

Research Group for Superheavy Elements

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The research objectives of this group are to understand chemical and nuclear properties of superheavy elements (SHEs) placed at the uppermost end of the Periodic Table and on the heaviest frontier of the nuclear chart. To clarify the chemical properties of SHEs, we investigate valence electronic structures of SHEs through experimental determinations of ionization potentials, redox potentials, and compound formations of SHEs. To elucidate the limits of stability of the heaviest nuclei, we investigate the shell structure of superheavy nuclei through experimental assignments of proton and neutron single-particle orbitals and through the evolution of nuclear deformation at the highest proton and neutron numbers.

Element 104, rutherfordium (Rf) is the first transactinoid element. From the simple extension of the Periodic Table of the Elements, Rf should belong to the group 4 transition metals. Although chemical properties of Rf are expected to be similar to those of lighter homologues Zr and Hf, some differences are found in HCl and HF solutions [1,2], which provides valuable information on the valence electronic structure of Rf.

Fluorido complex formation of Rf in HF/HNO₃ mixed solution [3]

In the present work, we have investigated the cation-exchange behavior of ²⁶¹Rf ($T_{1/2} = 78$ s) produced in the ²⁴⁸Cm(¹⁸O, 5n) reaction on a “one-atom-at-a-time” scale using an automated ion-exchange separation apparatus coupled with the detection system for alpha-spectroscopy (AIDA), together with its lighter group-4 homologs Zr and Hf, and the tetravalent pseudo-homolog Th in HF/HNO₃ mixed solution. The results demonstrate that distribution coefficients (K_d) of Rf in HF/0.10 M HNO₃ decrease with increasing concentration of the fluoride ion [F⁻] (Fig. 1). This resembles the behavior of the homologs, indicating the consecutive formation of fluorido complexes of Rf. We also measured the K_d values of Rf and the homologs as a function of the hydrogen ion concentration [H⁺] in the range of [F⁻] = 5.29×10^{-7} – 3.17×10^{-6} M. The $\log K_d$ values decrease linearly with an increase of $\log[H^+]$ with slopes between -2.1 and -2.5. This indicates that these elements are likely to form the same chemical compounds: mixture of [MF]³⁺ and [MF₂]²⁺ (M = Rf, Zr, Hf, and Th) in the studied solution. It is also ascertained that the fluorido complex formation of Rf is

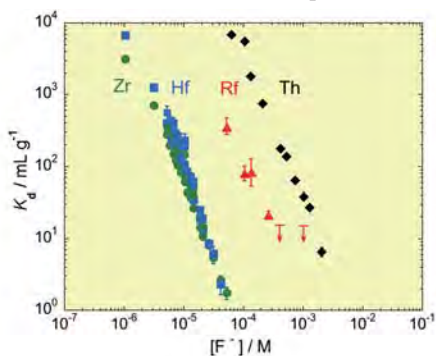


Fig. 1 Distribution coefficients, K_d , of Rf, Zr, Hf, and Th between a cation-exchange resin CK08Y and 0.10 M HNO₃ plotted as a function of [F⁻].

significantly weaker than that of Zr and Hf, but it is stronger than that of Th.

Sulfate complex formation of Rf in H₂SO₄/HNO₃ mixed solution [4]

The cation-exchange behavior of Rf was studied in 0.15–0.69 M H₂SO₄/HNO₃ mixed solutions ([H⁺] = 1.0 M) using AIDA. It was found that adsorption probabilities (%ads) of ²⁶¹Rf on cation-exchange resin decrease with an increase of [HSO₄⁻], showing a successive formation of Rf sulfate complexes. Rutherfordium exhibits a weaker complex formation tendency compared to the lighter homologues Zr and Hf. This is in good agreement with theoretical predictions including relativistic effects [5]. It was shown that the lower stability of the Rf complexes is due to the smaller ionic contribution to the chemical bond, which is caused by the relativistic stabilization of the 7s orbital, as well as the destabilization and spin-orbit splitting of the 6d orbitals. It is also in agreement with its larger ionic radius (76 pm) [6] in comparison with those of Zr (71 pm) and Hf (72 pm) [7]. We like to compare this results with our previous report for the complex formation with fluoride ions [2,3]. The trend of the fluoride complex formation in the group-4 elements is Zr = Hf > Rf > Th, being also in agreement with theoretical predictions [8]. The smaller ionic contribution to the metal–fluorine bonding was also responsible for the weaker fluoride complexation of Rf in comparison with that of Zr and Hf [8].

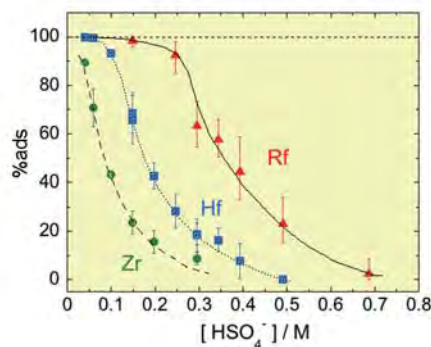


Fig. 2 Variations of adsorption probabilities, %ads, of Rf, Zr, and Hf on a cation-exchange resin CA08Y as a function of [HSO₄⁻] in the H₂SO₄/HNO₃ mixed solutions ([H⁺] = 1.0 M).

References

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