DOI: 10.1002/anie.200702872

Actinide Chemistry

Structure of the Homoleptic Thorium(IV) Aqua Ion $[Th(H_2O)_{10}]Br_4$**

*Richard E. Wilson, S. Skanthakumar, Peter C. Burns, and L. Soderholm**

Fundamental to the aqueous chemistry of an element is the structure of the solvated ion. The coordination number and bond lengths, together with ligand-exchange rates and mechanisms are necessary for a predictive and comprehensive understanding of chemical processes occurring in solution.[1] The structures of numerous di- and trivalent transition metals, metalloids, and lanthanide and actinide homoleptic aqua complexes have been elucidated by the isolation of their solid-state aqua salts using various sulfonate and bromate ligands.[2] The structural studies carried out on both the solid- and solution-state ions have resulted in a greater predictive ability and understanding regarding the forces governing ion solvation. Absent in this class of structures are any homoleptic aqua complexes of the tetravalent cations.

The inherent difficulty in isolating such structures stems from the Lewis acidity and hardness of these highly charged, small cations, which results in a propensity to inner-sphere anion coordination along with a tendency to undergo hydrolysis reactions. Thorium(IV) is the softest tetravalent ion that is stable in aqueous solution and therefore least susceptible to hydrolysis.[3] Guided by periodic trends in bonding and coordination, together with results from our earlier studies with actinide solution coordination and hydrolysis in nitrate and chloride media, we hypothesized that a softer anion, such as Br^-, would behave as a non-coordinating but stabilizing ion in aqueous solution.[4] A simple, monoatomic anion such as bromide is particularly attractive in such structural studies because it is easily represented in any complementary theoretical work.

Herein we report the structure of decaaquathorium(IV) bromide, $[Th(H_2O)_{10}]Br_4$ (Figure 1), isolated from a solution of Th^{IV} in concentrated hydrobromic acid. Crystal data reveal that the thorium ion is homoleptic and ten-coordinate; the first coordination sphere is occupied solely by water molecules.[5] The thorium atom resides on a special position with multiplicity of 2 and with 422 site symmetry (D_4 point symmetry). The first coordination shell has a bicapped square-antiprismatic geometry; eight water molecules give rise to a Th–O bond length of 2.492(3) Å and two marginally longer capping water molecules with Th–O bond lengths of 2.520(5) Å. The shorter Th–O bond corresponds to the eight prismatic oxygen atoms on the general site, and the two longer bonds from the capping oxygen atoms lie on a special position with fourfold rotational symmetry. As a consequence of the site symmetry for the capping oxygen atoms, the refined hydrogen positions reflect half occupancy. The

