STRUCTURE OF IRIDIUM(III) HYDRATION BASED ON AB INITIO QUANTUM MECHANICAL CHARGE FIELD MOLECULAR DYNAMICS SIMULATIONS

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ABSTRACT

Structural properties of Iridium(III) hydration have been studied based on an ab initio Quantum Mechanical Charge Field (QMCF) Molecular Dynamics (MD) Simulations. The most chemical-relevant region was treated by ab initio calculation at Hartree-Fock level. For the remaining region was calculated by Molecular Mechanics method. LANL2DZ ECP and DZP Dunning basis sets were applied to Ir^{3+} *ion and water, respectively. The average distance of Ir-O in the first hydration shell is 2.03 Å. The QMCF MD Simulation can detect only one complex structure with coordination number of 6 in the first hydration shell. Bond angle analysis shows that* Ir^{3+} *ion hydration in the first hydration shell has octahedral structure.*

Keywords: *ab initio, hydration structure, Iridium(III), MD simulations, QMCF study*

INTRODUCTION

Structural and dynamical properties of metal ion hydration are important data for understanding the interaction between metal ion and water [1]. Coordination characteristic of hydrated metal ion is correlated to the chemical properties, such as redox process, ligand exchange, reaction kinetics and also hydrolysis [1]. The structural and dynamical properties of hydrated metal ions can be obtained by experimental techniques and computer simulation methods [2-4].

The main experimental techniques are divided into two groups. The first methods are diffraction methods, such as X-ray and neutron diffraction (XRD and ND, respectively), and the second, spectroscopic methods, such as extended X-ray absorption fine structure (EXAFS) and nuclear magnetic resonance (NMR). Because of the limitation, only the NMR technique can investigate the dynamics of particles in the liquid system in 10^{-9} s order [3]. Unfortunately, all experimental methods have their limitations for investigating metal ion hydration properties. Even a novel Femtosecond Laser Pulse Spectroscopy method still has its limitation for investigating metal ion hydration properties [3]. This limitation can be solved by computer simulation methods [4]. They are Monte Carlo (MC) and Molecular Dynamic (MD) Simulations. This research used MD Simulation because it can give both structural and dynamical properties of metal ion hydration. In its development some methods of MD simulation are available such as Classical MD [3], Car-Parrinelo (CP) MD [3], Quantum Mechanical/Molecular Mechanical (QM/MM) MD [2-3] and a novel Quantum Mechanical Charge Field (QMCF) MD [5-10].

Iridium (Ir) and its compounds have important function as a catalyst, especially Iridium(III) [11-12]. For further development of Iridium(III)-based compounds and catalytic mechanism investigation, reactivity data of Ir^{3+} ion in liquid system is needed. The reactivity of Ir^{3+} ion in water can be shown by coordination characteristic of its hydration. A novel QMCF Molecular Dynamics (MD) Simulation method was applied in order to obtain the coordination property of Ir^{3+} ion. The QMCF MD simulation is QM/MM MD scheme development by utilizing electrostatic embedding technique to describe the interactions between the QM and MM regions. The QMCF MD method works without the solute-solvent potentials due to a large radius of the QM region [5]. This paper explains the structural properties of Ir^{3+} ion hydration. These properties are radial distribution of Ir^{3+}-O in first and second hydration shells, hydration number and bond angle distribution [7-10].

EXPERIMENTAL SECTION

Materials and instruments

This research is theoretical study that uses a model of liquid system. The model consists of 1 Ir^{3+} ion and 999 water molecules in a simulation box. The instrument is 1 unit of personal computer (Core2Quad

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Processor). Computational Programs are Gaussian 03 [13] package and the QMCFC package 1.3.1 developed by Theoretical Chemistry Institute (TCI), Innsbruck University, Austria [14].

Methods

Similar to QM/MM MD method, the chemical system is divided into two parts: First region is QM region where the chemically most relevant region is calculated by quantum mechanical calculation [2-4]. The remaining part of the system or MM region is treated by classical mechanics calculation. Although the theoretical treatment of interactions within the regions is straightforward, the coupling of the subsystems should be considered. The partition of the system according to QMCF MD method can be seen in Fig. 1. In the QMCF MD method the first region is QM region which consists of the core and the layer region. The remaining part is the MM region. In this method the solute or metal ion is placed in the center of the QM region. Because of the large distance of QM region only Coulombic interaction is applied for calculation [5].

