4006 *Inorg. Chem.* **2000,** *39,* 4006−4011

Steric Effects Control the Structure of the Solvated Lanthanum(III) Ion in Aqueous, Dimethyl Sulfoxide, and *N*,*N*′-Dimethylpropyleneurea Solution. An EXAFS and Large-Angle X-ray Scattering Study

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Received October 12, 1999

The structure of the solvated lanthanum(III) ion has been determined in aqueous, dimethyl sulfoxide, and *N*,*N*′-dimethylpropyleneurea solution by means of the EXAFS and large-angle X-ray scattering (LAXS) techniques. The close agreement between the EXAFS spectra of solid nonaaqualanthanum(III) trifluoromethanesulfonate and of an aqueous lanthanum(III) perchlorate solution shows that the hydrated lanthanum(III) ion in aqueous solution most probably has the same structure as in the solid, i.e., nine water molecules coordinated in a tricapped trigonal prismatic configuration. The data analysis from EXAFS and LAXS measurements of the aqueous solution resulted in the La−O bond distances 2.52(2) and 2.65(3) Å to the water molecules in the prism and the capping positions, respectively. The LAXS study shows a second hydration sphere consistent with approximately 18 water molecules at 4.63(2) Å. The EXAFS spectra of solid octakis(dimethyl sulfoxide)lanthanum(III) trifluoromethanesulfonate and a dimethyl sulfoxide solution of this salt are also similar. The data analysis of EXAFS and LAXS measurements assuming eight-coordination around lanthanum yielded an La−O bond distance of 2.50(2) Å, and an La···S distance of 3.70(3) Å, giving an La−O−S angle of 133(2)°. The EXAFS data of an *N*,*N*′-dimethylpropyleneurea solution of lanthanum(III) trifluoromethanesulfonate gave the La−O bond distance 2.438(4) Å and the La···C distance 3.41(2) Å, which correspond to an La−O−C angle of 131(2)°. The La−O bond distance is consistent with seven-coordination around lanthanum, on the basis of the variation of the ionic radii of the lanthanum(III) ion with different coordination numbers.

Introduction

Lanthanum has, being the first element in the lanthanide series, been the focus of many investigations of coordination chemical properties, including the solvation, of the elements in this series. The view that the coordination number of the hydrated lanthanide(III) ions changes from nine to eight in aqueous solution in the middle of the series,[1] ”the gadolinium break”, is widely accepted today. This is also supported in a number of review articles on the structure of hydrated and solvated metal ions in solution.[2−4]

In the solid state the lanthanum(III) ion is found to have a variety of hydration numbers and geometries since variations in the lattice energies with different anions may favor other coordination geometries than that in aqueous solution. The crystal structure of nonaaqualanthanum(III) trifluoromethanesulfonate, and the isostructural lanthanide(III) compounds, shows nine water molecules to be coordinated in a tricapped trigonal prism.[5,6] In this series of compounds lanthanum is the element with the smallest difference between the bond distances in the prism (6 × 2.519 Å) and to the capping positions (3 × 2.619 Å), 0.10 Å.[6] No octahydrate has been found in the solid state, but the lanthanide(III) ions coordinate eight oxygen atoms, forming distorted dodecahedrons (or rather bicapped trigonal prisms), in $[M(OH_2)_6(O_3SC_7H_7)_2](C_7H_7SO_3)\cdot 3H_2O$,[7] (M = Y, Sm, Gd, Dy, Ho, Er, Yb). Six-coordination in octahedral fashion is found in the hexaaqualanthanide(III) perchlorates, $[M(OH_2)_6(ClO_4)_3]$,[8] (M = La, Tb, Er); the La−O bond distance was reported as 2.48(3) Å after a large riding motion correction.[8]

A large-angle X-ray scattering (LAXS) investigation on an aqueous lanthanum(III) chloride solution gave a mean La−O distance of 2.58 Å for a hydration number of 9.1.[1] Later an isomorphous substitution method was applied on a lanthanum perchlorate solution, which resulted in eight water molecules at the La−O distance 2.57 Å in the inner coordination sphere, and a second hydration sphere at about 4.70 Å.[9] An EXAFS study on an aqueous solution of lanthanum(III) perchlorate, with a fixed coordination number of nine, resulted in a mean La−O bond distance of 2.545(2) Å.[10−12]

