Angewandte
Chemie

DOI: 10.1002/anie.200603947

Transplutonium Chemistry

The Structures and Optical Spectra of Hydrated Transplutonium Ions in the Solid State and in Solution**

Patric Lindqvist-Reis, Christos Apostolidis, Jean Rebizant, Alfred Morgenstern, Reinhardt Klenze, Olaf Walter, Thomas Fanghänel, and Richard G. Haire*

Basic knowledge about the coordination shell of hydrated actinide (An) ions and their dynamics is important for a sound thermodynamic description of the hydrolysis, complexation, and redox reactions of these ions in aqueous solution.[1] This information is necessary, for example, for the prediction of actinide migration in the aqueous systems of a nuclear repository and for the design of selective extraction agents for the separation of trivalent actinide (Am^{3+} and Cm^{3+}) and lanthanide (Ln) ions for partitioning and transmutation (P&T).[1b] However, owing to the redox instability of the lighter actinides and the very short half-lives of the heavier actinides, structural studies of An^{III} compounds are rare.[2] The lack of structural and thermodynamic data for An^{3+} ions can, to some extent, be bridged with data for Ln^{3+} ions with similar ionic radii.[1a]

Important structural information on nona-hydrated Ln^{3+} ions has been obtained primarily from crystallographic studies on the isotypic trifluoromethanesulfonate (triflate),[3] ethylsulfate,[4] and bromate series[5] $[Ln(H_2O)_9]X_3$ ($X = CF_3SO_3$, $EtOSO_3$, BrO_3). All three series feature highly symmetrical, tricapped trigonal-prismatic (TTP) cation entities that are stabilized by extensive hydrogen bonding to the neighboring anions. These hydrogen bonds are crucial for the attainment of nine-coordination for the heavier lanthanides, which normally prefer eight-coordination.[1a,d,6]

In analogy with the Ln^{III} series, we expect An^{3+} ions with larger ionic radii to be hydrated by nine water molecules, while a smooth transition from nine to eight has been suggested to occur between Cm^{3+} and Es^{3+}.[1a,7] Extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to derive hydration numbers and bond lengths for the aqua ions of U^{3+}–Cf^{3+}.[1c] The results show a decrease in the mean An–O bond length with increasing atomic number but no consistent trend in the hydration numbers.[1d] In a recent time-resolved, laser-induced fluorescence spectroscopic (TRLFS) study we showed that the $Cm^{3+}(aq)$ spectrum can be described by an equilibrium between octa- and nona-hydrated species with molar ratios of 1:9 at 20 °C and 4:6 at 200 °C.[8] Quantum chemical calculations including a polarizable-continuum model revealed D_3 symmetry for the $[M(H_2O)_9]^{3+}$ ($M = Nd$, Cm) species in solution.[9] Until now, only one nona-hydrate–An^{III} structure was known, namely $[Pu(H_2O)_9](CF_3SO_3)_3$ (**1**).[3f] Herein, we report the single-crystal X-ray structures of the transplutonium nona-hydrates $[M(H_2O)_9](CF_3SO_3)_3$ ($M = Am$ (**2**), Cm (**3**)) and their lanthanide counterpart ($M = Nd$ (**4**)). We also compare the 5f optical spectra of **2** and **3** with the spectra of their dilute aqueous solutions to deduce structural information for the aqua ions.

The studied compounds crystallize from their respective aqueous solutions isotypically with the lanthanide triflates in the hexagonal space group $P6_3/m$.[10] The metal ions, which are located in the (2c) site of $\bar{6}$ symmetry, are surrounded by six equidistant water oxygen atoms (O2) at the vertices of a trigonal prism and three capping water oxygen atoms (O1) in the equatorial plane at longer distances that are slightly displaced from the center of the rectangular surfaces. The TTP coordination of $[M(H_2O)_9]^{3+}$ (C_{3h} symmetry) is stabilized by hydrogen bonds to the triflate ions, which also control the orientation of the coordinated water molecules. Thus, the capping water molecules obtain a trigonal coordination with their hydrogen atoms symmetrically located above and below the equatorial plane, while the prismatically arranged water molecules are slightly tilted towards pyramidal coordination (Figure 1).