The layer region consists of the second shell water molecules which need not only Coulombic but also non-Coulombic interactions for describing their interactions with MM particles. According to this condition the forces in the subsystem of simulation box defined as:

$$F_J^{core} = F_J^{QM} \tag{1}$$

$$F_J^{layer} = F_J^{QM} + \sum_{I=1}^{M} F_{IJ}^{MM-nC} \tag{2}$$

$$F_J^{MM} = \sum_{\substack{I=1 \\ I \neq J}}^{M} F_{IJ}^{BJH} + \sum_{I=1}^{N_1+N_2} \frac{q_I^{QM} . q_J^{MM}}{r_{IJ}^{2}} + \sum_{I=1}^{N_2} F_{IJ}^{MM-nC} \tag{3}$$

Symbol of F_J^{core} corresponds to the quantum mechanical force acting on a particle *J* in the core zone, F_J^{layer} to the forces acting on a particle *J* located in the solvation layer, and F_J^{MM} to the forces acting on a particle *J* in the MM region. The forces acting on all atoms in the core region (N_1) consist of the QM forces F_J^{QM} plus the charge field interaction according to Coulomb's law. As mentioned before the non-Coulombic forces F_{IJ}^{MM-nC} between QM particles located in the layer region (N_2) and MM particles (M) have to be included via potential embedding. The force acting on an MM particle consists of three contributions, namely, the interactions with all other MM atoms (M) calculated on the basis of classical potential functions F_{IJ}^{MM}, the non-Coulombic interactions F_{IJ}^{MM-nC} with all layer atoms (N_2), and the charge field contributions with all QM atoms ($N_1 + N_2$). All Coulombic interactions between QM and MM atoms are obtained utilizing partial charges assigned to the QM atoms via population analysis. This assignment is performed in every step of the simulation. This step can accommodate the nature of interaction between polarizing particles such as highly charge Rh^{3+} or Ir^{3+} ion and water molecules [5].

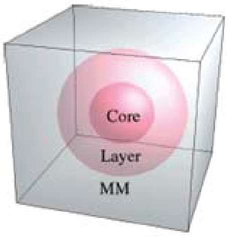

Fig 1. The simulation box partition in the QMCF MD method. The metal ion is located at the center of the box [5]

To give a more reliable description of the quantum mechanical region, the point charges of all MM particles are embedded in the Hamiltonian as a perturbation potential [5]:

$$H_{CF} = H_{HF} + V' \tag{4}$$

$$V' = \sum_{J=1}^{M} \frac{q_J}{r_{IJ}} \tag{5}$$

In order to obtain the best performance of computer simulation, calculation method has to be selected. Basis set and theory level of calculation are needed because of the application of ab initio calculation. Based on energy calculation of Ir^{3+}-n(H_2O) complexes (known as water cluster method) and the agreement with the experimental data, LANL2DZ ECP [17] and DZP Dunning [18] basis sets were used to Ir^{3+} ion and water molecule, respectively. For the details, another QMCF MD simulation protocols are explained in previous works [5-10].

RESULT AND DISCUSSION

Basis Set and Theory Level Selection

Interaction energies and geometry data of Ir^{3+}-n(H_2O) complexes from 2 candidates of basis set are calculated by 3 theory level of calculation such as Hartree-Fock (HF), Density Functional Theory (DFT) and the Post-SCF Möller-Plesset 2 (MP2). Two candidates of basis set are LANL2DZ ECP and SBKJC VDZ ECP which are frequently used to calculate transition metal ions [2-4]. Most previous works suggest the DZP Dunning basis set has to be used for water molecule in MD simulations [4-10]. Based on the calculation, the result of HF method is closed to MP2 (Table 1 and 2). Therefore, the HF method is selected as theory level of ab initio calculation.

Table 1. Interaction energies of Ir^{3+}-*n*(H_2O) and Ir-O distance of LANL2DZ ECP basis set at various ab initio theory level

The number of H_2O	Interaction energy (kcal/mol)			Ir-O distance (Å)		
	HF	DFT	MP2	HF	DFT	MP2
1	-144.04	-237.73	-159.23	1.95	1.84	1.95
2	-311.87	-408.51	-351.78	1.90	1.91	1.90
3	-332.10	-520.92	0.00	1.98	1.95	1.92
4	-484.13	-613.52	0.00	2.02	2.00	1.92
5	-566.54	-691.04	-634.57	2.06	2.07	2.06
6	-652.03	-753.63	-699.68	2.08	2.09	2.08

Table 2. Interaction energies of Ir^{3+}-*n*(H_2O) and Ir-O distance of SBKJC VDZ ECP basis set at various ab initio theory level

