be done research that examines more deeply about the interaction of solvents with solutes [7-8]. Mercury (II) is an electron pair acceptor that forms bonds with a high degree of covalence with ligands with soft atomic donors, and its special affinity with mercaptan (RSH) is known. Distorted four-tetrahedral coordination was found for mercury ions (II) in the S N, N-dimethylthioformamide donor solvent with strong electron-pair donor properties. Likewise, nitrogen donor ligands can form strong bonds. Ammonia is a solvent with very strong electron pair donor characteristics that are expected to form strong covalent bonds with mercury (II). Recently, tetraammine(mercury(II)) perchlorate crystals, [Hg(NH$_3$)$_4$]$^2+$ (ClO$_4$)$_2$, have been made by flowing ammonia gas into concentrated mercury (II) perchlorate solution. The crystal structure at 170 K has been reported with the distorted tetrahedral configuration around the mercury ion (II) [9]. Mercury (II) complexes with monodentate ligands often show flexible coordination geometry. In a solid state the arrangement of the ligand atoms is bound to be linear, trigonal or tetrahedral. The geometry of octahedral coordination is rare but occurs for example with O-and -N donor ligands in solid solvates eg [Hg(H$_2$O)$_3$](ClO$_4$)$_2$, [Hg(OS(CH$_3$)$_2$)$_3$] (ClO$_4$)$_2$, and [Hg(NC$_3$H$_5$)$_3$] (CF$_3$SO$_3$)$_2$, which crystallizes each of the aqueous solutions, dimethylsulfoxide and pyridine. Investigation of mercury(II) solvated in oxygen and nitrogen donor solvents, eg water, dimethylsulfoxide and pyridine in EXAFS and LAXS shows a labile sixth coordination with dynamic distortion of octahedral symmetry [10]. Study of the structure and dynamics of solvation of metal ions in solvents, especially water and ammonia, has an important role. Shell dynamics solvation of water molecules determines the process of chemical reactions. Some reactions only occur after the water molecules are removed from the solvation shell. Certain metal complexes with amino acids are important from biological and medical aspects, for example as antibacterial and antifungal. Metal ions in ammonia become an interesting system model because they are very relevant, because both amino acids and ammonia contain nitrogen and hydrogen atoms [11].

2. Method

2.1 Determination of Hg$^{2+}$ - H$_2$O coordinates in cartesian coordinates
The initial geometry of Hg$^{2+}$ in H$_2$O is modeled in three-dimensional cartesian coordinates by adjusting the angle and distance between atoms in the system. With the help of Gauss View, a structural form of the Hg$^{2+}$ - H$_2$O coordinate system can be produced [12].

2.2 Selection of the best basis sets
Based on several basis sets are recommended to be tested for basis set pairs that do not cause significant changes in charge to Hg$^{2+}$ ions, and have a bond energy curve profile to the distance of Hg$^{2+}$-O according to Lennard-Jones potential curve profile. In addition to those used also must have a base set superposition error value (basis sets superposition error, BSSE) which is relatively small. Next the best basis sets of pairs is used as a reference for calculating the pair and 3-body functional potential.
2.3 QM/MM DM simulation

QM/MM simulation is done after MM simulation. The final configuration stage results from the MM simulation is used as the initial configuration of the QM/MM simulation. MM/MM simulation is carried out at least 20ps. The distance of the MK area was determined by looking at the RDF results from the MM simulation trajectory analysis. By looking at the RDF chart from the trajectory analysis of molecular mechanics (MM) simulations, the first shell of hydration/hydration can be determined. The DM MK/MM simulation requires a softener function that is useful to allow water ligands to freely move from the MM area to the MK and vice versa. The softening function is used for the MK and MM transition areas of 0.2 Å. The system style is denoted by \( F_{system} \) with the equation as shown in the \( F_{system} \) equation = \( F_{MM} + S \left( F_{MK} - F_{MM} \right) \). \( F_{MM} \) is the force in the MK region, \( F_{MK/MM} \) is the MM style in the MK region, and \( S \) is the softener function. The use of this softener function allows water ligands to freely move from the MK to MM region or vice versa [13].