The metal–oxygen distances for prismatically arranged (O_{prism}) and capping (O_{cap}) oxygen atoms in **1**–**3** are plotted in Figure 2a together with those of the Ln^{III} triflates. The distances to O_{cap} are 0.10–0.11 Å longer than those to O_{prism}

---

[*] Dr. P. Lindqvist-Reis, Dr. R. Klenze
Institut für Nukleare Entsorgung
Forschungszentrum Karlsruhe
Postfach 3640, 76021 Karlsruhe (Germany)
Fax: (+49) 724-782-3927
E-mail: plr@ine.fzk.de

Dr. C. Apostolidis, Dr. J. Rebizant, Dr. A. Morgenstern,
Prof. Dr. T. Fanghänel
European Commission, Joint Research Centre
Institute for Transuranium Elements
Postfach 2340, 76125 Karlsruhe (Germany)

Dr. O. Walter
Institut für Technische Chemie
Forschungszentrum Karlsruhe
Postfach 3640, 76021 Karlsruhe (Germany)

Dr. R. G. Haire
Transuranium Research Laboratory
Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)

[**] The authors are indebted to OBES, USDOE, for providing ^{248}Cm through the former production program at Oak Ridge National Laboratory. We would like to thank the INE radiation safety officers for their assistance in providing a secure experimental setup, the scientists at the INE-Beamline for Actinide Research at ANKA, and Dr. Clemens Walther (INE-FZK) for his help with the laser fluorescence spectroscopy.

Supporting Information for this article (experimental and crystallographic details for **2**–**4**, and EXAFS, UV/Vis, TRLFS, and IR spectroscopic data) is available on the WWW under http://www.angewandte.org or from the author.

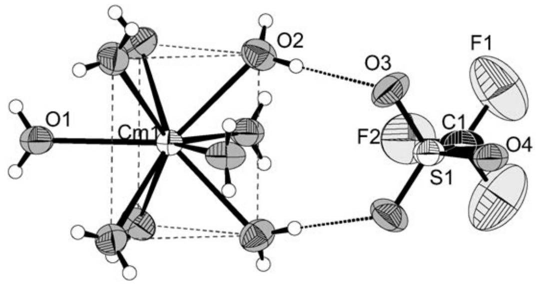

Figure 1. Structure of the $[An(H_2O)_9]^{3+}$ entity in **2** and **3** (**3** is shown; thermal ellipsoids set at 40% probability) hydrogen-bonded to $CF_3SO_3^-$. The TTP geometry and hydrogen-bonding are indicated by dashed lines. Selected bond lengths [Å] for **2**, **3**, and **1**[3f]: Am–O1 2.578(6), Am–O2 2.466(4); Cm–O1 2.565(8), Cm–O2 2.454(6); Pu–O1 2.574(3), Pu–O2 2.476(4).

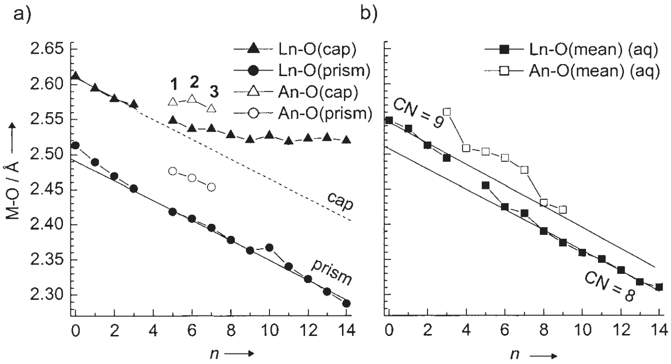

Figure 2. a) M–O bond lengths in the isotypic $[M(H_2O)_9](CF_3SO_3)_3$ (M = Ln, An) compounds (*n* = number of electrons in 4f or 5f orbitals).[3] The straight lines show the predicted M–O distances assuming (linear) Ln and An contractions of about 0.20 Å.[11] b) Mean M–O distances for Ln^{3+}(aq) and An^{3+}(aq) determined by EXAFS.[1c,6f,13]

