Anionic Fluoro Complex of Element 105, Db

Yoshitaka Kasamatsu,*[1,2] Atsushi Toyoshima,[1] Masato Asai,[1] Kazuaki Tsukada,[1] Zijie Li,[1] Yasuo Ishii,[1] Hayato Toume,[1] Tetsuya K. Sato,[1] Takahiro Kikuchi,[1] Ichiro Nishinaka,[1] Yuichiro Nagame,[1] Hiromitsu Haba,[2] Hidetoshi Kikunaga,[2] Yuki Kudou,[2] Yasuji Oura,[3] Kazuhiko Akiyama,[3] Wataru Sato,[4] Kazuhiro Ooe,[4] Hiroyuki Fujisawa,[4] Atsushi Shinohara,[4] Shin-ichi Goto,[5] Taichi Hasegawa,[5] Hisaaki Kudo,[5] Tomohiro Nanri,[6] Mikio Araki,[6] Norikazu Kinoshita,[6] Akihiko Yokoyama,[7] Fangli Fan,[8] Zhi Qin,[8] Christoph E. Düllmann,[9] Matthias Schädel,[9] and Jens V. Kratz[10]

[1]*Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Naka-gun, Ibaraki 319-1195*

[2]*Nishina Center for Accelerator Based Science, RIKEN, Wako 351-0198*

[3]*Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397*

[4]*Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043*

[5]*Faculty of Science, Niigata University, Niigata 950-2181*

[6]*Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192*

[7]*Institute of Science and Engineering, Kanazawa University, Kanazawa 920-1192*

[8]*Institute of Modern Physics, Chinese Academy of Science, Lanzhou 730000, P. R. China*

[9]*GSI Helmholtzzentrum für Schwerionenforschung GmbH, D-64291 Darmstadt, Germany*

[10]*Institut für Kernchemie Universität Mainz, D-55099 Mainz, Germany*

(Received August 27, 2009; CL-090785; E-mail: kasamatsu@riken.jp)

We report on the characteristic anion-exchange behavior of the *superheavy* element dubnium (Db) with atomic number $Z = 105$ in HF/HNO_3 solution at the fluoride ion concentration $[F^-] = 0.003$ M. The result clearly demonstrates that the fluoro complex formation of Db is significantly different from that of the group-5 homologue Ta in the 6th period of the periodic table while the behavior of Db is similar to that of the lighter homologue Nb in the 5th period.

Transactinide elements (superheavy elements) with $Z \geq 104$ are produced at accelerators using heavy-ion-induced nuclear reactions. Because of their low production rates and short half-lives, chemical experiments with these elements must be performed on a one-atom-at-a-time scale. Thus, chemical characterization of these elements at the uppermost end of the periodic table is extremely challenging as well as fascinating.[1] In the past, the chemical behavior of Db, the group-5 element in the 7th period of the periodic table, in aqueous phases has been investigated using the nuclides ^{262}Db ($T_{1/2} = 34$ s) and ^{263}Db ($T_{1/2} = 27$ s) by comparison with each behavior of the lighter homologues, Nb and Ta, and also of the pentavalent pseudo-homologue Pa.[1,2] Little is, however, known about the chemical properties of Db because of the constraint of one-atom-at-a-time experiments.

In our previous work,[3] the anion-exchange behavior of Db in 13.9 M HF solution was studied with the rapid chemical separation apparatus AIDA with which the anion- and cation-exchange behavior of element 104 (Rf) in HF and HF/HNO_3 solutions was successfully investigated.[4–6] It was found that the distribution coefficient (K_d) of Db is smaller than those of Nb and Ta that presumably form $[MF_6]^-$ and/or $[MF_7]^{2-}$ (M = Nb and Ta) in 13.9 M HF. The behavior of Db was also compared with that of Pa for reference. While the K_d values of these anionic fluoro complexes on the resin decreases in the sequence of Ta $\approx$ Nb $>$ Db $\geq$ Pa, the chemical species of Db was not determined. In solutions with more dilute fluoride ion concentration $[F^-]$, Nb is known to form fluoro–oxo complexes, whereas Ta forms fluoro complexes.[7] In fact, we have ascertained the significantly different anion-exchange behavior between Nb and Ta in the HF/HNO_3 mixed solution ($[F^-] \leq 0.01$ M);[8] see Figure 1. It is, therefore, of great interest to explore how Db behaves in anion-exchange chromatography in the dilute $[F^-]$ solution. In this report, we present a successful measurement of the K_d value of Db in 0.31 M HF/0.10 M HNO_3 solution ($[F^-] = 0.003$ M), where Nb and Ta form $[NbOF_4]^-$ and $[TaF_6]^-$, respectively,[7,8] and briefly discuss the chemical form of Db.