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10.1021/ic991208s CCC: $19.00

Table 1. Concentrations (mol·dm^{-3}), Density (ρ), and Linear Absorption Coefficient (μ) for MoKα X-ray Radiation of the Solutions Used in the EAXFS and Large Angle X-ray Scattering Measurements

solution	[La^{3+}]	[X^-]	[H^+]	[solvent]	ρ/g·cm^{-3}	μ/cm^{-1}
$La(ClO_4)_3$ in water[a,b]	0.662	3.856	1.870	46.12	1.306	7.10
$La(CF_3SO_3)_3$ in Me_2SO[a,b]	0.750	2.250		11.35	1.341	10.45
$La(CF_3SO_3)_3$ in DMPU[a]	0.080	0.240		7.96	1.068	

[a] EXAFS. [b] LAXS.

The solvation number of the lanthanide(III) ion in *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA) are reported to be about eight in both solvents, thus lower than the corresponding hydration number in aqueous solution.[10,11] The lanthanum(III) ion is solvated by eight dimethyl sulfoxide (DMSO) molecules in the solid $[La(OS(CH_3)_2)_8][Cr(NCS)_6]$ with La−O bond distances in the range 2.46−2.51 Å,[13] and by eight pyridine 1-oxide molecules in the solid $[La(ONC_5H_5)_8](ClO_4)_3$ with an average La−O bond distance of 2.497 Å in a distorted square antiprism.[14] Our attempts to determine the crystal structures of the solid iodide, perchlorate, and trifluoromethanesulfonate salts with the dimethyl sulfoxide-solvated lanthanum(III) ion have so far failed since the crystals gave too few reflections.

The accuracy in the determination of the coordination number is fairly low in the LAXS and EXAFS methods. However, there is a strong correlation between the observed bond distances and the coordination number, since the ionic radii of metal ions in general increase significantly with increasing coordination number. The ionic radii of the lanthanum(III) ion are estimated to be 1.03, 1.10, 1.16, and 1.22 Å in six-, seven-, eight-, and nine-coordination, respectively.[15]

The steric influence of the ligands on the coordination of the lanthanum(III) ion seems to be strong, and to obtain further insight into its coordination chemistry, which is of importance for the interpretation of thermodynamic and kinetic studies, this structural investigation was performed in the oxygen donor solvents water, dimethyl sulfoxide, and *N*,*N*′-(dimethylpropylene)urea (DMPU) using EXAFS and LAXS techniques. The coordination number of the hydrated lanthanum(III) ion has previously not been fully established in aqueous solution, and the reported nine-coordination with only one La−O bond distance seems somewhat unlikely as nine-coordination normally results in a tricapped trigonal prism; see above. The lanthanum(III) ion seems to have a lower coordination number in dimethyl sulfoxide than in water; see above. *N*,*N*′-Dimethylpropyleneurea is an unusually bulky solvent molecule,[16] often forcing the metal ion to adapt a lower coordination number than for most other solvates of monodentate oxygen donor solvents.[17]

