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A Coordination Chemistry Study of Solvated Thorium(IV) Ions in Two Oxygen-Donor Solvents

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The structures of the dimethyl sulfoxide (dmso) and *N*,*N*′-dimethylpropyleneurea (dmpu) solvated thorium(IV) ions have been studied in solution by extended X-ray absorption fine structure (EXAFS), and the structure of the solid oxonium bis[nonakis(κ*O*-dimethyl sulfoxide)]thorium(IV) trifluoromethanesulfonate dihydrate, $(H_3O)[Th((CH_3)_2SO)_9]_2(CF_3SO_3)_9{\cdot}2H_2O$ (**1**) has been determined by single-crystal X-ray diffraction and EXAFS. Compound **1** was crystallized by evaporating a saturated dmso solution. It consists of two individual nonakis(κ*O*-dimethyl sulfoxide)thorium(IV) units, both of which have a tricapped trigonal prismatic configuration, as also found in nonakis(dimethyl sulfoxide)thorium(IV) perchlorate previously reported. Mean Th–O bond lengths of 2.47 and 2.43 Å are found for the two structural units, respectively, for which the differences may be explained by differences in occupancy and temperature factors. The EXAFS data of **1** revealed mean Th–O and S–O bond lengths of 2.449(3) and 1.525(3) Å, respectively, and a Th–O–S bond angle of 135.2(5)° to give a Th···S distance of 3.665(7) Å. In dmso solution, the mean Th–O and S–O bond lengths are 2.447(3) and 1.534(3) Å, respectively, the Th–O–S bond angle is 133.5(5)°, and there is a Th···S distance of 3.672(7) Å. The Th–O bond-length distribution is somewhat asymmetric in both samples with $R_{\max}$ values of 2.424 and 2.422 Å for **1** and solution, respectively. In dmpu solution, the Th–O and C–O bond lengths are 2.404(5) and 1.264(2) Å, respectively, and there is a Th–O–C angle of 157.1(5)° to give a Th···C distance of 3.594(7) Å. The observed Th–O bond length indicates strongly that thorium(IV) is eight-coordinate in dmpu.

Introduction

The physicochemical properties and the spatial demands on coordination of solvents play an important role in the chemistry of metal ions in solution.[1–3] The properties and characteristics exhibited, such as reactivity, color, and complex formation ability sometimes vary profoundly depending on the solvent used.[4–9] Dimethyl sulfoxide (dmso) is an important polar aprotic solvent that dissolves both polar and nonpolar compounds well and is fully miscible with water as well as many organic solvents.[10] It is also capable of solvating both soft and hard metal ions well, thereby making dmso frequently used as solvent or cosolvent for chemical reactions that involving metal salts as, for example, Finkelstein reactions and nucleophilic substitutions.[11] Hard metal ions coordinate dmso through the oxygen atom, whereas much softer metal ions such as the platinum group metals may coordinate dmso either through sulfur or oxygen in the same solvate complex.[12] Transfer thermodynamics show that dmso solvates hard metal ions stronger than water does.[13] Crystalline compounds with dmso-solvated metal ions are frequently used as precursors in nonaqueous inorganic synthesis.[14,15]

N,*N*′-Dimethylpropyleneurea (dmpu) is a versatile solvent and cosolvent for syntheses of pharmaceuticals, agrochemical materials, dyes, and polymers.[16,17] It has high thermal and chemical stability under both acidic and alkaline conditions, high dielectric constant, high dipole moment, and low toxicity (Table 1).[18] As a space-demanding ligand upon coordination, dmpu often causes metal ions to attain a lower coordination number (CN) in comparison to the corresponding hydrates and dmso solvates.[19–26]

Table 1. Selected physicochemical properties of solvents discussed in the study.

Solvent	Sum formula	Donor atom	Melting point [°C]	Boiling point [°C]	D_s[a]	ε_r[b]	μ [D]
water	H_2O	O	0.0	100	17.0	78.5	1.85
dmpu	$C_6H_{12}N_2O$	O	–23.8	246	34.0	36.1	4.23
dmso	C_2H_6SO	O or S	18.5	189	27.5	48.0	3.96

[a] Donor strength (D_s) is a more complete quantitative measure of Lewis basicity (see ref.[3]). [b] The permittivity (ε_r) is relative to that of vacuum, $\varepsilon_0 \approx 8.854 \times 10^{-12}$ F m^{-1}.