The number of H_2O	Interaction energy (kcal/mol)			Ir-O distance (Å)		
	HF	DFT	MP2	HF	DFT	MP2
1	-171.33	-238.33	-202.39	1.97	1.85	1.85
2	-311.96	-411.02	-357.98	1.91	1.92	1.91
3	-302.89	-522.36	-465.72	2.15	2.02	1.97
4	-513.96	-615.57	-	2.04	2.02	-
5	-587.63	-695.03	-	2.07	2.07	-
6	-652.95	-757.84	-	2.10	2.09	-

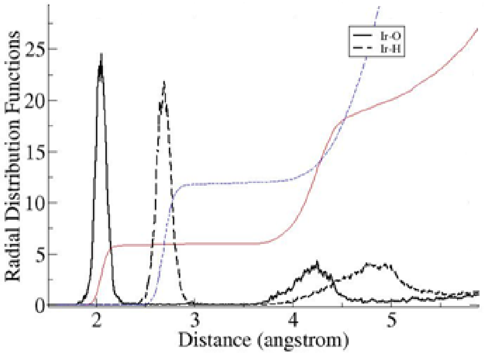

Fig 2. The radial distribution function curve that is obtained by QMCF MD simulations of Ir^{3+} ion in water. Two peaks describe the abundance and location of water molecules from the Ir^{3+} ion. The first sharp peak is first hydration shell and the second broad peak is second hydration shell.

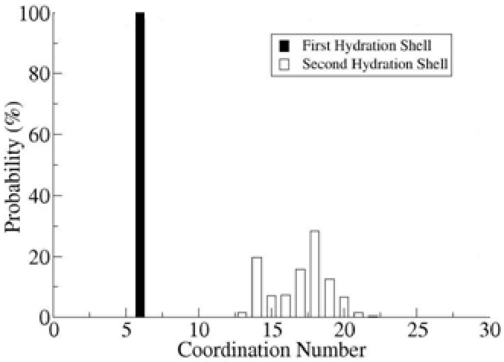

Fig 3. The CND data are obtained by QMCF MD simulations of Ir^{3+} ion in water. These data describe the number of water molecules in the first and second hydration shell. Coordination number of 6 is occurred in the first hydration shell

After ab initio theory level is obtained the suitable basis set for Ir^{3+} is determined by geometry structure analysis of $[Ir(H_2O)_6]^{3+}$ complex. The LANL2DZ ECP gives closed results to the experimental data. The Basis Set Superposition Error (BSSE) value of this basis set is also small. BSSE (in kcal/mol) for LANL2DZ ECP and SBKJC VDZ ECP basis set are 5.02 and 82.10, respectively. Based on these data, the LANL2DZ ECP is selected for Ir^{3+} ion calculation.

Structure of Ir^{3+} ion in Water

Average distance of Ir-O

Radial distribution functions (RDFs) of Ir^{3+}-O obtained from this research is plotted in Fig. 2. This figure shows the two well-distinguished regions. Two peaks in Fig. 2 show the occurrence of water molecules. The first sharp-high peak on the interval of 1.8 – 2.3 Å is the first hydration shell and the broad peak on 3.6 – 4.8 Å is the second hydration shell. There is no water molecule in the region between 2.5 – 3.5 Å. Based on the Ir^{3+}-O RDFs the largest radial distribution value of water molecules in first hydration shell is located at 2.03 Å (see Fig. 2). This means that the average distance between water molecules and Ir^{3+} ion in first hydration shell is 2.03 Å. This information can complete the structural property of Ir^{3+} ion in water which can not be obtained by experimental method [17].

Table 4. Maximum (r_M,Å) and Minimum (r_m,Å) peak of The Radial Distribution Function ($g_{Ir(III)-O}$) and The average Coordination Number of First ($CN_{av,1}$) and Second Hydration Shell ($CN_{av,2}$) of Ir^{3+} ion in water by QMCF MD Simulations

Methods	r_{M1}	r_{m1}	r_{M2}	r_{m2}	$CN_{av,1}$	$CN_{av,2}$
QMCF MD Simulation	2.03	2.30	4.30	4.80	6	13 - 22
Experimental method [17-18]	2.03 – 2.06	n.a	n.a	n.a	6	n.a

n.a = not available.