Experimental Section

Preparation of Samples. An aqueous lanthanum(III) trifluoromethanesulfonate solution was prepared by adding trifluoromethanesulfonic acid (Riedel-deHaën, purum) dropwise to a lanthanum(III) oxide−water slurry until dissolution, and the mixture was thereafter refluxed for at least 2 h. The volume of this solution was reduced by evaporation, and single crystals of nonaaqualanthanum(III) trifluoromethanesulfonate were obtained upon cooling in a refrigerator. Anhydrous lanthanum(III) trifluoromethanesulfonate was obtained by boiling off all water and excess trifluoromethanesulfonic acid, and drying the solid in an oven at 190 °C.[18] The dimethyl sulfoxide and *N*,*N*′-dimethylpropyleneurea solutions were prepared by dissolving weighed amounts of anhydrous lanthanum(III) trifluoromethanesulfonate in the freshly distilled solvent. An aqueous lanthanum(III) perchlorate solution was prepared by dissolving lanthanum(III) oxide in dilute perchloric acid (AnalR, 70%). Solid hexaaqualanthanum(III) perchlorate was prepared in the same way as nonaaqualanthanum(III) trifluoromethanesulfonate; see above. Solid octakis(dimethyl sulfoxide)lanthanum(III) trifluoromethanesulfonate and iodide were obtained by slowly cooling dimethyl sulfoxide solutions saturated at ca. 40 °C with the anhydrous salts (Aldrich) to room temperature. Hexaaqualanthanum(III) perchlorate was dissolved in a minimum volume of acetone, and 6 equiv of 2,2-dimethoxypropane (Merck) was added to the solution to react with water, forming acetone and methanol. 8 equiv of dimethyl sulfoxide was added to this mixture, which was stirred for 5 min, and the volume was thereafter reduced ca. 50% by evaporation. Octakis(dimethyl sulfoxide)lanthanum(III) perchlorate precipitated immediately on cooling, and it was recrystallized in dimethyl sulfoxide. The lanthanum(III) content of the solids and solutions was analyzed by EDTA titration using xylenol orange as indicator.[19,20] The composition of the studied solutions is given in Table 1, and the analyses of the solids were in agreement with the given composition. All the studied solution systems have been checked for ion-pair formation by means of conductometry. The three systems presented in this paper are all completely dissociated, also in concentrated solution.

WARNING! *Organic solvates of perchlorate salts are powerful explosives and should be handled with great caution.*[21,22]

EXAFS. The La L_{III}-edge X-ray absorption data were collected in transmission mode, or in fluorescence mode using a Lytle detector (cf. Table 2), at beam line 4-1 at the Stanford Synchrotron Radiation Laboratory (SSRL), under dedicated conditions; SSRL operates at 3.0 GeV and a maximum current of 100 mA. Data were only collected up to $k \approx 9$ Å^{-1} since the La L_{II}-edge appears at 5891 eV.[23] Monochromatic X-ray radiation was obtained by a Si[111] double monochromator, which was detuned to 30% of the maximum intensity at the end of the scans to reduce higher order harmonics. The solutions were kept in cells with 6.3 μm X-ray polypropylene foil windows and 1−5 mm Teflon spacers. The solids were diluted with boron nitride (BN) to give an absorption change over the edge of about one logarithmic unit. Energy calibration of the X-ray absorption spectra were performed by recording the edge spectrum of a lanthanum foil repeatedly during the data collection, and assigning its first L_{III}-edge inflection point to 5483 eV.[23] The sample absorption was too high to allow simultaneous recording of the foil. Typically 3−4 scans of the solutions and 2−3 scans of the solids were accumulated and averaged.

Large-Angle X-ray Scattering. The scattering from the free surface of an aqueous solution of lanthanum(III) perchlorate and a dimethyl sulfoxide solution of lanthanum(III) trifluoromethanesulfonate was measured by means of a large-angle $\theta-\theta$ diffractometer described elsewhere,[24] using Mo Kα radiation, $\lambda = 0.7107$ Å. The scattered radiation was monochromatized by a focusing LiF crystal monochromator, and the intensity was recorded at 450 discrete points in the range $1° < \theta < 65°$; 2θ is the scattering angle. A total of 100 000 counts

