

## Dinuclear complexes of tetravalent cerium in an aqueous perchloric acid solution

Tetravalent cerium (Ce(IV)) is a widely known inorganic oxidizing agent, particularly in the field of organic synthesis [1]. More recently, Ce(IV) has attracted considerable attention as an electron sacrificial oxidant in studies of the photocatalytic oxidation of water to produce H<sub>2</sub> and O<sub>2</sub> for energy sources [2]. Since its compounds are commercially available and reasonably priced, a continuous demand for Ce(IV) is still anticipated in various basic and applied research fields.

For a powerful chemical reagent, Ce(IV) is often employed in the form of an aqueous solution, meaning that Ce(IV) species interact with the target substances to be oxidized or activated as aquo species. The nature of Ce(IV) aquo species is, however, far less well understood, as compared with that of trivalent cerium (Ce(III)). Several preceding studies have also implied the formation of soluble polymeric species with oxo- and/or OH-bridging, although their speciation and structure are not yet identified. Despite this finding, Ce(IV) aquo species in applied chemical and biochemical research are generally regarded as a monomeric species. Obviously, the chemical reactions

related to Ce(IV) species depend strongly on whether they exist only as monomeric species in the system, or if they form other polymeric species. For instance, the most plausible role of Ce(IV) aquo species in the photocatalytic oxidation of water is as a "single-electron" oxidant, which indirectly produces active metal oxo complexes through two-step single electron transfer reactions [2]. However, if Ce(IV) species interact with the targets as a dimer, the formation of the metal oxo complexes may take place via a one-step two-electron transfer event, or the bridging oxo/OH groups in the dimer may directly cause the introduction of oxo group into the target complexes. From these viewpoints, detailed characterization of Ce(IV) aquo species must be indispensable for elucidating the appropriate reaction schemes in which Ce(IV) species play an important role. Therefore, the EXAFS and DFT calculation studies for identifying the speciation and complex structure of Ce(IV) aquo species in an aqueous perchloric acid (HClO<sub>4</sub>) solution were performed [3]. The studies were carried out at **BL11XU**.

An X-ray absorption study of lanthanides is

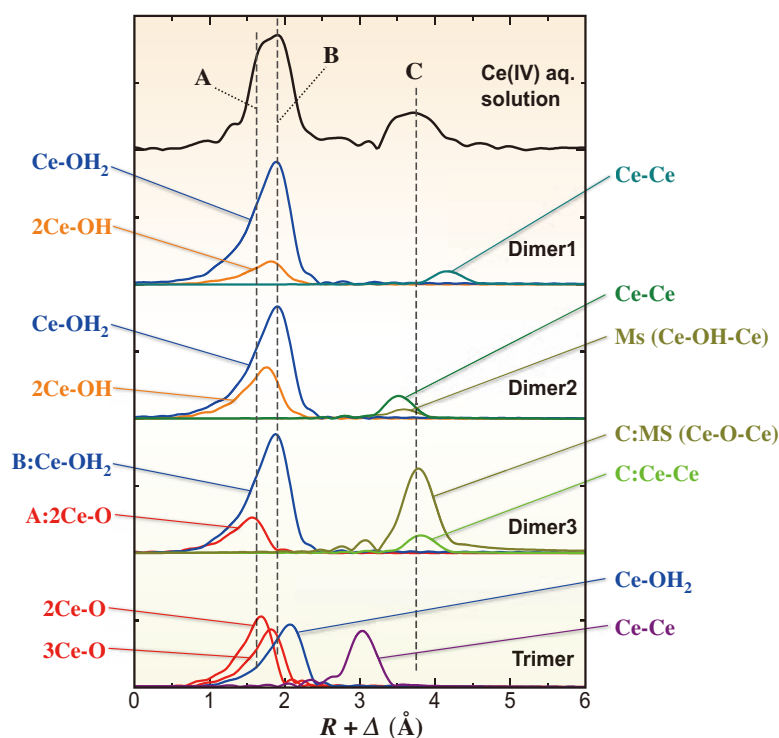


Fig. 1. Fourier transformed Ce *K*-edge EXAFS spectrum for Ce(IV) in 2 M HClO<sub>4</sub> (top, black) and the simulated spectra for the DFT-optimized complexes illustrated in Fig. 2 (colored data in the lower spectra). **A**, **B**, and **C** positions denote dominant components in the raw data (black spectrum in the first column), and those agreed well with three peaks of **Dimer 3**. The Ce concentration in the solution samples was 0.05 M. Each color was used only for distinction of each atomic distance in the same simulated spectrum. MS: multiple scattering derived from the Ce–OH–Ce arrangement.