The metal–oxygen bond lengths in seventy-six structures of actinoid(IV) ions with organic ligands [out of 142 with any oxygen-donor ligand (Table 2) including homoleptic solvates of thorium(IV), uranium(IV), and neptunium(IV)] have been summarized recently.[27] The homoleptic dmso-

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solvated uranium(IV) ion is reported to be eight- or nine-coordinate depending on preparation route,[28] whereas neptunium(VI) (NpO_2^{2+}) and uranium(VI) (UO_2^{2+}) binds four or five dmso molecules in a plane perpendicular to the oxo groups.[29–31] Hydrated thorium(IV) predominates in strongly acidic aqueous solution, with hydrolysis occurring as pH increases.[27] Thorium(IV) is nine-coordinate in solid nonakis(κ*O*-dimethyl sulfoxide)thorium(IV) perchlorate, $[Th(dmso)_9](ClO_4)_4$, in which nine dmso oxygen atoms form a distorted tricapped trigonal prism with a mean Th–O bond length of 2.455 Å.[32] A nine-coordinate thorium solvate with eight dmso molecules and one chloride ion has been reported as well.[33] Thorium(IV) chloride does not dissociate in diphenyl sulfoxide and precipitates as tetrachlorotetrakis(diphenyl sulfoxide)thorium(IV) $[ThCl_4(OS–(C_6H_5)_2)_4]$, molecules.[34] The structures of two dmso-solvated uranium(IV) chloride complexes are reported, one with six dmso molecules and two chloride ions coordinated, and the other with seven dmso molecules and one chloride atom coordinated with a total CN of eight,[35,36] whereas dioxouranium(VI) is solvated either by four or five dmso molecules.[29,30]

Table 2. The mean An^{IV}–O bond lengths for complexes and salts with mono- and bidentate neutral and anionic oxygen-donor ligands and their respective coordination number (CN). The number of structures obtained from the literature for each actinoid ion and coordination number is given within the curly brackets. Full references are listed for each element in Tables S4–S7 in the literature.[27]

CN	*d*(Th–O) [Å]	*d*(U–O) [Å]	*d*(Np–O) [Å]	*d*(Pu–O) [Å]
6	2.301 {2}	2.277 {2}	n/a	n/a
7	2.357 {1}	n/a	n/a	n/a
8	2.415 {25}	2.363 {18}	2.338 {7}	2.329 {7}
9	2.451{20}	2.409 {3}	2.403 {2}	2.386 {1}
10	2.504 {21}	2.456 {7}	2.454 {1}	2.429 {1}
11	2.537 {3}	n/a	n/a	n/a
12	2.581 {15}	2.510 {3}	2.504 {2}	2.484 {1}

Two other tetravalent metal ions, zirconium(IV) and hafnium(IV), are eight-coordinate in acidic aqueous and dimethyl sulfoxide solution with square antiprismatic configuration, both in the solid state and solution.[37] Hafnium(IV) chloride does not dissociate in *N*,*N′*-dimethylpropyleneurea, likely due to lower permittivity of dmpu in comparison to dmso; an octahedral $[HfCl_4(dmpu)_2]$ complex is formed.[37]

The aim of this study was to determine the structures of dmso- and dmpu-solvated thorium(IV) in solution and the solid state by using extended X-ray absorption fine structure (EXAFS) and crystallography. This study is a continuation of our previous study of the coordination chemistry of thorium(IV) in aqueous media.[27]

Results and Discussion

Crystal Structure of $(H_3O)[Th\{(CH_3)_2SO\}_9]_2(CF_3SO_3)_9\cdot 2H_2O$ (1)

The crystal structure of **1** was solved and refined in the monoclinic space group *P*2$_1$ (no. 4) (Table 3). It consists of two crystallographically independent nonakis(κ-*O*-dimethyl sulfoxide)thorium(IV) structural units with a tricapped trigonal prismatic configuration, *ttp* (Figure 1 and Figures S1–S3 in the Supporting Information). In addition to the nine crystallographically independent trifluoromethanesulfonate anions found in the unit cell, three water molecules (oxygen atoms) are present; one of them, likely O200, is required to be protonated for charge neutrality. One additional oxygen may be present in a fourth void (approx. 121 Å^3) in the unit cell; however, no stable refinement was possible for such an oxygen in this position.

Table 3. Selected crystal data and structure refinement details for **1**.