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Table 2. EXAFS Determinations of Bond Distances, d/Å, Debye–Waller Factors (σ^2) Given as σ/Å, and Number of Distances, n, of the Solvated Lanthanum(III) Ions in Solids and Solutions at Room Temperature[a]

solvent	state	interaction	d	σ	n	ΔE_o	S_o^2
water	solid[b]	La–O	2.519[d]	0.067(4)	6	−11.3(3)	0.88(2)
		La–O	2.619[d]	0.094(6)	3		
		La–O–O	3.597[d]	0.055(16)	12		
	solution[b]	La–O	2.515(8)	0.057(9)	6	−11.3[f]	0.90(2)
		La–O	2.64(2)	0.07(2)	3		
		La–O–O	3.60[e]	0.055[e]	12		
Me_2SO	solid[c]	La–O	2.486(3)	0.093(5)	8	−10.4[f]	0.90(4)
		La···S	3.675(6)	0.093(5)	8		
		La–O–S	3.85(2)	0.10(2)	16		
	solution[c]	La–O	2.504(3)	0.063(4)	8	−10.4(3)	0.73(2)
		La···S	3.675(6)	0.087(6)	8		
		La–O–S	3.828(12)	0.082(12)	16		
DMPU	solution[c]	La–O	2.438(4)	0.078(4)	7	−8.5(3)	0.68(3)
		La···C	3.410(12)	0.089(12)	7		
		La–O–C[g]	3.66(3)	0.14(2)	14		
		MS	4.12(4)	0.12(2)	28		
		MS	4.37(5)	0.11(2)	28		

[a] The shift of the threshold energy, ΔE_o/eV, and the amplitude reduction factor, S_o^2, are given. Standard deviations estimated from the noise level at high k values in the EXAFS data are given within parentheses for refined parameters. [b] Data collection in transmission geometry. [c] Data collection in fluorescence mode. [d] Distances kept constant at the crystal structure values, ref 6. [e] The parameter is not refined. [f] The ΔE_o value was fixed to the refined value for the sample with the best data quality and with the same configuration around lanthanum. [g] It is not possible to resolve the La–O–C and La–O–C–O distances expected at 3.56 and 3.71 Å, respectively.

were accumulated at each point, and the entire angular range was scanned twice, which corresponds to a statistical error of about 0.3%. The divergence of the primary X-ray beam was limited by 1°, $^1/_4$°, or $^1/_{12}$° slits for different θ regions, with overlapping data for scaling purposes.[24] The solutions were contained in an open Teflon cup enclosed in a half-cylindrical radiation shield with a beryllium window.

Data Treatment. EXAFS. The EXAFS functions were extracted using standard procedures for preedge subtraction, spline removal, and data normalization[25] using the EXAFSPAK program package.[26] An anomalous feature, obviously deviating from the oscillations in the scattering pattern, and previously attributed to a double electron transition, $2p4d \rightarrow 5d^2$, is observed at $k \approx 5.8$ Å^{-1} in all EXAFS spectra of the lanthanum(III) samples studied;[27,28] see Figure 1. This feature was eliminated by means of the deglitching procedure in the EXAFSPAK program package. To extract quantitative information, the k^3-weighted EXAFS oscillations were analyzed by nonlinear least-squares fitting of a model function with an ab initio calculated phase and amplitude backscattering parameters obtained by means of the FEFF program (version 6.01).[29] These parameters were calculated from $LaO_6O'_3$, LaO_8, and LaO_6 clusters in tricapped trigonal, square antiprismatic, and octahedral configurations, respectively, and three-leg La–O–S (angle 130°) and La–O–C (135°) scattering pathways for the dimethyl sulfoxide and *N,N'*-dimethylpropyleneurea solvates, respectively, and the parameters were applied when the corresponding assumed coordination figure was refined. The backscattering parameters for all pathways shorter than 5.3 Å have been calculated, but only those giving significant contributions to the EXAFS function were included in the final calculations; see Table 2. The k range used in the analyses was typically 2–9 Å^{-1}, and all refinements have been performed on deglitched unfiltered data. The EXAFS data recorded for the solid nonaaqualanthanum(III) trifluoromethanesulfonate compound with bond distances known from the crystal structure were used to determine the shift of the threshold energy, ΔE_o, which then was used for the aqueous solution. The amplitude reduction factor, S_o^2, was refined for constant coordination numbers, and found to be in the normal range, about 0.90, for all samples except the dimethyl sulfoxide and *N,N'*-dimethylpropyleneurea solutions; see Table 2. The reason for the lower S_o^2 value in the dimethyl sulfoxide solution is probably self-absorption since the sulfur atoms absorb strongly in the wavelength range used in the EXAFS studies of lanthanum, and for the *N,N'*-dimethylpropyleneurea solution probably the low concentration and the limited k-range used for the refinement (see Figure 2).