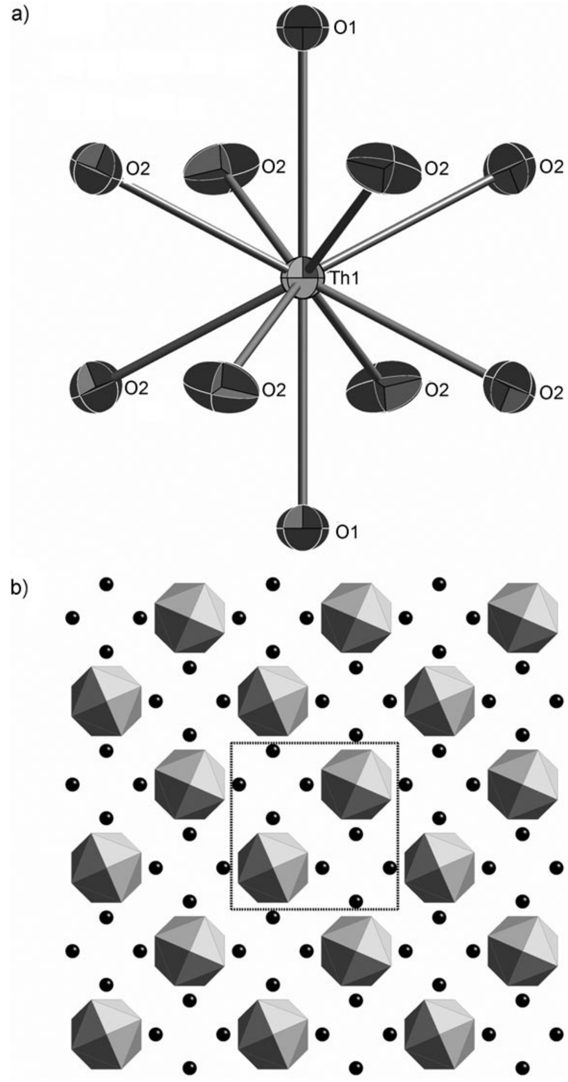

Figure 1. a) ORTEP of $[Th(H_2O)_{10}]Br_4$. Thermal ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. b) Crystal packing projected down the *c* axis. The thorium decaaqua moiety is shown as a polyhedron, and the bromide ions are black dots. The broken line indicates the unit cell.

---

[*] Dr. R. E. Wilson, Dr. S. Skanthakumar, Dr. L. Soderholm
Chemistry Division
Argonne National Laboratory
Argonne, IL 60439
Fax: (+1) 630-252-4225
E-mail: ls@anl.gov
Prof. P. C. Burns
Department of Civil Engineering and Geological Sciences
University of Notre Dame
Notre Dame, IN 46556

[**] Work at ANL was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under contract DE-AC02-06CH11357.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

charge-balancing bromide ions are located on a special position of eightfold multiplicity and twofold rotational symmetry. Significant hydrogen bonding between the bromide ion and the coordinated water exists, with six Br···H distances of 2.30–2.38 Å. Whereas high symmetry is exhibited by the water about the thorium atom, the water distribution about the Br^- ion is considerably asymmetric.

The water coordination number and geometry in the solid state is unequivocally demonstrated from the crystal data. However, this does not necessarily mean the same structure occurs with the dissolved thorium cation. X-ray absorption spectroscopy (XAS) studies of thorium aqua coordination in aqueous solutions have provided coordination numbers ranging from nine to twelve.[6] Wide-angle X-ray scattering experiments (WAXS) have determined a coordination number as low as eight, while semi-empirical and modern theoretical methods have suggested aqua coordination between nine and twelve.[7–9] Using the high-energy (92 keV) X-rays available at the Advanced Photon Source, Sector 11-ID-B,[10] we obtained scattering data from a dissolved sample of $[Th(H_2O)_{10}]Br_4$ in water. The advantages of using high-energy X-rays include a wider Q-space range available and lower absorption, which permits transmission experiments on aqueous solutions.[11] Thorium near-neighbor correlations are clearly visible from the pair-distribution function (PDF, Figure 2), which was obtained following a Fourier transform of scattering data after subtracting correlations not involving thorium.[12]

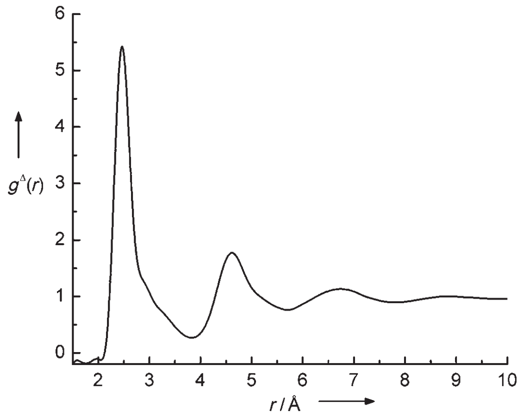

Figure 2. Pair-distribution function $g^A(r)$ for a 0.76 molal solution of $[Th(H_2O)_{10}]Br_4$.

There are three notable features in the PDF, the assignment of which are assisted by the structure of the solid-state sample. The first intense peak centered at 2.46(1) Å is attributed primarily to Th–O_{water} correlations. Also easily discernable are correlations at about 4.6 and 6.6 Å, which are assigned to thorium second- and third-coordination shells with water, as demonstrated in molecular dynamics simulations.[9]