for **1**–**3**, in agreement with observations with the early lanthanides. Owing to the lanthanide contraction, the distances $M-O_{prism}$ display an almost linear decrease across the series.[11] An analogous decrease (actinide contraction) with a similar slope is seen for the distances to O_{prism} for **1**–**3**. However, the situation is quite different for O_{cap}: while in the lanthanide series both distances decrease with approximately the same slope up to about Nd, for elements heavier than Gd the distances to O_{cap} are almost constant at about 2.52 Å. A similar effect may occur for the heavier actinides. It is interesting to note that the distance to O_{cap} of **1** departs by about 0.02 Å from this linear decrease with decreasing ionic radii, and is even shorter than that of **2**. Even though we expect a slight decrease in the unit-cell dimensions for **1** at low temperature (200 K, as was observed for **4**), this shrinkage of the distance to O_{cap} may indicate a higher degree of covalency in the Pu–O bonds than for the heavier actinides (see Figure 2a and Table 1 in the Supporting Information).[7c,12]

The difference between the distances to O_{prism} and O_{cap} is partly due to the hydrogen bonding between the water molecules and the triflate ions, and partly due to steric crowding of the water ligands.[3a,e,5c] The latter effect becomes increasingly important with decreasing ionic radius and results in a "pushing out" of the capping water molecules from the coordination sphere that becomes obvious at the end of the Ln^{III} triflate series (Figure 2a). In the Ln^{III} bromate series the decrease in the distances to O_{cap} is comparable to that in the triflate series, although the difference between both distances is considerably smaller.[5] This observation shows that the $[M(H_2O)_9]^{3+}$ coordination geometry is very sensitive to the hydrogen bonding to the anions in the second coordination shell.

The hydrogen bonding to the second hydration sphere in aqueous solution is much more flexible and the hydration numbers are therefore governed by the Ln^{3+} and An^{3+} ionic radii. X-ray and neutron diffraction, and, subsequently, EXAFS studies, have shown that the ions in the middle of the Ln^{3+}(aq) series change hydration number from nine to eight.[6] This (smooth) transition gives rise to the familiar "S-shape" in the Ln–O distance plot when progressing through the series. We note that the corresponding feature in the actinide series is between Cm and Cf (Figure 2b). The derived An–O mean bond lengths for Pu^{3+}(aq) and Am^{3+}(aq) (2.51 and 2.48–2.51 Å, respectively)[1d,13a,b] are comparable to those of **1** (2.51 Å) and **2** (2.50 Å), while the distances reported for Cm^{3+}(aq) (2.45–2.47 Å)[1a,c] are slightly shorter than the mean Cm–O distance of **3** (2.49 Å). The present Cm^{3+}(aq) EXAFS data show an asymmetric distribution of 8.5(8) water molecules at the mean Cm–O distance (2.477(5) Å; see the Supporting Information). This asymmetry is consistent with a TTP coordination geometry, while the shorter bond length compared to **3** is explained by the presence of about 10% of octa-hydrated ions.[8]

Figure 3a shows the electronic absorption spectra of Am^{3+}(aq) and $[Am(H_2O)_9]^{3+}$ in **2** at room temperature. Both spectra show a pronounced agreement in the peak maxima, line widths, and intensities of the crystal-field (CF) transitions in the region 250–460 nm, whereas the most