3. Result and Discussion

3.1. The best basis sets

The activity that was carried out for the first time in DM MM simulation research on Hg\(^{2+}\) ion in water was to determine the set of base atoms. The first step is to find the type of set of atoms that are most suitable for use in DM/MM simulation. The types of support base groups can be known through taking the basis of various research journals that have been conducted. The calculation method used in the base set selection process is a method at Hartree-Fock theory level. The publication of several previous studies, shows that a specific set of support bases for the hydration system of Hg\(^{2+}\) ion in water (H\(_2\)O) is not yet available. Some previous studies that carried out research related to Mercury atoms used different sets of bases. The set of support bases that are commonly used for research in simulations for Mercury atoms include: LANL2DZ ECP, DZVP, DZVPP.

![Energy Potential curves at various distances of the Hg\(^{2+}\)-H\(_2\)O system](image)

**Figure 1.** Energy Potential curves at various distances of the Hg\(^{2+}\)-H\(_2\)O system

Based on the set of bases that have been used by previous researchers, this study begins with a series of trials to find the basis of the most suitable for the hydration system studied. In addition to being based on the basis set that has been used by previous researchers, in order to find the appropriate base set, testing is also conducted on the base set that has an Electron core potential. This is done because Mercury atoms are located in the transition class in the periodic system (class IIB transition elements. Thus the base set analyzed consists of 5 (five) base sets, namely: three types containing ECP: LANL2DZ,
CRENBLJC, DEF2-SVP, base set for H and O atoms, used in this study is the set of DZP-Dunning bases that have been tested for reliability. Based on trials of several basis sets (LANL2DZ ECP, CRENBLJC ECP and DEF2-SVP), a base set that best matches the four hydration systems to be studied and the corresponding base set forms the Lennard-Jones potential curve, the corresponding base set is DEF2-SVP for Mercury and DZP-Dunning atoms for O and H atoms. The graph of potential profile with distance and angle variations is shown in figure 1. After obtaining a suitable base set, the base set that is in accordance with the hydration system is used in the simulation for the system studied, namely: hydration of Hg$^{2+}$ ion in water.

3.2. The 2-body and 3-body Potential

3.2.1. The 2-body potential equations for Hg$^{2+}$–H$_2$O. The first step is to determine the 2-body potential equation of the Hg$^{2+}$-H$_2$O system. Determination of the 2-body potential equation of Hg$^{2+}$-H$_2$O, is carried out by collecting energy points. Energy points are collected by placing water molecules (H$_2$O) in the center of cartesian coordinates, (0,0,0), while Hg$^{2+}$ ions are placed around the water coordinates (H$_2$O), with distances varied from 1.4 Å to with 15 Å, with varying angles $\theta$ and $\phi$. Variation of angle $\theta$ is determined starting from 0$^\circ$ to 180$^\circ$ ($0^\circ \leq \theta \leq 180^\circ$), while for angles $\phi$ starting from 0$^\circ$ to 90$^\circ$ ($0^\circ \leq \phi \leq 90^\circ$). Data on energy points of potential energy at various distances and angles $\theta$ and angle $\phi$ are then processed further through a 2 body fitting program with the most suitable modification of the rank. The form of pair potential equation of Hg-H$_2$O is as follows:

$$
E_{2bd}^{fit} = \frac{q_{Hg(ii)} q_i}{r} + \frac{A_0}{r^2} + \frac{B_0}{r^6} + \frac{C_0}{r^{11}} + \frac{D_0}{r^{12}} + \sum_{i=1}^{3} \left( \frac{q_{Hg(ii)} q_i}{r_i} + \frac{A_H}{r_i^4} + \frac{B_H}{r_i^5} + \frac{C_H}{r_i^6} + \frac{D_H}{r_i^{12}} \right)
$$

where $a,b,c,d, A_i, Bi, Ci$, dan $Di$ is a fitting parameter, rMi, is the i-atom distance from the Hg$^{2+}$ and H$_2$O ions, qi is the i-atomic charge of the H$_2$O molecule, and $q_{4m}$ is the total charge of Hg$^{2+}$ ion. The results of the analysis of energy points on a variety of distances and variations in angles $\theta$ and $\phi$ of the Hg$^{2+}$-H$_2$O system are presented in table 1.