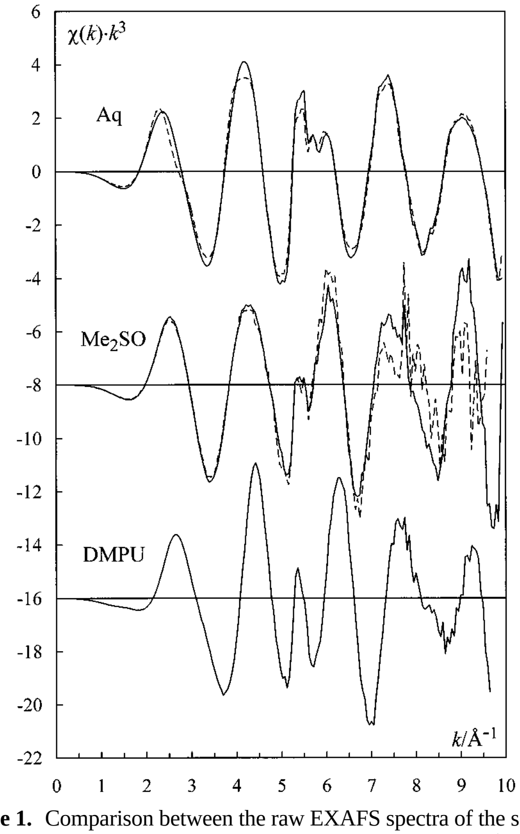

Figure 1. Comparison between the raw EXAFS spectra of the solvated lanthanum(III) ion in aqueous, dimethyl sulfoxide, and *N,N'*-(dimethylpropylene)urea solution (solid lines) and the corresponding solid solvates (dashed lines).

LAXS. The data sets obtained were treated by means of the KURVLR program.[30] The experimental intensities were normalized to

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a stoichiometric unit of volume containing one lanthanum atom, using the scattering factors f for neutral atoms, including corrections for anomalous dispersion, $\Delta f'$ and $\Delta f''$,[31] and values for Compton scattering.[32] Least-squares refinements of the model parameters were carried out by using the STEPLR program,[33] where the expression $U = \sum s[i_{\mathrm{exptl}}(s) - i_{\mathrm{calcd}}(s)]^2$ is minimized. The refinement of the model parameters was made for data in the high s region where the intensity contribution from the diffuse and long-range interactions can be neglected. Prior to the refinements a Fourier back-transformation was made, removing spurious nonphysical peaks below 1.2 Å in the experimental radial distribution function (RDF),[34] to obtain a better alignment of the intensity function, $i_{\mathrm{exptl}}(s)$. Due to the low linear absorption coefficients of the solutions studied, corrections for angle-dependent absorption effects and for multiple scattering were applied.[30] The starting models for the hydrate and the dimethyl sulfoxide solvate have been taken from the corresponding solid solvates,[6,13] and the initial parameter values for the hydrated perchlorate ion from the literature.[35]

Results and Discussion

Hydrated Lanthanum(III) Ion. The XANES and EXAFS spectra of the solid nonaaqualanthanum(III) trifluoromethanesulfonate and of the aqueous solution of lanthanum(III) perchlorate are almost identical, respectively, strongly indicating very similar local structure around the hydrated lanthanum(III) ion in both samples; cf. Figures 1 and S1, which is given in the Supporting Information. For the aqueous solution a model function was fitted to the unfiltered EXAFS data assuming a tricapped trigonal prismatic configuration around lanthanum, and fixing the ΔE_o value to that obtained from solid nonaaqualanthanum(III) trifluoromethanesulfonate. This resulted in La−O bond distances of 2.515(8) Å to the six oxygen atoms in the prism and 2.64(2) Å to the three capping ones; see Table 2. The fit of the experimental data is shown in Figure 2, the contribution from each separate scattering path is given in Figure S2, and the Fourier transforms are given in Figure S3. Fits with an eight-coordinated model were less good, ca. 10% higher error square sum, than the fit with a tricapped trigonal prismatic model.