	1
Formula	$C_{45}H_{115}F_{27}O_{48}S_{27}Th_2$
M_r [amu]	3267.34
Crystal size [mm]	0.25 (min.); 0.35 (max.)
Crystal system	monoclinic
Space group	*P*2$_1$
Z	2
a [Å]	11.899(2)
b [Å]	43.531(6)
c [Å]	12.534(2)
β [°]	90.882(2)
V_{cell} [Å^3]	6491.8(15)
h, *k*, *l*	–12 to 13, –51 to 51, –14 to 14
T [K]	296(2)
F(000)	1740
θ range [°]	2.42–24.88
Max./min. transmission	0.7455/0.4327
Number of reflections	34455
Unique reflections/[$I > 2\sigma(I)$]	21561/19116
R_1, wR_2 [$I > 2\sigma(I)$]	0.0629/0.1451
R_1, wR_2 [all data]	0.0721/0.1494
Goodness of fit	1.099
Number of parameters/restraints	1390/364
Residual electron density [e Å^{-3}]	1.443/–2.921

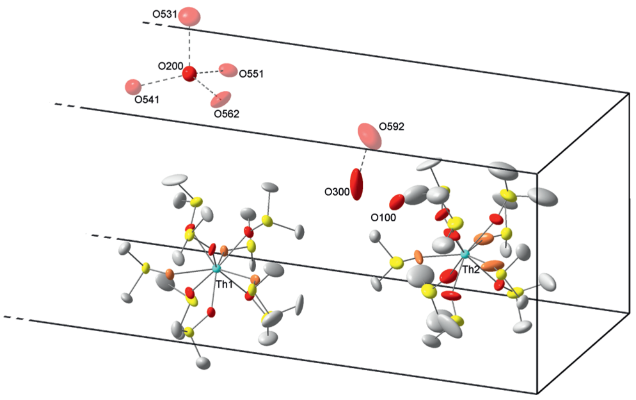

Figure 1. Representation of the crystallographically independent atoms in **1**, in which the dmso oxygen atoms in capping positions are orange. The trifluoromethanesulfonate counterions, alternate position sulfur atoms on Th2, and hydrogen atoms have been removed for clarity. However, the counterion oxygen atoms within 3 Å of the water oxygens are included (shaded) in an attempt to indicate possible hydrogen-bonding capabilities; see Figure S1 in the Supporting Information. The thermal ellipsoids are set at 30% probability.

The mean Th1–O_{dmso} bond length is 2.47 Å, with the three capping dmso molecules bound at longer mean bond length relative to the prismatic ones, 2.498 and 2.455 Å, respectively. The mean Th2–O_{dmso} bond length is 2.43 Å after riding motion correction, with mean distances for the capping and prismatic positions of 2.455 and 2.415 Å, respectively. The oxygen atomic positions around Th1 have normal temperature thermal ellipsoids, whereas those around Th2 are unusually large and cause a much larger uncertainty in distances and angles (Figure S3 in the Supporting Information). Refinements with alternate positions of the Th2 oxygen atoms were attempted but unsuccessful. The short distances are most likely an effect of the highly irregular ellipsoids, and more appropriate values can be obtained through a geometrical correction on the crystallographic end result; once applied, as expected, the mean capping value surpasses the corresponding mean prism value and is in better agreement with that for Th1 (Table S1 and Figure S4).

The sulfur atoms in the dmso ligands bound to Th2 were refined with alternative positions with occupancy factors around 50 %, which could contribute to less well-defined positions for the entire dmso molecule.[25] Additional interference from the presence of the highly absorbing thorium atoms also makes it more difficult to refine the positions of the lighter atoms. The possibility of incorrect space-group assignment may be yet another factor to consider, but if this is the case, the data quality is too low to allow for a stable refinement in a space group of a lower symmetry. It is common that nine-coordinate actinoid ions bind capping ligands at slightly longer bond length,[27,32,38] as also observed in **1**, and we believe that there should be no doubt that thorium(IV) in fact is nine-coordinate in the crystalline state.

EXAFS Study of 1

The Th–O and S–O bond lengths in **1** were refined to 2.449(3) and 1.525(2) Å, and the Th–O–S angle to 135.2(5)°, thus giving a Th···S distance of 3.665(7) Å (Figure 2 and Table 4). The structure parameters are in good agreement with those of **1** (2.45 Å) and $[Th(dmso)_9](ClO_4)_4$ (2.455 Å). As EXAFS is a non-lattice-dependent method, the results from the EXAFS study independently support the results from the crystallographic investigation.