generally performed at their  $L_{III}$ -edges (5–10 keV). However, the available range of their EXAFS spectra (in particular lighter lanthanides including Ce) is rather narrow. Furthermore, the spectra often suffer from the multi-electron excitation effect (MEE), which increases errors in determining coordination numbers and interatomic distances from EXAFS data [4]. To avoid the interference of MEE, we have collected the XAS spectra of our samples at the Ce  $K$ -edge (40.443 keV). This also enables us to obtain EXAFS spectra with a wider  $k$ -range, providing higher distance resolution on the data analysis for EXAFS. The EXAFS Fourier transform (FT) of the Ce(IV) aquo species (black spectrum in Fig. 1) exhibits two well-defined peaks at approximately  $R+\Delta = 1.8$  and 3.7. The first peak at  $R+\Delta = 1.8$  Å corresponds to the coordination of water molecules and possibly hydroxide ions. On the other hand, we can interpret the second peak at  $R+\Delta = 3.7$  Å as either the scattering from heavy atoms or the enhanced multiple scattering of linear coordinating ligands. Since perchlorate ions are highly unlikely to coordinate to Ce(IV), the second peak can be assigned to the scattering from distant Ce atoms. This clearly indicates the presence of polymeric Ce(IV) species in the present sample solution.

To probe the probable structural arrangement of polymeric Ce(IV) species, DFT geometry optimization was carried out for di- and trinuclear Ce(IV) complexes

in the aqueous phase. The geometry optimization was converged for three dinuclear and one trinuclear complexes, as shown in Fig. 2. The simulated EXAFS-FT spectra of these DFT-optimized complexes (colored spectra in Fig. 2; each color was used only for distinction of each atomic distance in the same simulated spectrum) indicate that the Ce–Ce peak for the **Trimer** appears at a much shorter  $R$ -range than the observed second peak at  $R+\Delta = 3.7$  Å, and its Ce–O( $H_2O$ ) peak also deviates from the observed first peak at  $R+\Delta = 2.0$  Å. Therefore, it is more reasonable to assign the peak at  $R+\Delta = 3.7$  Å to dinuclear complexes, rather than tri- or larger polymeric ones. On the basis of the detailed analysis of EXAFS data and the results of DFT calculation, we concluded that the “single oxo-bridging” dinuclear complex (**Dimer3**) is the most dominant form of the Ce(IV) species in the aqueous solution. The dinuclear complexes shown in Fig. 2 are energetically close to one another, implying that all of these species are potentially involved in the dimerization process of Ce(IV), although the final species is likely to settle into the “single oxo-bridging” structure. The bridging-oxo (and potentially OH) groups of the dinuclear complex are expected to be chemically active. Therefore, they possibly contribute to the remarkably high reactivity of Ce(IV) aqueous solution, in addition to its large reduction potential.

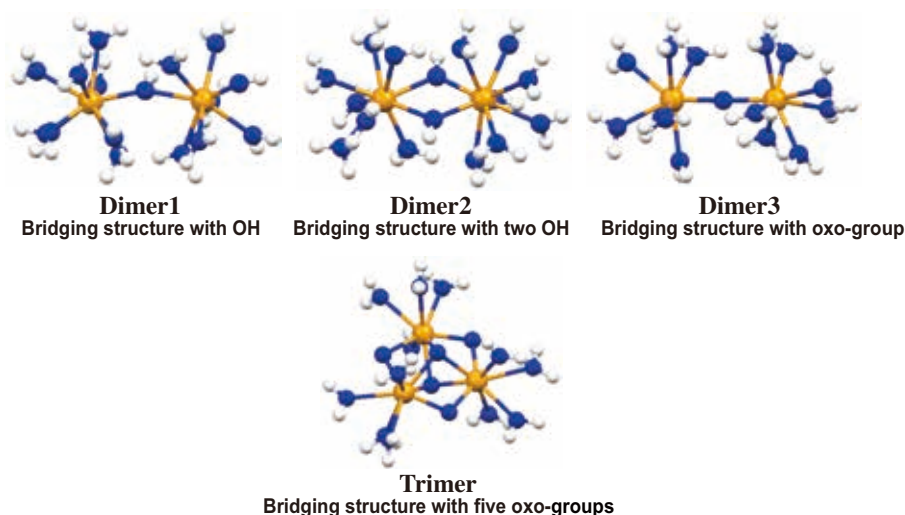


Fig. 2. Di- and tri-nuclear complex structures optimized using molecular orbital calculations based on the DFT theory (yellow: Ce(IV), blue: oxygen, white: hydrogen). **Dimer 3** is most probable.

Atsushi Ikeda-Ohno and Tsuyoshi Yaita\*

SPring-8/JAEA

\*Email: yaita@spring8.or.jp

#### References

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