| Table 1. The optimized parameters of the analytical two-body potential and three-body correction functions |
|-------------------|-----------------|-----------------|-----------------|-----------------|
| 2-body            | A (kcal mol$^{-1}$) | B (kcal mol$^{-1}$) | C (kcal mol$^{-1}$) | D (kcal mol$^{-1}$) |
| Hg(II)-O          | -4291.14         | 181896.74       | -802564.93       | 3691064.19       |
| Hg(II)-H          | -644.85          | 12474.54        | -2081.79         | 551.51           |
| 3-body            | A$_1$ (kcal mol$^{-1}$ Å$^{-1}$) | A$_2$ (kcal mol$^{-1}$ Å$^{-1}$) | A$_3$ (kcal mol$^{-1}$ Å$^{-1}$) |
| O-Hg(II)-O        | 4.474            | 0.551           | 0.590            |

A, B, C and D are parameters of the potential pair equation (kcal/mol Å) 

3.2.2. Determination of 3-body potential equations for H$_2$O–Hg$^{2+}$–H$_2$O. The preparation of 3-body potential is needed, this is done in order to minimize the influence of many body interactions between water molecules and or ammonia molecules. Collection of energy points in determining 3-body potential equations for hydration of mercury ions in water using the turbomol program (scan3bd). The steps in determining a 3-body potential equation are similar to steps when determining potential 2-body potential equations. Interaction energy is collected in various geometric configurations by varying the distances (r1 and r2) of mercury ions with
water and. The interaction energy points are carried out at a distance of 1.5 Å to 7.0 Å at various variations of tau (τ) and angle φ. The angle τ used is selected from 0° to 180°, while the angle φ is determined from 90° to 180°. After obtaining energy points at various distances and various angles φ and τ, fitting is done to obtain the 3-body equation. The potential equation for 3-body hydration system is Hg\(^{2+}\) ion in water (H\(_2\)O–Hg\(^{2+}\)–H\(_2\)O). Form 3-body potential equations for hydration:

\[
V_{3bd} = a_1 e^{-a_2 (r_1 + r_2)} e^{-a_3 r_3} (\text{CL} - r_1)^2 \text{CL} - (r_2)^2
\]

information:
- \(V_{3bd}\): function of potential 3-body equation
- \(\text{CL}\): the cut-off limit which is normally set to 6.0 Å, at a distance above 6.0 Å the interaction is outside the 3-body potential count
- \(r_1\): distance of Hg with O\(_1\) (Å)
- \(r_2\): distance of Hg with O\(_2\) (Å)
- \(r_3\): distance of O\(_1\) with O\(_2\) (Å)
- \(a_1, a_2, a_3\): parameters of potential 3-body equations

Energy points obtained from variations in distance (r1 and r2) and on variations in angles φ and τ which were collected in the determination of the 3-body equation for the Hg\(^{2+}\) ion system in water in this study were 10,560, the obtained energy interaction points then fitting is done by using the fit3bd program for water. The parameters of the potential equation for 3-hydration body Hg\(^{2+}\) in water are presented in table 1.

### 3.3. Structure of hydration of Hg\(^{2+}\) ions

#### 3.3.1. Radial Distribution functions (RDF)

RDF or distance distribution function in this hydration system states the function of the distance distribution of water molecules (H\(_2\)O) to Hg\(^{2+}\) ions. The distance of the central ion with the oxygen atom from the water molecule is denoted by Hg\(^{2+}\)-O, the distance distribution function (RDF) for the hydration system of Hg\(^{2+}\) ion in water in molecular dynamics/quantum mechanics simulations is presented in figure 2.

![RDF of Hg\(^{2+}\) ion in water](image)

**Figure 2.** RDF of Hg\(^{2+}\) ion in water are obtained by the QM/MM MD simulations.
A summary of the results of the RDF analysis of the hydration of the Hg$^{2+}$ ion system in water is presented in table 2.