Dimethyl Sulfoxide and *N*,*N*′-Dimethylpropyleneurea Solvated Thorium(IV) Ions in Solution

Refinements of the EXAFS study of the dmso-solvated thorium(IV) ion gave mean Th–O and S–O bond lengths of 2.447(3) and 1.534(2) Å, respectively, and a Th–O–S bond angle of 133.5(5)°, thereby giving a Th···S distance of 3.672(7) Å (Table 4 and Figure 2), which is in close agreement with the structure of **1**. The M–O–S angle can be used as an indicator of whether the electron-pair acceptor has soft or hard binding properties.[25,26,39,40] The Th–O–S angle of around 134° indicates that thorium(IV) is a hard electron-pair acceptor with similar binding properties to the lanthanoids (e.g., the La–O–S angle is 135° in dmso solution).[41] The Th–O distance has a significant distribution asymmetry, which strongly supports the notion that the bond length to the capping positions is longer than to the prismatic ones as also found in the solid state (Table 4 and

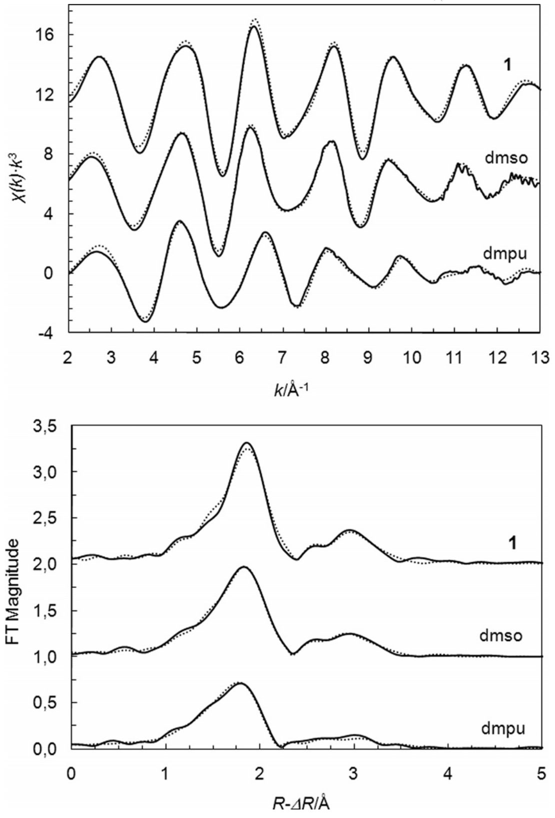

Figure 2. (a) Fit of EXAFS data and (b) its respective Fourier transform for **1**, and the dmso and dmpu solutions (dotted line: model, black line: experimental data).

Table 4. Mean bond lengths, *d* [Å], number of distances, *N*, and Debye–Waller coefficients, σ^2 [Å^2], and the third cumulant factor, C_3 [Å^3], $C_3 = \beta\cdot\sigma^3$, in the EXAFS studies of the dmso- and dmpu-solvated thorium(IV) ions in solution, respectively, and of **1** at room temperature.

Sample	Parameter	N	d/R_m [angle in °]	σ^2	C_3
1	Th–O	9	2.449(3)/2.424	0.0089(3)	3.0×10^{-4}
	S–O	9	1.525(2)	0.0012(2)	0
	∠Th–O–S	9	135.2(5)		
	Th···S[a]	9	3.665(7)	0.0120(5)	0
dmso	Th–O	9	2.447(3)/2.422	0.0078(3)	4.9×10^{-4}
	S–O	9	1.534(2)	0.0023(2)	0
	∠Th–O–S	9	133.5(5)		
	Th···S[a]	9	3.672(7)	0.0120(5)	0
dmpu	Th–O	8	2.404(3)/2.374	0.0077(3)	1.8×10^{-4}
	C–O	8	1.264(2)	0.0041(2)	0
	∠Th–O–C	8	157.1(5)		
	Th···C[a]	8	3.594(7)	0.0050(5)	0

[a] Calculated from the refined parameters.

the literature[31]), but the difference is too small to be refined from the present data. The obtained mean Th–O bond length, 2.447 Å, fits very well within the range expected for nine-coordination (Figures 3 and 4).