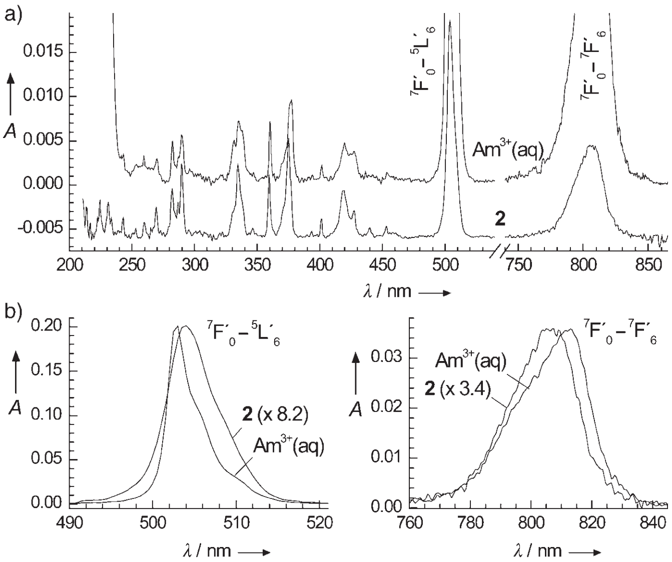

Figure 3. UV/Vis electronic absorption spectra of **2** and Am^{3+}(aq) (4.9 mM $Am(CF_3SO_3)_3$ in 1.4 M HCF_3SO_3; optical path = 1.0 mm) at room temperature: a) the region 200–860 nm; b) the bands near 503 and 810 nm.

intense and broad bands near 503 and 810 nm show some differences in the intensity distributions of the various spectral components (Figure 3b). Rajnak and Couture have analyzed the CF transitions of $[Nd(H_2O)_9](EtSO_4)_3$ and $[Er(H_2O)_6Cl_2]Cl_2$ in comparison with Nd^{3+}(aq) and Er^{3+}(aq) in frozen aqueous solutions and have derived nine- (D_{3h}) and eightfold (D_{4d}) coordination, respectively, for the aqua ions.[14] In a similar study, Carnall compared the absorption spectra of the hexagonal $AmCl_3$ and La:$AmCl_3$ salts at 4.2 K with those of Am^{3+}(aq) at 298 and 77 K, and found a nearly one-to-one correspondence between the relatively few (symmetry-allowed) CF transitions.[15] He thus concluded that the same local symmetry, approximately D_{3h}, exists, with a similarly weak CF strength, for the Am^{3+}–aqua ion as in the solid hosts. These findings are confirmed by the striking similarities between the spectra of Am^{3+}(aq) and **2** in Figure 3a. Good agreement was also found between absorption spectra of Pu^{3+}(aq) and **1** at room temperature.[3f] However, as the CF transitions are poorly resolved in those spectra, it is difficult to deduce conclusive structural information for Pu^{3+}(aq).

The half-filled 5f shell of Cm^{3+} gives rise to a large energy gap (approx. 17000 cm^{-1}) between the ground state ($^8S'_{7/2}$) and the lowest excited state ($^6D'_{7/2}$), which results in interesting luminescence properties.[1e] The room-temperature emission spectra of $[Cm:Y(H_2O)_9](CF_3SO_3)_3$ (Cm:Y ≈ 1 ppm; **3a**) and neat **3** (see the Supporting Information) are identical, while that of Cm^{3+}(aq) is notably red-shifted (by about 2 nm) and is nearly twice as broad (Figure 4a). The reason for the red-shift and the broadening for this aqua ion is revealed by analyzing the $^8S'_{7/2} \rightarrow {}^6D'_{7/2}$ excitation spectrum, which provides the energies and relative intensities for all four $^6D'_{7/2}$ CF levels (denoted as A1–A4). As can be seen in Figure 4b, the absorption profiles show general agreement for **3a** and Cm^{3+}(aq),[16] with similar intensity distributions and overall splitting of the component bands; however, the separation between A1 and A2 is larger for the aqua ion (about 90 cm^{-1}) than for **3a** (53 cm^{-1}).[17] Therefore, because both levels are populated to a different extent at room temperature (the higher-lying A3 and A4 levels are scarcely populated), the emission spectrum of Cm^{3+}(aq) is red-shifted and broadened compared to **3a**. In total, the spectroscopic agreement suggests a similar TTP coordination for Cm^{3+}(aq) to that found for Am^{3+}(aq).

