

Change in the chemical state of [AuCl_{4-n}(OH)_n]⁻ complex ion (n=0-4) by the substitution of Cl⁻ with OH⁻

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The behavior of gold in natural water is of considerable interest in geochemistry. To elucidate the behavior of gold in natural water, some studies on the adsorption behavior of dissolved Au(III) complex ion on the surface of minerals have been conducted using [AuCl₄]⁻ complex ion as source of gold. The [AuCl₄]⁻ complex ion is stable under acidic condition and it hydrolyzes to [AuCl_{4-n}(OH)_n]⁻ as pH increases. In our previous study, it was found that Au(III) complex ion hardly adsorbs on alumina and goethite around pH 4, but adsorbs at higher pH 4. From this result, one of the driving force of the adsorption of Au(III) complex ion on minerals is considered to be the hydrolysis. However, it has still been uncertain why the adsorption of Au(III) complex ion on mineral is associated with the hydrolysis. The aim of this study is to calculate the chemical state of [AuCl_{4-n}(OH)_n]⁻ complex ion in each composition and discuss the above reason.

Based on the crystal structure of anhydrous potassium tetrachloroaurate, the structures of tetrachloroaurate ion and its hydrolytic species, [AuCl_{4-n}(OH)_n]⁻, were optimized by DFT calculation. Based on the optimization, the first principle MO calculation were performed using the relativistic DV-X α method developed by Rosen et al. and improved later by Adachi et al..

From the calculation result of the net charge, it is concluded that the ionic property of Au increases as hydrolysis proceeds. Especially, when [AuCl₄]⁻ transforms to [AuCl₃(OH)]⁻, the change in the net charge of Au is largest compared with those of other transformations. From the values of the bond overlap population, Au-Cl and Au-O interactions are concluded to be the single bond. Moreover, it was revealed that the electronic polarization of Au-O interaction is larger than that of Au-Cl interaction. Consequently, the adsorption of Au(III) complex ion on minerals may be driven by the relatively strong electronic polarization of the Au-O bond associated with hydrolysis.