Ab Initio investigation of chloroaqualead (II) complexes as possible corrosion products in Super Critical Water Cooled Reactor (SCWR)

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Abstract

One of the undesirable processes hindering development of Generation IV SCWR is the possibility of corrosion of construction material. Formation of corrosion products such as metal-ligand complexes is poorly understood both experimentally and computationally. It is essentialto predict and control its water chemistry to ensure sustainability of SCWR. Pressurized and heated solutions are challenging for experimental research; computational method becomes an important research tool. A series of *ab initio* calculations of chloroaqualead (II) complexes have been performed at HF, MP2 and B3LYP levels of theory with CEP-121G, LANL2DZ, SDD basis sets for Pb and 6-31G*, 6-31+G*, 6-311+G* for water.

1. Introduction

Due to the increased world energy demand, in 2001, Generation IV International Forum (GIF), consisting of 10 different countries including Canada has proposed six innovative concepts of Generation IV nuclear reactors. The idea is to maintain original CANDU (Canadian Deuterium Uranium) concept, originally developed by Atomic Energy of Canada Limited (AECL), but to enhance both design and application, promisinghigher safety, better performance, increased sustainability (by optimizing fuel usage and minimization of waste production), and longer design life (up to 60 years; lower financial risk for investment) [1-12]. One of the Generation IV conceptual designs is Supercritical Water Cooled Reactor (SCWR). Performance and efficiency of SCWR depends on extreme operating conditions (625ºC and 25 MPa). SCWR offers many benefits over current Light Water Reactor (LWR) such as: higher thermal efficiency (~ 45% vs. 33% of current LWR) obtained by expansion of turbines due to direct-cycle pressure tube, and simplifiedsingle phase coolant with high enthalpy [8-14].SCWR utilizes Super Critical Water (SCW) as a working fluid. SCW refers to water above 374 ºC and 22.1 MPa. SCW is a single phase fluid with no distinct liquid and gas phases and acts as a dense gas [8- 14]. SCWcan very quickly become oxidative environment, which may result in corrosion of construction material. The long term sustainability ofSCWRlargely depends on the ability to predict and control water chemistry inside the reactor in order to minimize corrosion associated with the new design. The proposed structural material for Canadian-SCWR are Fe-Ni-Cr and zirconium alloys. Corrosion could produce the following metal species of interest: Mn^{3+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{+}, Zn^{2+}, Pb^{2+}, ZrO^{2+}, Cr^{3+}, CrO_4^{2-} and their hydrolysis products [3-4, 11-15]. The metal specie of interest for this research isPb^{2+} (lead), which exists as an impurity within theproposed Fe-Ni-Cr and zirconium alloys. Trace amount of lead are major cause of the embrittlement and crack propagation via

stress corrosion cracking and thus is important to be researched with respect to development of SCWR [16]. At elevated temperatures and pressures, traces of Pb^{2+} tend to dissolve from the construction material into the SCW[10].SCW has low density and acts as a non-polar solvent, thus is unable to fully dissolve ions as it would in subcritical region. Undissolved lead has a tendency to make neutral complexes with surrounding anions (Cl^- and OH^-), and H_2O, and/or NH_3. $Cl^-$is introduced to the SCW environment via condenser leakage from the river water, OH^- from the feedwater or it can be added for pH adjustment (NH_3). Owing to direct-cycle conceptual design, any metal-ligand speciesformed will be carried with a coolant out of the core and will be deposited on the fuels or turbines causing general corrosion[10, 12]. Formation of such corrosion complexes is poorly understood both experimentally and computationally, thus require thorough research [11].Experimental research involving SCW conditions is difficult giving advantage to computational methods as an excellentstarting point. In this study, a comprehensive *ab initio* calculations of chloroaqualead (II) complexes, $[PbCl_n(H_2O)_m]^{2-n}$, were performed up to and including hexacoordinate species. The ultimate goal of this study is to contribute to development of an appropriate chemistry water control strategy for SCWR concept, and to contribute to sustainable development of feasible SCWR.