The similar luminescence lifetimes of **3** and **3a** ((66 ± 2) and (63 ± 2) µs, respectively) indicate negligible interactions between neighboring Cm^{3+} ions in the neat compound. These lifetimes are virtually identical to that of Cm^{3+}(aq) ((65 ± 2) µs; see the Supporting Information), which shows that the quenching by energy transfer to the OH vibrational overtones of the water ligands is the same in the solids and in solution.[1e,8]

In summary, the single-crystal X-ray structures and 5f electronic absorption spectra of highly symmetric Am^{III} and Cm^{III} nona-hydrates have been reported for the first time. The structures of $[M(H_2O)_9](CF_3SO_3)_3$ (M = Pu (**1**),[3f] Am (**2**), Cm (**3**)) provide new and valuable knowledge about the isotypic An^{III} and Ln^{III} series. A comparison of the nona-hydrated structures of **2** and **3** with the EXAFS-derived structures for the aqua ions of Am^{3+} and Cm^{3+}, together with their respective 5f optical spectra, clearly indicates the prevailing ninefold TTP coordination for the hydrated ions in solution. Such basic knowledge is of key importance for the understanding of the aqueous as well as the extraction chemistry of these actinides.

Received: September 26, 2006
Published online: January 3, 2007

Keywords: actinides · coordination modes · EXAFS spectroscopy · hydrates · X-ray diffraction

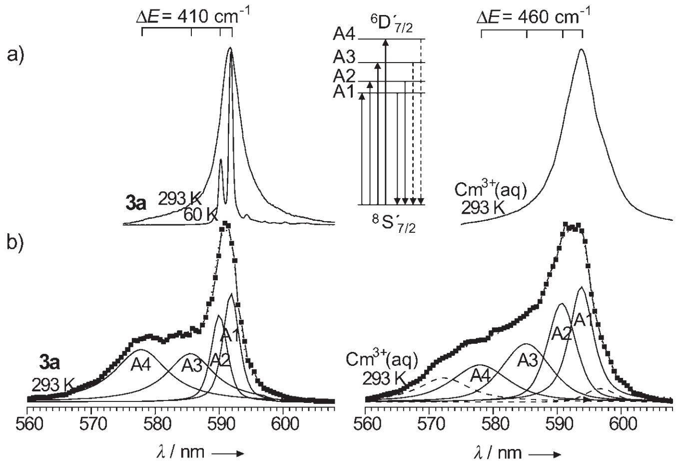

Figure 4. a) $^6D'_{7/2} \rightarrow {}^8S'_{7/2}$ emission (λ_{exc} = 397 nm) and b) $^8S'_{7/2} \rightarrow {}^6D'_{7/2}$ excitation spectra of Cm^{3+} in **3a** and 0.1 M $HClO_4$ aqueous solution. Note that the A1 and A2 component bands of **3a** are resolved at ≈ 60 K;[17] peak deconvolution of the excitation spectrum at room temperature was performed to obtain peak positions for A3 and A4. A similar procedure was used for Cm^{3+}(aq) (see the Supporting Information for details).

---

[1] For recent reviews, see: a) G. R. Choppin, M. P. Jensen in *The Chemistry of the Actinide and Transactinide Elements*, *Vols. 4 and 5* (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger, J. J. Katz), 3rd ed., Springer, Dordrecht, **2006**, pp. 2524–2621; b) K. L. Nash, C. Madic, J. N. Mathur, J. Lacquement in *The Chemistry of the Actinide and Transactinide Elements*, *Vols. 4* and *5* (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger, J. J. Katz), 3rd ed., Springer, Dordrecht, **2006**, pp. 2622–2798; c) L. Soderholm, M. Antonio in *The Chemistry of the Actinide and Transactinide Elements*, *Vols. 4 and 5* (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger, J. J. Katz), 3rd ed., Springer, Dordrecht, **2006**, pp. 3086–3198; d) S. Cotton, *Lanthanide and Actinide Chemistry*, Wiley, Chichester, **2006**; e) N. M. Edelstein, R. Klenze, T. Fanghänel, S. Hubert, *Coord. Chem. Rev.* **2006**, *250*, 948.
[2] Only a few crystal structures of Cm^{III} and Cf^{III} compounds have been published, see: R. E. Sykora, Z. Assefa, R. G. Haire, T. E. Albrecht-Schmitt, *J. Solid State Chem.* **2004**, *177*, 4413; R. E. Sykora, Z. Assefa, R. G. Haire, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2005**, *44*, 5667; N. A. Stump, G. M. Murray, G. D. Del Cul, R. G. Haire, J. R. Peterson, *Radiochim. Acta* **1993**, *61*, 129; R. E. Sykora, Z. Assefa, R. G. Haire, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2006**, *45*, 475.
[3] a) J. M. Harrowfield, D. L. Kepert, J. M. Patrick, A. H. White, *Aust. J. Chem.* **1983**, *36*, 483; b) C. O. Paiva Santos, E. E. Castellano, L. C. Machado, G. Vicentini, *Inorg. Chim.* Acta