The RDF of the aqueous lanthanum(III) perchlorate solution from the LAXS study shows three major peaks at 1.4, 2.5, and 4.6 Å, which correspond to the Cl−O bond distance of the perchlorate ions, and the La−O$_\mathrm{I}$ and La···O$_\mathrm{II}$ distances to the first and second hydration spheres, respectively; see Figure 3. A least-squares refinement gave a satisfactory fit for a tricapped trigonal prismatic model with six water molecules at 2.515(15) Å and three at 2.66(3) Å. The results from the EXAFS and LAXS studies are in satisfactory agreement, and the La−O bond distances do not differ significantly from those of the solid nonaaqualanthanum(III) trifluoromethanesulfonate. The La···O$_\mathrm{II}$ distance to the second hydration sphere was refined to 4.63(2) Å; see Table 3 and Figure 3. A fit of LAXS data with a square antiprismatic configuration around the lanthanum(III) ion resulted in a slightly inferior fit (ca. 10% increase of the error square sum). Furthermore, the obtained mean value of the La−O bond distance, 2.546(11) Å, is significantly longer than normally found for eight-coordinated lanthanum(III) complexes; see the Introduction.

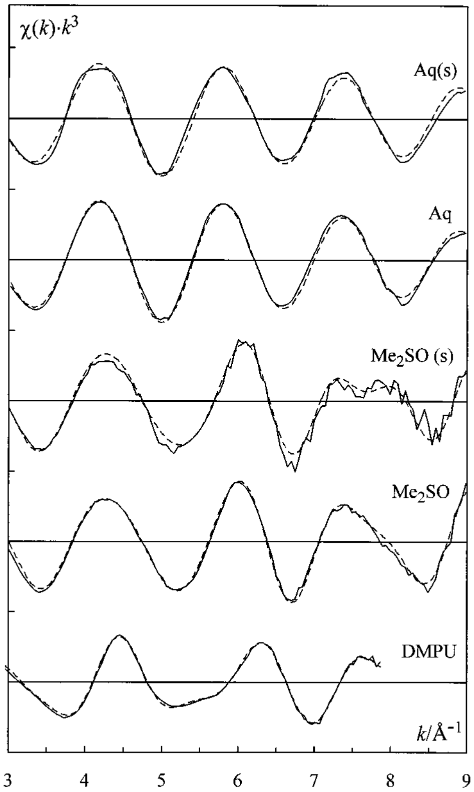

Figure 2. Calculated scattering paths from the program FEFF (dashed lines): Aq(s), solid nonaaqualanthanum(III) trifluoromethanesulfonate; Aq, aqueous solution of lanthanum(III) perchlorate; Me$_2$SO(s), solid octakis(dimethyl sulfoxide)lanthanum(III) trifluoromethanesulfonate; Me$_2$SO, dimethyl sulfoxide solution of lanthanum(III) trifluoromethanesulfonate; DMPU, *N*,*N*′-dimethylpropyleneurea solution of lanthanum(III) trifluoromethanesulfonate.