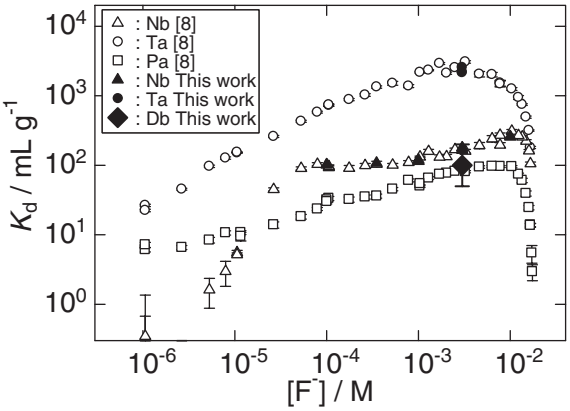

Figure 1. Distribution coefficients, K_d, of Nb, Ta, Pa, and Db on the anion-exchange resin in HF/0.1 M HNO_3 depending on the fluoride ion concentration.

Dubnium-262 was produced in the ^{248}Cm(^{19}F, 5*n*) reaction with a production rate of about 0.5 atoms per min at the JAEA tandem accelerator.[9] The beam energy ranged from 102.1 to 103.8 MeV in the ^{248}Cm target (1.4 mg cm^{-2}), and the average beam current was 440 particle nA. Reaction products recoiling out of the target were continuously transported by a He/KF gas-jet system from the target chamber to the collection site of the newly developed rapid ion-exchange apparatus located in the chemistry laboratory.[10] After collection for 83.4 s, the products were dissolved in 300 μL of 0.31 M HF/0.10 M HNO_3 and subsequently fed onto the microcolumn (1.0-mm i.d. × 3.5-mm long) filled with the anion-exchange resin MCI GEL CA08Y (particle size of 25 μm) at a flow rate of 1.2 mL min^{-1}. The elu-

ate was collected as Fraction 1 on a 15 × 300-mm tantalum sheet (0.15-mm thickness) which was continuously moving toward an α-particle detection chamber at 2.0 cm s^{-1}. The sample on the sheet was automatically evaporated to dryness with a halogen heat lamp and then subjected to the α-particle measurement for 75 s in the chamber equipped with an array of 12 silicon PIN photodiodes.[10] Remaining products on the resin were stripped with 290 μL of 0.015 M HF/6.0 M HNO_3. The eluate was collected on another Ta sheet as Fraction 2 followed by the same procedures for sample preparation and measurement. The α-particle measurement was started 14 and 38 s after the end of product collection for Fractions 1 and 2, respectively. The above procedure was repeated 1222 times. In the ^{248}Cm target, Gd (39%-enriched ^{152}Gd) was admixed to simultaneously produce ^{169}Ta through the Gd(^{19}F, *xn*) reactions. After the α-particle measurement, the samples on the sheets were assayed by γ-ray spectrometry with a Ge detector to monitor the transport efficiency of the gas-jet system and to determine the chemical yield and the adsorption behavior of ^{169}Ta. In separate experiments, the nuclides ^{90}Nb and ^{178m}Ta were produced in the Zr/Hf(*p*, *xn*) reactions, and ^{88}Nb and ^{170}Ta were produced in the Ge/Gd(^{19}F, *xn*) reactions. Then, the anion-exchange behavior of Nb and Ta was studied in the same way as that for Db. Elution curves of the nuclides were obtained by γ-ray spectrometry for eluate fractions.

α-Particle energies of ^{262}Db and its daughter nuclide ^{258}Lr ($T_{1/2} = 3.9$ s) are in the range from 8.3 to 8.7 MeV.[9] In this work, α events detected in the energy range of 8.1–8.7 MeV were assigned to the decays of ^{262}Db and ^{258}Lr taking into account the energy resolution of 60–150 keV in full width at half-maximum. A total of 26 α events were registered in this energy range. It should be noted that the α events in this range were almost free from interfering events originating from other products. After subtracting the background count rate of 7.5×10^{-7} counts/s for each detector, the number of α events ascribed to the decays of ^{262}Db and ^{258}Lr was 9.7 for Fraction 1 and 7.6 for Fraction 2. One time-correlated α particle pair of ^{262}Db and ^{258}Lr was also detected. The cross section of ^{262}Db was evaluated to be 1–2 nb from the α-decay events with a 30% detection efficiency, 60% chemical yield, α-decay branches of 64% for ^{262}Db and 100% for ^{258}Lr, and a 25% transport efficiency of the gas-jet system.[9] This value is in good agreement with our previously measured value of 1.5 ± 0.4 nb.[3,9]

The adsorption probability (*%ads*) of Db on the resin was determined to be 56^{+16}_{-13}% from the α-decay counts detected in both Fractions 1 and 2. The asymmetric error limits were evaluated from the counting statistics of the observed α events at the 68% confidence level for Poisson distributed variables.[11] The *%ads* values of Nb and Ta under the same conditions as for Db were evaluated from their elution curves to be 76 ± 2% and >99%, respectively. The K_d values of Nb and Ta were also determined from their elution curves,[4,5] and the values agree well with those from the previous batchwise experiment[8] as shown in Figure 1. This indicates that chemical equilibrium is reached in the fluoride complexation and ion-exchange process of these elements under the present conditions. The K_d value of Db plotted in Figure 1 was evaluated from its *%ads* in the same way as described in refs 4 and 5. It is found that the adsorption of Db on the resin is considerably weaker than that of Ta and is similar to that of Nb and also Pa. From the discussion on the fluoro complexes of the group-5 elements based on their K_d values,[8] the present result suggests that Db would form an fluoro–oxo complex $[DbOF_4]^-$ like Nb, but not $[DbF_6]^-$ like Ta. Note that the K_d value of Db is also close to that of Pa that forms $[PaOF_5]^{2-}$ and/or $[PaF_7]^{2-}$.[8,12,13] Formation of complexes with the −2 charge state such as $[DbOF_5]^{2-}$ and $[DbF_7]^{2-}$ could be suggested for Db. To unequivocally clarify the fluoride complexation of Db, further systematic study of Db as a function of $[F^-]$ and $[NO_3^-]$ is required.