2. Methods

Ab initio calculations were performed using the Gaussian03 [17] software through ACEnet (Atlantic Computational Excellence Network) [18]. The molecular geometries were optimized using a stepping stone approach, in which the geometries were optimized sequentially at different levels of theory(HF (Hartree-Fock), MP2 (second-order Møller-Plesset perturbation theory) and B3LYP (Hybrid Density Functional Theory)).6-31G*, 6-31+G* and 6-311+G* basis sets were used for small atoms (oxygen (O), hydrogen (H), chloride (Cl)), while Pb was investigated using effective core potential (ECP) basis sets (CEP-121G, LANL2DZ and SDD) [19].Geometry convergence at each level was followed by frequency calculations.The Hessian (FOpt=CalcFC) was evaluated at the beginning of each optimization in order to assist geometry convergence of the following levels. Optimized geometry (geom=allcheck) was used in the subsequent optimizations. The Z-matrixwas used to speed up calculations by constraining molecule to a specific symmetry.The stability of molecular symmetry was characterized by the vibrational frequencies from the Hessian.Potential energy surface (PES) was scanned starting with the highest symmetry structures, subsequently reducing the symmetry of the structure based on imaginary frequency modes (denoted as negative by the software) until the lowest energy minima structure was found.The eigenvectors of the imaginary frequencies pointed towards the new structural orientation where molecule is at the true minimum (all real frequencies). Geometry optimizations were carried out to completion for all levels of theories in a sequence even when one or more levels did not converge to local minima. This ensured that no energy minima were missed. Frequency analysis and pictures of optimized molecular structures were obtained utilizing visualization program called MOLDEN [20].

3. Results

The goal of molecular optimization of chloroaqualead (II) complexes was to find the most stable coordinated structures. The result include calculations at HF, MP2 and B3LYP levels of theory coupled with CEP-121G, LANL2DZ and SDDbasis sets for Pb, and 6-31G*, 6-31+G* and 6-311+G* for small

atoms. Complexes were investigated both in the presence and absence of water for the stability comparison. The absolute minimum energy structures are presentedin Figures 1, 2 and 3.

3.1 Monochloroaqualead (II) Complexes, $[PbCl_1(H_2O)_n]^{1+}$, where n=0-5

The anhydrous complex, $[PbCl_1]^{1+}$, proved to be the most stable at the highest symmetry $C_{\infty v}$ structure.$[PbCl_1(H_2O)_1]^{1+}$ was desymmeterized from C_{2v}, along imaginary B_1 mode, skeletal deformation, to the most stable C_s structure.$[PbCl_1(H_2O)_2]^{1+}$, was reverted from C_{2v} structure along B_1 and B_2 modesto C_s #1 and C_s #2, which converged to the same absolute energy minima.$[PbCl_1(H_2O)_3]^{1+}$ was reverted fromC_{3v}along imaginary A_2 mode, water twisting mode, to C_3 structure. Furthermore, C_3 structure was reverted along imaginary E mode, skeletal deformation, to C_s which proved to be at absolute minima for all attempted levels. $[PbCl_1(H_2O)_4]^{1+}$was constrained C_{4v} (2 forms) andfound to be the most stable for: C_{4v} #2 , C_4 and C_1 structure. $[PbCl_1(H_2O)_5]^{1+}$was initially constrained at 5 different C_{2v} structures. The lowest energy C_{2v} structure wasreverted along A_2 mode to C_2 structure and along B_1 mode to $C_s$structure (imaginary frequencies). $[PbCl_1(H_2O)_5]^{1+}$_C_s structure was reverted along imaginary A" mode to the most stable C_1 structure. $[PbCl_1(H_2O)_6]^{1+}$wasinitially constrained to C_{3v} symmetry (4 forms). Currently, $[PbCl_1(H_2O)_6]^{1+}$_C_{3v} #1 and #3 are being desymmeterized to $C_s$and C_3 structure.

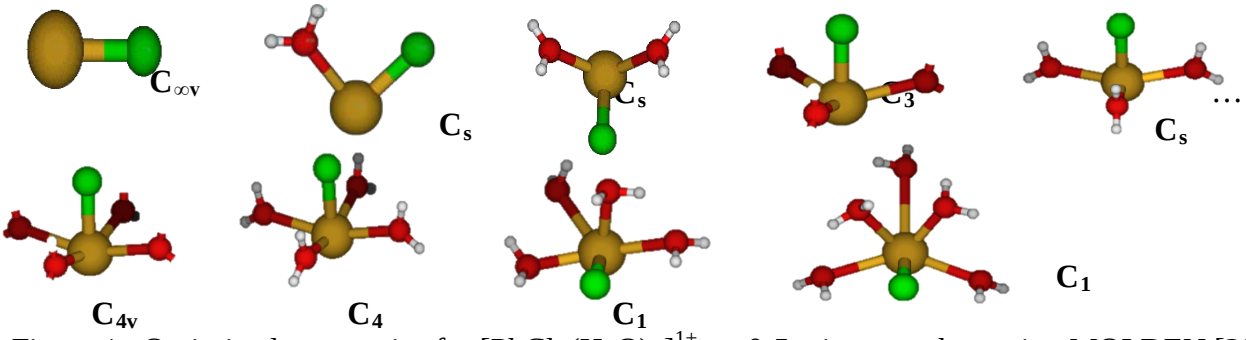

Figure 1 Optimized geometries for $[PbCl_1(H_2O)_n]^{1+}$, n=0-5, pictures taken using MOLDEN [20]