Analysis of the peak at 2.46 Å establishes correlation of the thorium coordination in solution with that of the solid state. The distance for the Th–O_{water} bond in solution is slightly shorter than the average bond length of 2.498(4) Å found in the crystal structure. This slight contraction in solution versus solid-state distances is not uncommon and is not indicative of a change in coordination number.[12] A quantitative assessment of the coordination number can be made by integrating the scattering peak, the intensity of which is dependent upon the number of electrons contributing to the scattering pair. Integrating over the distance range of 2.16–3.22 Å determines that there are 101(3) electrons contributing to the peak. Thus, the 101(3) electrons correspond to 10.1(3) water molecules coordinating to thorium in the solution, which is consistent with the solid-state structure. From these data, we see no evidence for the inner-sphere coordination of bromide to thorium, though chloride inner-sphere coordination is known to occur.[7]

The high-energy X-ray scattering (HEXS) data from solution measurements confirm that the first coordination sphere of the homoleptic thorium aqua ion in the solid state is conserved upon dissolution in water. Although the agreement in coordination number is excellent, it is not possible to rule out an equilibrium in solution of 9-, 10-, and/or 11-coordinate thorium. Molecular dynamics simulations and quantum mechanical calculations presented by Tsushima et al.[8,9] find there to be only very small differences in energy between the 9-, 10-, and 12-coordinate structures. As can be seen in Figure 2, the HEXS data show strong thorium correlations in solution beyond the first coordination sphere, at 4.6 Å and 6.60 Å. The necessity of including such correlations in calculations of solute energetics has been clearly demonstrated, particularly when only small energy differences exist between different coordination environments.[13]

With the exception of the compound reported herein, the highest coordination number for homoleptic aqua complexes is nine, observed universally for the lanthanide ions in the solid state. Complex hydrates of thorium have been observed previously, such as the nine coordinate tricapped trigonal-prismatic heptaaqua complex $[ThCl_2(H_2O)_7]^{2+}$ and the ten-coordinate bicapped square-antiprismatic hexaaqua complex $[Th(SO_4)_2(H_2O)_6]\cdot 2H_2O$.[14] Additionally, several mono-, tri-, and tetraaqua complexes of U^{IV} are known, as well as a nine-coordinate octaaquabromouranium(IV) complex, $[UBr(H_2O)_8]Br_3\cdot H_2O$.[15] However, the homoleptic tenfold aqua coordination reported herein is unique among aqua-ion crystal structures. We have demonstrated that the tenfold coordination for the thorium aqua ion is common to both the solution and solid state, indicating its inherence to the chemistry of the thorium ion itself. Therefore, the magnitude and balance of the forces (such as ion–dipole, dipole–dipole, coulomb) thought to govern the coordination of the solvated ion must be quantified for a predictive and comprehensive understanding.

Refinement and development of theoretical models in concert with continued experimentation will provide valuable developments for increased predictive capability for metal-ion aqueous chemistry. To this end, further scattering experiments are underway to quantify the second-shell correlations of thorium in aqueous hydrobromic acid.

Experimental Section

Caution! ^{232}Th is an alpha-emitting radioisotope and as such is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials. The compound $[\mathrm{Th(H_2O)_{10}}]\mathrm{Br_4}$ (**1**) was synthesized by the dissolution of $^{232}\mathrm{Th(NO_3)_4}{\cdot}x\,\mathrm{H_2O}$ (1 g) in water followed by precipitation with aqueous ammonia, and then washing of the precipitate with water until the supernatant was neutral. The precipitate was dissolved in concentrated HBr (5 mL). Reducing the solution volume to 1 mL by boiling produced crystals of **1** upon cooling the solution. The crystals were collected by filtration and dried in air. An FT-IR spectrum of **1** is available in the Supporting Information.

For HEXS experiments, compound **1** (278 mg) was dissolved in water (0.5 g) and placed in a Kapton capillary and further contained, as required for actinide samples. Scattering data were collected at the Advanced Photon Source, Argonne National Laboratory, on wiggler beamline 11-ID-B, BESSRC. Scattered intensity was collected at two detector distances, corresponding to $Q_{\max} = 15$ Å^{-1} and 35 Å^{-1} using an amorphous silicon flat-panel X-ray detector (GE Healthcare). Final data treatment reflects a merging of these two data sets followed by treatment described previously.[16]

Received: June 28, 2007

Keywords: actinides · coordination modes · hydrates · thorium · X-ray diffraction

---

[1] Y. Marcus, *Ion Solvation*, Wiley, New York, **1985**.