1985, *110*, 83; c) A. Chatterjee, E. N. Maslen, K. J. Watson, *Acta Crystallogr. Sect. B* **1988**, *44*, 381; d) C. Bisi Castellani, O. Carugo, M. Giusti, *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 1089; e) A. Abbasi, P. Lindqvist-Reis, L. Eriksson, D. Sandström, S. Lidin, I. Persson, M. Sandström, *Chem. Eur. J.* **2005**, *11*, 4065; f) J. H. Matonic, B. L. Scott, M. P. Neu, *Inorg. Chem.* **2001**, *40*, 2638.

[4] For a comprehensive study of $[Ln(H_2O)_9](EtOSO_3)_3$ (Ln = Ln–Lu, except Pm) at 171 K, see: R. E. Gerkin, W. J. Reppart, *Acta Crystallogr. Sect. C* **1984**, *40*, 781.

[5] Note that there has been some controversy regarding the choice of space group, see ref. [5d] for a review: a) L. Helmholz, *J. Am. Chem. Soc.* **1939**, *61*, 1544; b) S. K. Sikka, *Acta Crystallogr. Sect. A* **1969**, *25*, 621; c) J. Albertsson, I. Elding, *Acta Crystallogr. Sect. B* **1977**, *33*, 1460; d) R. E. Gerkin, W. J. Reppart, *Acta Crystallogr. Sect. C* **1987**, *43*, 623; e) E. Moret, F. Nicolo, J.-C. Bünzli, G. Chapuis, *J. Less-Common Met.* **1991**, *171*, 273; f) A. Abbasi, L. Eriksson, *Acta Crystallogr. Sect. E* **2006**, *62*, m126.

[6] a) A. Habenschuss, F. H. Spedding, *J. Chem. Phys.* **1979**, *70*, 2797; A. Habenschuss, F. H. Spedding, *J. Chem. Phys.* **1979**, *70*, 3758; A. Habenschuss, F. H. Spedding, *J. Chem. Phys.* **1980**, *73*, 442; b) G. Johansson, H. Wakita, *Inorg. Chem.* **1985**, *24*, 3047; c) G. Johansson, H. Yokoyama, *Inorg. Chem.* **1990**, *29*, 2460; d) T. Yamaguchi, M. Nomura, H. Wakita, H. Ohtaki, *J. Chem. Phys.* **1988**, *89*, 5153; e) C. Cossy, A. C. Barnes, J. E. Enderby, A. Merbach, *J. Chem. Phys.* **1989**, *90*, 3254; f) S. Ishiguro, Y. Umebayashi, K. Kato, R. Takahashi, K. Ozutsumi, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 3607.

[7] a) B. Fourest, J. Duplessis, F. David, *Radiochim. Acta* **1984**, *36*, 191; b) F. H. David, B. Fourest, *New J. Chem.* **1997**, *21*, 167; c) F. H. David, V. Vokhmin, *New J. Chem.* **2003**, *27*, 1627.

[8] P. Lindqvist-Reis, R. Klenze, G. Schubert, T. Fanghänel, *J. Phys. Chem. B* **2005**, *109*, 3077.