**Table 2.** Characterization values of RDF for Hg$^{2+}$ ions in water are obtained by the QM/MM simulations

| Simulation Method | $\alpha$-$\beta$ | $r_{M1}$ | $r_{m1}$ | $n_1$ | $r_{M2}$ | $r_{m2}$ |
|-------------------|------------------|---------|---------|-------|---------|---------|
| QM/MM             | Hg$^{2+}$-O      | 2.1     | 2.7     | 6.0   | 4.2     | 5.5     |
|                   | Hg$^{2+}$-H      | 2.7     | 3.4     | 12.4  | 4.2     | 6.9     |

explanation:
$\alpha$-$\beta$: ligand atom(β)-center atom (α)
$r_{M1}/r_{M2}$: the maximum peak of the first and second solvation shell (Å)
$r_{m1}/r_{m2}$: the minimum peak of the first and second solvation shell (Å)
$n_1$: number of ligands in the first shell

3.3.2. **Coordination Number Distribution (CND).** CND or distribution of coordination numbers, illustrates the distribution of coordination numbers that have central ions with related ligands. The number of coordination numbers or ligands during the hydration simulation of Hg$^{2+}$ in water with the method of quantum mechanics/molecular mechanics is presented in figure 3.

**Figure 3.** Distributions of the coordination numbers calculated within the first and second solvation shell of Hg$^{2+}$ in water based on QM/MM MD simulation

Figure 3 is a CND graph from the simulation of Hg$^{2+}$ ions in water. The figure gives information that the number of ligands surrounding the central atom for the hydration system of Hg$^{2+}$ ion in water the number of ligands is 6. So it can be said that the complex ion Hg(H$_2$O)$_6^{2+}$ which is formed is an ion molecule that is less stable enough. The number of ligands in the second shell looks quite high. This fact shows that the ligand in the second shell is very dynamic and flexible.
3.3.3. **Angular Distribution Function (ADF).** ADF or angle distribution function is a function that describes the distribution of angles during the molecular dynamics simulation takes place. ADF provides information about the bond angle distribution formed between ligand 1 (atom O₁) - central ion (Hg) - ligand 2 (atom O₂). The ADF for the Hg²⁺ ion in water is presented in figure 4.

Figure 4 The O-Hg²⁺-O angle (°) distribution of solvation structure of Cd²⁺ in water based on QM/MM MD simulation

Figure 4 shows that the angle O₁-Hg²⁺-O₂ is between 90° and 175°. The graph shows the two highest peak angles, at 90°. While the angle of one ranges from 175°. Based on the results of the analysis of RDF, CND, and ADF above, it can be concluded that the hydration structure of Hg ions in water forms a distorted octahedral.

Figure 5. Snapshot of the first solvation shell of Hg²⁺ in water during the hybrid QM/MM MD simulations
Graph of ligand exchange hydration of Hg$^{2+}$ ion in water, shows the hydration dynamics between Hg$^{2+}$ ions and water molecules during the simulation process. In addition to information on the hydration distance of Hg$^{2+}$ ions with water molecules, it is also seen the number of ligands that hydrate both in the first and the second shell. This ligand exchange chart can also show the presence or absence of water ligands from the first shell to the second shell and vice versa from the outer shell to the deeper shell. The presence or absence of ligand exchange during the ongoing simulation is presented in figure 6.

Figure 6 is a ligand exchange graph from a simulation and Hg$^{2+}$ ion in water. It was seen during the simulation that it had never experienced a ligand move either towards the first shell or towards the second shell. This shows that the hydration structure of Hg$^{2+}$ ion molecules in water is quite stable, in this case the Hg$^{2+}$ ion binds 6 water molecules as ligands. Ligand exchange is seen in the second of shell to the bulk phase, from the graph shows the dynamics of the movement of water molecules, both the movement from the second shell to the third shell and the bulk phase, and vice versa from the bulk phase or the third shell to the second shell.

![Graph of ligand exchange hydration](image)

**Figure 6.** No water ligands migration between first and second solvation shell are observed: the ligand exchanges of H$_2$O are observed between the second solvation shell and bulk.

4. **Conclusion**

The Hg$^{2+}$ ion in water binds 6 water molecules as ligands. Hydration of Hg$^{2+}$ ions has a distorted octahedral structure. The residence time of ligands of water in the hydration of Hg$^{2+}$ ions is relatively long, and thus the first shell solvation are stable.

5. **References**

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