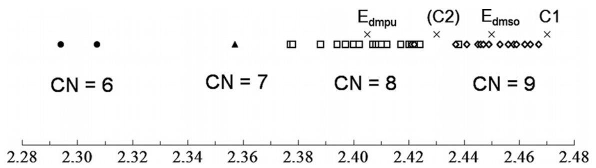

Figure 3. Overview of the previously reported Th^{IV}–O bond lengths and their corresponding coordination numbers in oxygen-donor ligands as reported in the literature[27]; ● CN = 6, ▲ CN = 7, □ CN = 8, ◇ CN = 9, × the data obtained in that study. C1 shows the mean Th–O bond length for Th1 in **1** (proper value), whereas (C2) shows the mean Th–O bond length for Th2 in **1** (with geometric correction applied). E_{dmso} and E_{dmpu} are the Th–O bond lengths obtained by EXAFS for solvated thorium(IV) in dmso solution and solid, and dmpu solution, respectively.

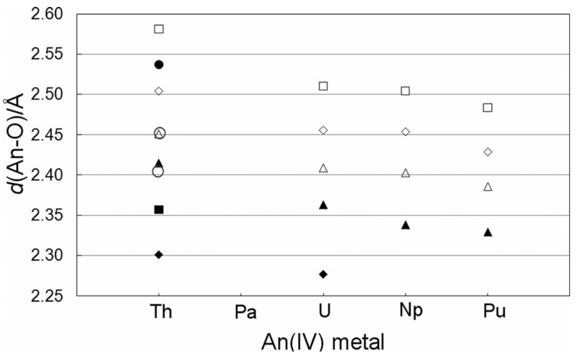

Figure 4. Overview of the An^{IV}–O bond lengths and their corresponding coordination numbers from crystallographic data of oxygen-donor ligands (Tables S4–S7 in the literature[27]); ♦ CN = 6, ■ CN = 7, ▲ CN = 8, Δ CN = 9, ◇ CN = 10, ● CN = 11, □ CN = 12) ○ EXAFS Th–O bond length in this work.

The EXAFS study of the dmpu-solvated thorium(IV) ion revealed mean Th–O and C–O bond lengths of 2.404(3) and 1.264(2) Å, respectively, and a Th–O–C bond angle of 157.1(5)°, thereby giving a Th···C distance of 2.594(7) Å (Figure 2 and Table 4). The obtained mean Th–O bond length (2.404 Å) fits very well within the range expected for eight-coordination (Figures 3 and 4). The large Th–O–C bond angle, 157°, is similar to those observed in the dmpu-solvated lanthanoid(III) ions (158–165°).[43] It is apparent that the coordination of such space-demanding ligands as dmpu causes a decrease in CN; the same trend is observed in dmpu-solvated lanthanoid(III) ions.[42] The higher coordination number for thorium(IV) relative to lighter lanthanoid(III) ions with larger ionic radii than thorium(IV) in dmpu solution is probably caused by the higher charge and thereby stronger M–O bonds. The actual configuration in solution, without a crystal structure to compare with, is difficult to determine, but a square antiprismatic configuration is by far the most common for eight-coordinate complexes and is most likely present also here. Our attempts to crystallize dmpu-solvated thorium(IV) failed.

Conclusion

The dmso-solvated thorium(IV) ion is nine-coordinate in both solution and the solid state with mean Th–O bond lengths of 2.45 Å. The dmso-solvated lanthanoid(III) ions are eight-coordinate.[19] The lower charge of lanthanoid(III) ions relative to actinoid(IV) ions results in lower charge density, which seems to be the reason for higher CN, even though the An–O bond length in the dmso-solvated actinoid(IV) ions is shorter than for the lanthanoid(III) ions.

The dmpu-solvated thorium(IV) is eight-coordinate in solution, with a mean Th–O bond length of 2.40 Å. The lower CN in dmpu solvate is caused by space-demanding properties upon coordination of the dmpu molecule.

Experimental Section

Chemicals: $[Th(H_2O)_6(OSO_2CF_3)_3][Th(H_2O)_3(OSO_2CF_3)_6]$ was prepared in the same way as described in ref.[27] Dimethyl sulfoxide (Merck) and *N*,*N'*-dimethylpropyleneurea (Aldrich) were distilled under reduced pressure over calcium hydride (Merck) at $T < 400$ K before use.