[9] a) U. Cosentino, A. Villa, D. Pitea, G. Moro, V. Barone, *J. Phys. Chem. B* **2000**, *104*, 8001; b) T. X. Yang, B. E. Bursten, *Inorg. Chem.* **2006**, *45*, 5291.

[10] Crystal data: a) $C_3H_{18}AmF_9O_{18}S_3$ (**2**), $M_r = 852.34\ \mathrm{g\,mol^{-1}}$, hexagonal, $P6_3/m$, $a = 13.8536(25)$, $c = 7.4622(22)$ Å, $V = 1240.3(5)$ Å^3, $Z = 2$, $T = 293(2)$ K, crystal size = 0.03 × 0.04 × 0.31 mm^3, $\rho_{\mathrm{calcd}} = 2.282\ \mathrm{g\,cm^{-3}}$, $\mu\mathrm{Mo}_{K\alpha} = 3.353\ \mathrm{mm^{-1}}$, $\theta_{\max} = 22.97°$, measured/independent reflections = 3752/629 ($R_{\mathrm{int}} = 0.0529$), $S = 1.131$, final $R1 = 0.0240$ (for 538 data $I > 2\sigma(I)$), $wR2 = 0.0557$ (all data); b) $C_3H_{18}CmF_9O_{18}S_3$ (**3**), $M_r = 856.34\ \mathrm{g\,mol^{-1}}$, hexagonal, $P6_3/m$, $a = 13.8352(19)$, $c = 7.4526(13)$ Å, $V = 1235.4(3)$ Å^3, $Z = 2$, $T = 293(2)$ K, crystal size = 0.04 × 0.05 × 0.45 mm^3, $\rho_{\mathrm{calcd}} = 2.302\ \mathrm{g\,cm^{-3}}$, $\mu\mathrm{Mo}_{K\alpha} = 3.487\ \mathrm{mm^{-1}}$, $\theta_{\max} = 22.93°$, measured/independent reflections = 3723/623 ($R_{\mathrm{int}} = 0.01418$), $S = 1.130$, final $R1 = 0.0307$ (for 511 data $I > 2\sigma(I)$), $wR2 = 0.0714$ (all data). CCDC-618933 (**2**), -618934 (**3**), and -618935 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] It has been claimed that the Ln contraction over the 4f series follows a quadratic decay, see: E. A. Quadrelli, *Inorg. Chem.* **2002**, *41*, 167.

[12] G. R. Choppin, *J. Alloys Compd.* **2002**, *344*, 55.

[13] a) P. G. Allen, J. J. Bucher, D. K. Shuh, N. M. Edelstein, I. Craig, *Inorg. Chem.* **2000**, *39*, 595; b) T. Stumpf, C. Hennig, A. Bauer, M. A. Denecke, T. Fanghänel, *Radiochim. Acta* **2004**, *92*, 133; c) M. Weigl, M. A. Denecke, P. J. Panack, A. Geist, K. Gompper, *Dalton Trans.* **2005**, 1281; erratum: M. Weigl, M. A. Denecke, P. J. Panack, A. Geist, K. Gompper, *Dalton Trans.* **2005**, 1865.

[14] K. Rajnak, L. Couture, *Chem. Phys.* **1981**, *55*, 331; L. Couture, K. Rajnak, *Chem. Phys.* **1984**, *85*, 315.

[15] W. T. Carnall, *J. Less-Common Met.* **1989**, *156*, 221, and references therein.

[16] Note that the excitation spectrum of Cm^{3+}(aq) in Figure 4b agrees with the absorption spectrum in: W. T. Carnal, K. Rajnak, *J. Chem. Phys.* **1975**, *63*, 3510.

[17] The bands A1–A4 were deduced by peak deconvolution of the excitation spectra with additional information for A1 and A2 from the emission spectra at low temperature, i.e., from Figure 4a for **3a** and from ref. [8] for Cm^{3+}(aq). Note that because the 60 K spectrum was found to be blue-shifted with 0.5 nm (15 cm^{-1}) compared to the room-temperature spectrum, for clarity the 60 K spectrum has been red-shifted with 0.5 nm in Figure 4a (see the Supporting Information).