3.2 Dichloroaqualead (II) Complexes, $[PbCl_2(H_2O)_n]^0$, where n=0-4.

The anhydrous $[PbCl_2]^0$ complex, was desymmeterized from $D_{\infty h}$ along the Π_{IU} mode, skeletal deformation mode, to the most stable C_{2v} structure. $[PbCl_2(H_2O)_1]^0$ was reverted from $C_{2v}$to C_s, which was further reverted to the lowest energy minima C_1 structure. $[PbCl_2(H_2O)_2]^0$ complexwas reverted from D_{2h} symmetry to the most stable C_{2v} structure. $[PbCl_2(H_2O)_3]^0$ was reverted fromD_{3h}, to C_{3v}structure,which was in turn reverted along A_2 (water twisting mode) and E (skeletal deformation mode) to C_3 and C_s structure, respectively. C_3 structure was found to be unstable structure (one detached chloride ligand). C_s structure was stable, but contains imaginary A" mode (indicative of C_1 structure).$[PbCl_2(H_2O)_3]^0$ requires further desymmeterization.
$[PbCl_2(H_2O)_4]^0$ was reverted from D_{4h} #1 along A_{2g}, water wagging mode, to C_{4h}(not the lowest energy minima), along A_{2u} mode, skeletal deformation mode, to C_{4v}(not the lowest energy minima) and along B_{2u} mode, skeletal deformation mode, to D_{2d}(stable, but not absolute minima). D_{4h} #1 was reverted along E_g mode, water twisting mode, to C_s(containing imaginary frequencies). Hence, $[PbCl_2(H_2O)_4]^0$ complex needs to be further investigated.

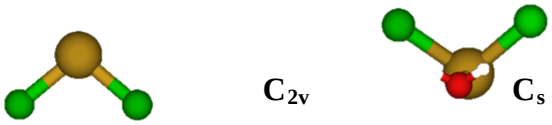

Figure 2 Optimized geometries for $[PbCl_2(H_2O)_n]^0$, n=0-1, pictures taken using MOLDEN [20]

3.3 Trichloroaqualead (II) Complexes, $[PbCl_3(H_2O)_n]^-$, where n=0-3.

The anhydrous $[PbCl_3]^-$was desymmetrized from D_{3h} structure along imaginary A" mode, skeletal deformation, to the most stable C_{3v} structure. $[PbCl_3(H_2O)_1]^-$was constrained to C_{2v} structure (two forms). Hence, C_{2v} #1 was reverted along B_1 and B_2 mode to C_s #1 and C_s #2. C_s #1 was found to be the most stable structure. $[PbCl_3(H_2O)_2]^-$was initially optimized at C_{2v} structure (two forms). Thus, C_{2v} #2 structure was reverted to C_s and C_2(both contained negative frequencies), suggesting furtherinvestigation. $[PbCl_3(H_2O)_3]^-$was initially optimized at 4 different forms of C_{2v} structures, which contained imaginary frequencies. Further desymmetrization of $[PbCl_3(H_2O)_3]^-$is necessary.

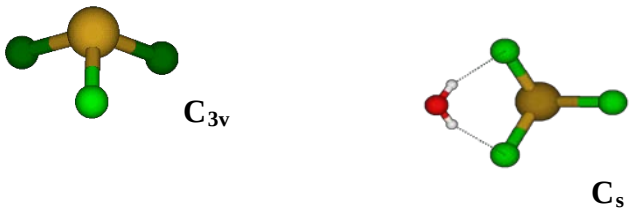

Figure 3 Optimized geometries for $[PbCl_3(H_2O)_n]^-$, n=0-1, pictures taken using MOLDEN [20]

3.4 Tetrachloroaqualead (II) Complexes, $[PbCl_4(H_2O)_n]^{2-}$, where n=0-2.

The anhydrous $[PbCl_4]^{2-}$was reverted from D_{4h} structure, along A_{2u} mode, skeletal deformation mode, to C_{4v} (contained imaginary frequencies) andalong B_{2u} mode, skeletal deformation, to the most stable D_{2d} structure. $[PbCl_4(H_2O)_1]^{2-}$was initially optimized to C_{2v} structure (2 forms), but contained imaginary frequencies suggesting further desymmetrization. $[PbCl_4(H_2O)_2]^{2-}$was initially constrained to D_{2h} structure (2 forms).The next step is to desymmeterizelower D_{2h} structure.

4. Conclusion

Comprehensive*ab initio* calculations were performed on chloroaqualead (II) complexes at HF, MP2 and B3LYP levels of theory coupled with CEP-121G, LANL2DZ, SDD basis sets for Pb and 6-31G*, 6-31+G*, 6-311+G* for H, O and Cl. This work provides foundation for future computational studies of possible SCWR corrosion products such as lead with hydroxide (OH^-) and ammonia (NH_3).

5. References

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