References and Notes

1 M. Schädel, *Angew. Chem., Int. Ed.* **2006**, *45*, 368.
2 W. Paulus, J. V. Kratz, E. Strub, S. Zauner, W. Brüchle, V. Pershina, M. Schädel, B. Schausten, J. L. Adams, K. E. Gregorich, D. C. Hoffman, M. R. Lane, C. Laue, D. M. Lee, C. A. McGrath, D. K. Shaughnessy, D. A. Strellis, E. R. Sylwester, *Radiochim. Acta* **1999**, *84*, 69, and references therein.
3 K. Tsukada, H. Haba, M. Asai, A. Toyoshima, K. Akiyama, Y. Kasamatsu, I. Nishinaka, S. Ichikawa, K. Yasuda, Y. Miyamoto, K. Hashimoto, Y. Nagame, S. Goto, H. Kudo, W. Sato, A. Shinohara, Y. Oura, K. Sueki, H. Kikunaga, N. Kinoshita, A. Yokoyama, M. Schädel, W. Brüchle, J. V. Kratz, *Radiochim. Acta* **2009**, *97*, 83.
4 H. Haba, K. Tsukada, M. Asai, A. Toyoshima, K. Akiyama, I. Nishinaka, M. Hirata, T. Yaita, S. Ichikawa, Y. Nagame, K. Yasuda, Y. Miyamoto, T. Kaneko, S. Goto, S. Ono, T. Hirai, H. Kudo, M. Shigekawa, A. Shinohara, Y. Oura, H. Nakahara, K. Sueki, H. Kikunaga, N. Kinoshita, N. Tsuruga, A. Yokoyama, M. Sakama, S. Enomoto, M. Schädel, W. Brüchle, J. V. Kratz, *J. Am. Chem. Soc.* **2004**, *126*, 5219.
5 A. Toyoshima, H. Haba, K. Tsukada, M. Asai, K. Akiyama, S. Goto, Y. Ishii, I. Nishinaka, T. K. Sato, Y. Nagame, W. Sato, Y. Tani, H. Hasegawa, K. Matsuo, D. Saika, Y. Kitamoto, A. Shinohara, M. Ito, J. Saito, H. Kudo, A. Yokoyama, M. Sakama, K. Sueki, Y. Oura, H. Nakahara, M. Schädel, W. Brüchle, J. V. Kratz, *Radiochim. Acta* **2008**, *96*, 125.
6 Y. Ishii, A. Toyoshima, K. Tsukada, M. Asai, H. Toume, I. Nishinaka, Y. Nagame, S. Miyashita, T. Mori, H. Suganuma, H. Haba, M. Sakamaki, S. Goto, H. Kudo, K. Akiyama, Y. Oura, H. Nakahara, Y. Tashiro, A. Shinohara, M. Schädel, W. Brüchle, V. Pershina, J. V. Kratz, *Chem. Lett.* **2008**, *37*, 288.
7 O. L. Keller, A. Chethan-Strode, *Inorg. Chem.* **1966**, *5*, 367.
8 Y. Kasamatsu, A. Toyoshima, H. Haba, H. Toume, K. Tsukada, K. Akiyama, T. Yoshimura, Y. Nagame, *J. Radioanal. Nucl. Chem.* **2009**, *279*, 371, and references therein.
9 Y. Nagame, M. Asai, H. Haba, S. Goto, K. Tsukada, I. Nishinaka, K. Nishio, S. Ichikawa, A. Toyoshima, K. Akiyama, H. Nakahara, M. Sakama, M. Schädel, J. V. Kratz, H. W. Gäggeler, A. Türler, *J. Nucl. Radiochem. Sci.* **2002**, *3*, 85.
10 K. Tsukada, Y. Kasamatsu, M. Asai, A. Toyoshima, Y. Ishii, H. Toume, Y. Nagame, *JAEA-Rev. 2008-054* **2008**, p. 67.
11 W. Brüchle, *Radiochim. Acta* **2003**, *91*, 71.
12 *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed., ed. by L. R. Morss, N. M. Edelstein, J. Fuger, Springer, Dordrecht. **2006**, Vol. 1, Chap. 4, pp. 212–218.
13 M. V. Di Giandomenico, C. Le Naour, E. Simoni, D. Guillaumont, Ph. Moisy, C. Hennig, S. D. Conradson, C. Den Auwer, *Radiochim. Acta* **2009**, *97*, 347.

Published on the web (Advance View) October 17, 2009; doi:10.1246/cl.2009.1084