[2] A. Chatterjee, E. N. Maslen, K. J. Watson, *Acta Crystallogr. Sect. B* **1988**, *44*, 381.

[3] Based on Shannon ionic radii, Th$^{\mathrm{IV}}$ is the largest tetravalent ion in the Periodic Table. R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751.

[4] R. E. Wilson, S. Skanthkumar, G. Sigmon, P. C. Burns, L. Soderholm, *Inorg. Chem.* **2007**, *46*, 2368.

[5] Crystal Data: $[\mathrm{Th(H_2O)_{10}}]\mathrm{Br_4}$, $M_r = 731.84$ g mol^{-1}, crystal size $= 0.20 \times 0.05 \times 0.05$ mm^3, tetragonal, $P4/nnc$, $a = b = 9.800(1)$, $c = 8.377(1)$ Å, $\alpha = \beta = \gamma = 90.00°$, $Z = 2$, ρcalcd $= 3.021$ g cm^{-3}, $\mu = 19.223$ mm^{-1}, Mo$_{\mathrm{K}\alpha}$ 0.71073 Å, $T = 298$ K, 2Θmax $= 33.07°$, measured reflections 11957, independent reflections 752, $R_{\mathrm{int}} = 0.0957$, $R = 0.0209$ $wR2 = 0.0540$ ($I > 2\sigma I$), GOOF $= 0.986$, residual density (max/min) 2.906/−0.985. Data were collected on a Bruker APEX II diffractometer. A semi-empirical correction for absorption was carried out using the program XPREP with the crystal modeled as an ellipsoid. The thorium atom was identified by direct methods and the structure refined by subsequent full-matrix least-squares refinement on F^2. Hydrogen atoms were identified in the difference Fourier and refined isotropically using a constrained distance of 0.98 Å from the parent oxygen atom. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-418199.

[6] H. Moll, M. A. Denecke, F. Jalilehvand, M. Sandstrom, I. Grenthe, *Inorg. Chem.* **1999**, *38*, 1795; V. Neck, R. Muller, M. Bouby, M. Altmaier, J. Rothe, M. A. Denecke, J. I. Kim, *Radiochim. Acta* **2002**, *90*, 485; J. Rothe, M. A. Denecke, V. Neck, R. Mueller, J. I. Kim, *Inorg. Chem.* **2002**, *41*, 249.

[7] G. Johansson, M. Magini, H. Ohtaki, *J. Solution Chem.* **1991**, *20*, 775.

[8] S. Tsushima, T. X. Yang, Y. Mochizuki, Y. Okamoto, *Chem. Phys. Lett.* **2003**, *375*, 204; T. X. Yang, S. Tsushima, A. Suzuki, *J. Phys. Chem. A* **2001**, *105*, 10439; T. X. Yang, S. Tsushima, A. Suzuki, *J. Solid State Chem.* **2003**, *171*, 235.

[9] T. X. Yang, S. Tsushima, A. Suzuki, *Chem. Phys. Lett.* **2002**, *360*, 534.

[10] M. A. Beno, C. Kurtz, A. Munkholm, U. Rutt, M. Engbretson, G. Jennings, J. Linton, G. S. Knapp, P. A. Montano, *Nucl. Instrum. Methods Phys. Res. Sect. A* **2001**, *467*, 694.

[11] L. Soderholm, S. Skanthakumar, J. Neuefeind, *Anal. Bioanal. Chem.* **2005**, *383*, 48.

[12] S. Skanthakumar, M. R. Antonio, R. E. Wilson, L. Soderholm, *Inorg. Chem.* **2007**, *46*, 3485.

[13] K. E. Gutowski, D. A. Dixon, *J. Phys. Chem. A* **2006**, *110*, 8840.

[14] J. Habash, A. J. Smith, *Acta Crystallogr. Sect. C* **1983**, *39*, 413; R. D. Rogers, *Lanthanide Actinide Res.* **1989**, *3*, 71.

[15] D. Rabinovich, G. L. Schimek, W. T. Pennington, J. B. Nielsen, K. D. Abney, *Acta Crystallogr. Sect. C* **1998**, *54*, 1740.

[16] S. Skanthakumar, L. Soderholm, *Mater. Res. Soc. Symp. Proc.* **2006**, *893*, 411.