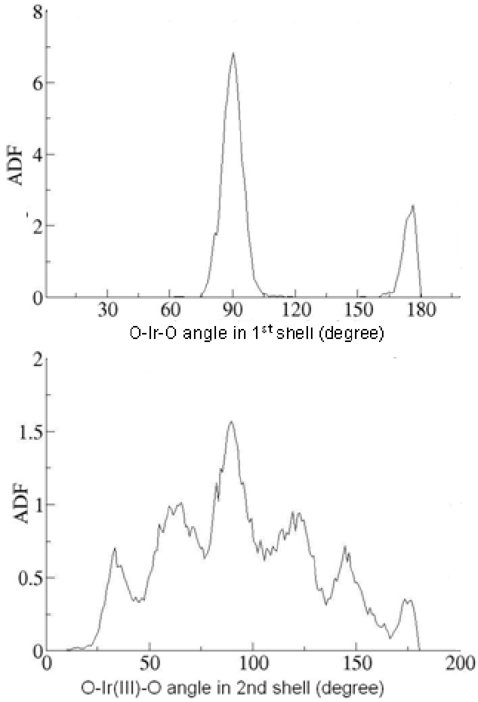

Fig 4. Angular Distribution Functions curve of O-Ir^{3+}-O angles obtained by QMCF MD Simulations. There are 2 peaks in the 1st hydration shell and 6 peaks in the 2nd shell. Orientation of water molecules in 2nd shell is more flexible than the 1st shell.

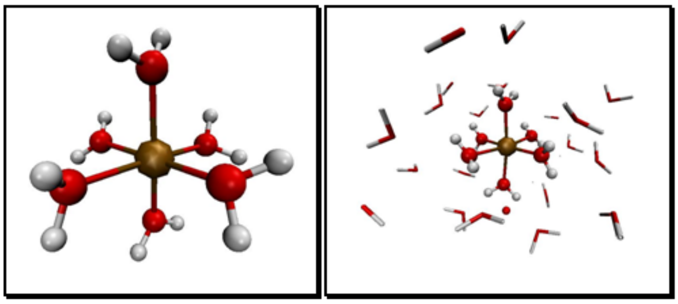

Fig 5. Snapshots of the 1st hydration shell (left) and 2nd shell (right) of Ir^{3+} ion structure in water based on QMCF MD simulations. In the 2nd shell, the $[Ir(H_2O)_6]^{3+}$ complex is surrounded by a lot of water molecules (stick model).

Coordination number

Coordination properties can be obtained by integration of the first and the second hydration shell curve. The first curve yields hydration number of 6 for Ir^{3+} ion in first hydration shell (see Fig. 3). The Coordination Number Distribution (CND) of 6 in the first hydration shell has 100% probability. It explains that only 1 complex structure is occurred in the first hydration shell. This six-coordinated complex in the first hydration shell was also obtained by experimental method [17]. Data from RDF and CND analysis can be seen in Table 4.

More than one coordination number is occurred in the second hydration shell. There are 13 – 22 water molecules in the second hydration shell (see Fig. 3). The large probabilities are located at 14 and 18 which have 22% and 30%, respectively. The coordination number in second hydration shell can complete the structural properties of Ir^{3+} ion in water that are not available from experimental method [17]. Investigation of structural properties of Ir^{3+} ion in water by RDFs and CND curves show that the first hydration shell is more rigid than the second shell.

Bond Angle of O-Ir-O

The Angular Distribution Function (ADF) of O-Ir^{3+}-O angles is plotted in Fig. 4. The ADF obtained from QMCF MD simulation displays two peaks which are located at ~90° and ~180°. The first maximum peak is located at 91° is caused by two neighboring Oxygen atoms. The second peak has a maximum value 178° indicating an octahedral structure of Ir^{3+}-water complex in the first hydration shell. This result is also obtained by experimental work [17].

Different O-Ir^{3+}-O angle distributions are obtained in second hydration shell. There are 6 peaks of angles are obtained by ab initio QMCF MD simulation. These angles are 30°, 60°, 90°, 120°, 145° and 178° which indicate the more flexible structure of Ir^{3+} ion hydration in the second hydration shell than the first shell. The 90° angle is the average water molecules orientation in the second hydration shell (Fig. 4). Water molecules orientation in the second hydration shell from QMCF MD completes structural properties of Ir^{3+} ion in water that could not be obtained by experimental technique.

The molecular shape of Ir^{3+} ion structure in the first hydration shell is the stable octahedral structure. More than one structure can be occurred in the second hydration shell (Fig. 5).

CONCLUSION

Applying the QMCF MD simulation can detect the stable six-hydrated structure in the first hydration shell of Ir^{3+} ion in water. It also can give data that can not be access by experimental methods.

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