THE NEW VALUES OF IONIC RADII OF Rf^{4+}, Db^{5+} AND Sg^{6+}

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The knowledge of accurate values of ionic radii (IR) is necessary to determine such important thermodynamic functions of ions as enthalpy and entropy of hydration, standard electrode potentials, etc. Ionic radii are usually obtained from X-ray diffraction data for oxides or fluorides. Unfortunately, elements heavier than fermium are produced in non-weighable amounts, so that the experimental structural data for these elements are not available. Until now, experimental ionic radii of transactinides have not been reported. In order to plan experiments with transactinides and to interpret the results, accurate thermodynamic functions based on ionic radii have to be known. Some procedures make it possible to predict ionic radii of ions in cases where experimental measurements are difficult or impossible. Commonly used calculations of ionic radii based on the correlation between IR and the maximum radial charge density ($R_{max,nl}$) for the heaviest elements give overestimated values. The reason for this is the decreased electron charge density in the outermost p orbitals due to the significant splitting of p orbitals into $p_{1/2}$ and $p_{3/2}$. Electrons in the $p_{1/2}$ orbital are more strongly bonded than in the $p_{3/2}$ orbital and therefore R_{max} for $p_{1/2}$ is smaller than R_{max} for $p_{3/2}$. As a result the cloud of the p electrons is more diffuse and is shifted toward the nucleus. In particular, the electron charge density at $R_{max}p_{3/2}$ becomes smaller than at $R_{max}p$ in the absence of splitting, so that ligands can penetrate deeper into the outermost shell of the cation. As a result the metal-ligand distance decreases and the IR/R_{max} ratio for heavy cations becomes smaller than for their lighter analogs. Using a linear extrapolation procedure with $2j+1$ weighted expectation radii,

$$<\bar{r}_{np}> = \frac{4<r_{np3/2}> + 2<r_{np1/2}>}{6},$$

instead of $R_{max}np_{3/2}$, new values of IR for Rf^{4+}, Db^{5+} and Sg^{6+} were calculated. These IR values are 75 pm instead of 79 pm for Rf^{4+}, 67 pm instead of 74 pm for Db^{5+} and 64 pm for Sg^{6+}. Fig.
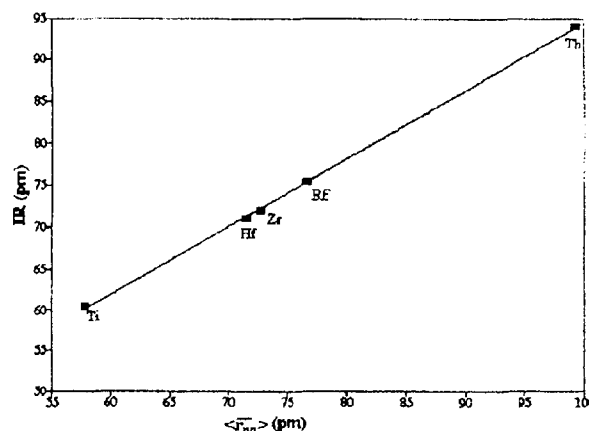

Fig. The ionic radius as a function of the $2j+1$ weighted expectation radius $<\bar{r}_{np}> = \dfrac{4<r_{np3/2}> + 2<r_{np1/2}>}{6}$ in group 4 cations.

presents, as an example, the dependence of IR on $<\bar{r}_{np}>$ for group 4 elements. Because the IR values of Rf^{4+} and Db^{5+} calculated in this work are almost the same as those of their congeners in rows 5 and 6, one can also expect the properties of ionic compounds e.g. oxides or fluorides to be very similar. However, there are experimental and calculation data [1, 2] showing that in some cases Rf^{4+} and Db^{5+} behave more like much larger pseudohomologous Th^{4+} and Pa^{5+} than their congeners in rows 5 and 6. This indicates that not only ionic radius is responsible for complexation and hydrolysis of transactinides. The promotion energy may also be an important factor.

References

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STEREOCHEMICAL CHARACTER OF s^2 LONE PAIR IN Bi^{3+} AQUA CATION

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The inert pair effect is characteristic for the p block elements. Lone electron pair can either be an s^2 pair or occupy one of the hybrid orbitals. In the case of Bi^{3+} the lone pair character depends on the ligand. In fluorides and oxides the lone pair is stereochemically inactive but in other complexes e.g. chlorides, bromides or tropolonates, the s^2 pair occupies the hybrid orbital [1]. According to Cotton and Wilkinson [2] there is no evidence for the existence of simple $[Bi(H_2O)_n]^{3+}$ ion. In aqueous perchlorate solutions, such species as $Bi_6O_6^{6+}$, $[Bi_6(OH)_{12}]^{6+}$ and $[Bi_6O_6(OH)_3]^{3+}$ are formed as a result of association and hydrolysis. However, Suganuma, Ono and Hataye [3] found only the mononuclear complexes $Bi(H_2O)_6^{3+}$ and $Bi(OH)_n(H_2O)_{6-n}^{(3-n)+}$ in aqueous solutions with ultratrace concentrations of Bi^{3+}. Radioisotope methods with ^{212}Bi, which have been applied in our studies, permit to study extremely diluted Bi^{3+} aqueous solutions at concentrations down to 10^{-15}-10^{-16} mol dm^{-3}. Under these conditions, the probability of collisions between Bi^{3+} ions is negligible, therefore, no polynuclear bismuth (III) ions are formed. The aim of our studies was to explain the character of $6s^2$ lone pair