Preparation of Solutions: Thorium dmso- and dmpu-solvated complexes were obtained by dropwise addition of dmso or dmpu into $[Th(H_2O)_6(OSO_2CF_3)_3][Th(H_2O)_3(OSO_2CF_3)_6]$ at around 100 °C, which resulted in a yellow dmso solution (**A**), and a pink dmpu solution (**B**), followed by slow cooling to room temperature (approx. $C_{Th} = 0.1$ mol dm^{-3}).

Preparation of Salts: $[Th(H_2O)_6(OSO_2CF_3)_3][Th(H_2O)_3(OSO_2CF_3)_6]$ was dissolved to saturation in freshly distilled dimethyl sulfoxide at 313 K. Slow cooling to room temperature allowed solid **1** to precipitate as pale yellow crystals.

Caution! Thorium-232 used in the study is radioactive, and has a specific activity of 4.06 MBq kg^{-1} with a half-life through α decay of 1.41×10^{10} years. Its daughters, radium-228 and thorium-228, are strong β and γ emitters![43]

EXAFS Data Collection: EXAFS measurements of the solutions **A** and **B**, and the solid **1** were performed at the thorium L_3 X-ray absorption edge. The data were collected at the bending magnet beamline 2–3 at the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA, which operated at 3.0 GeV and a maximum current of 100 mA. The EXAFS station was equipped with an Si[220] double-crystal monochromator. Higher-order harmonics were reduced by detuning the second monochromator crystal to reflect 60% of maximum intensity at the end of the scans. Solid $[Th(H_2O)_8(ClO_4)](ClO_4)_3 \cdot H_2O$ diluted with BN was used as reference, and the energy of the first inflection point on the edge was set to 16309 eV.[44] All measurements were performed in transmission mode. For each sample, 3 to 4 scans were averaged after energy calibration by means of the EXAFSPAK program package.[45]

EXAFS Data Analysis: The EXAFSPAK[45] and GNXAS[46–48] program packages were used for the data treatment. The GNXAS code is based on the calculation of the EXAFS signal and a subsequent refinement of the structural parameters. The GNXAS method accounts for multiple scattering (MS) paths, with correct treatment of the configurational average of all the MS signals to allow fitting of correlated distances and bond-length variances (Debye–Waller factors). A correct description of the first coordination sphere of the studied complex has to account for asymmetry in the distribution of the ion–solvent distances. Therefore the Th–O two-body signals associated with the first coordination shells were modeled with Γ-like distribution functions that depend on four parameters: the coordination number N, the average distance R, the mean-square variation σ, and the skewness β. The β term is related to the third cumulant C_3 through the relation $C_3 = \sigma^3\beta$, and R is the first moment of the function $4\pi\int g(r)r^2\mathrm{d}r$. It is important to stress that R is the average distance and not the position of the maximum of the distribution (R_m).

The standard deviations given for the refined parameters are obtained from k^2- or k^3-weighted least-squares refinements of the EXAFS function $\chi(k)$ and do not include systematic errors of the measurements. These statistical error estimates provide a measure of the precision of the results and allow reasonable comparisons (e.g., of the significance of relative shifts in the distances). However, the variations in the refined parameters, including the shift of the E_0 value (for which $k = 0$) using different models and data ranges indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.005 to 0.02 Å for well-defined interactions. The "standard deviations" given in the text have been increased accordingly to include estimated additional effects of systematic errors.

Single-Crystal X-ray Diffraction: Individual data sets were collected on several crystals with the best end result presented here. The data quality is lower than that which is normally achieved in similar measurements, likely due to a combination of low crystal quality and unfavorable absorption conditions; nevertheless, the information obtained is satisfactory for the relevant discussion of the CN of thorium(IV). The crystallographic data sets were obtained with a Bruker Apex-II CCD diffractometer and graphite monochromator using Mo-K_α ($\lambda = 0.71073$ Å) radiation at ambient room temperature. The structure was subsequently solved by standard direct methods in the SHELXL program package, and refined by full-matrix least-squares on F^2, with hydrogen atom positions calculated geometrically. Several additional constraints and restraints were applied to both the dimethyl sulfoxide ligands and the trifluormethanesulfonate counterions to stabilize the refinement in the beginning and were removed when possible after each refinement step. Selected crystal and experimental data are summarized in Table 3.

Supporting Information (see footnote on the first page of this article): Surrounding of O200 in **1** and the unit cell showing two independent thorium(IV) units and trifluoromethansulfonate ions.

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