Dimethyl Sulfoxide-Solvated Lanthanum(III) Ion. The XANES and EXAFS regions of solid octakis(dimethyl sulfoxide)lanthanum(III) trifluoromethanesulfonate and a dimethyl sulfoxide solution of this salt are similar but with some deviation for $k > 7$ Å^{-1}; see Figures 1 and S1, respectively. Curve-fitting of model functions assuming eight-coordination gave the mean La−O bond distances 2.486(3) and 2.504(3) Å for the solid solvate and the dimethyl sulfoxide solution, respectively. The distances of the La···S backscattering and of the three-leg La−O−S pathways were refined to 3.675(6) and 3.85(2) Å, and 3.675(6) and 3.828(12) Å, for the solid and the dimethyl sulfoxide solution, respectively; see Table 2 and Figure 2. The contributions from the individual scattering pathways are shown in Figure S2, and the Fourier transforms in Figure S3. A mean La−O−S angle of 132(2)° emerges from the La−O and La···S distances, and the length of the three-leg La−O−S scattering path, assuming an S−O bond distance of 1.52 ± 0.01 Å.[16] The crystal structures of octakis(dimethyl sulfoxide)lanthanum(III) trifluoromethanesulfonate, perchlorate, and iodide were not possible to solve because only a small number of reflections were observed, all at small scattering angles, indicating a high degree of disorder in these structures. This is not surprising since several solid dimethyl sulfoxide solvates of three-valent metal ions display alternative positions of the sulfur atoms corresponding to an inversion of the dimethyl sulfoxide ligands.[17] The observed mean La−O bond and La···S distances in solid octakis(dimethyl sulfoxide)lanthanum(III) trifluoromethanesulfonate are in good agreement with those in solid [La(OS(CH$_3$)$_2$)$_8$][Cr(NCS)$_6$].[13]

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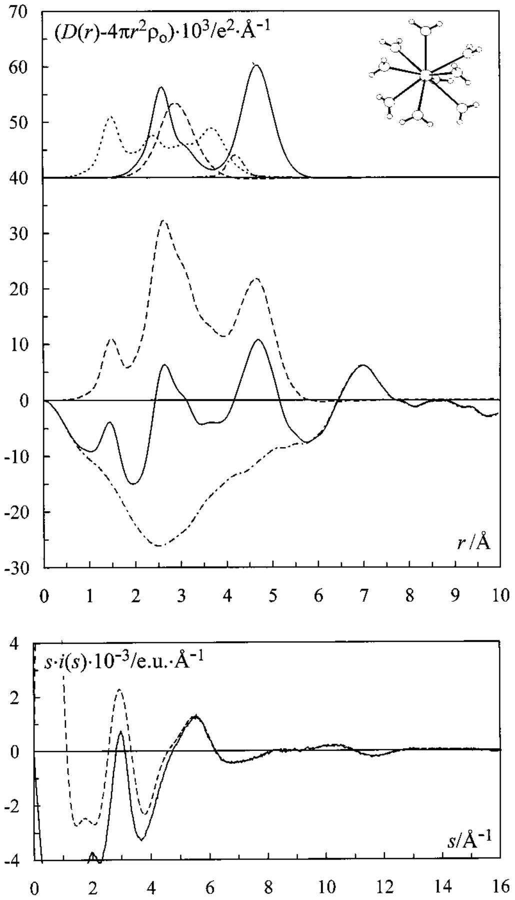

Figure 3. LAXS for 0.66 mol·dm^{-3} lanthanum(III) perchlorate in acidified aqueous solution: (upper) separate model contributions with parameters from Table 2 (solid line, first (La−O$_I$) and second (La···O$_{II}$) hydration spheres; dashes, hydrated perchlorate ion; dots, bulk water); (middle) radial distribution functions, $D(r) - 4\pi r^2\rho_o$, and the sum of the calculated peak shapes (solid line, experimental; dashes, model; dots, difference experimental − model function); (lower) structure-dependent LAXS intensity functions multiplied by the scattering variable, $si(s)$ versus s (solid line, experimental data; dashes, model function).

Table 3. LAXS Determinations of Bond Distances, d/Å, Displacement Factors, σ_l/Å,[a] and Number of Distances, n, of the Solvated Lanthanum(III) Ions in Aqueous and Dimethyl Sulfoxide Solution at Room Temperature[b]

solvent	interaction	d	σ_l	n
water	La−O	2.515(15)	0.046(3)	6
	La−O	2.66(2)	0.056(4)	3
	La···O	4.63(2)	0.12(1)	18
DMSO	La−O	2.50(2)	0.09(1)	8
	La···S	3.725(6)	0.18(1)	8

[a] σ_l is the parameter of the Debye−Waller factor in the LAXS equation, $\exp(-2\sigma_l s^2)$. [b] Estimated standard deviations are given within parentheses for refined parameters.

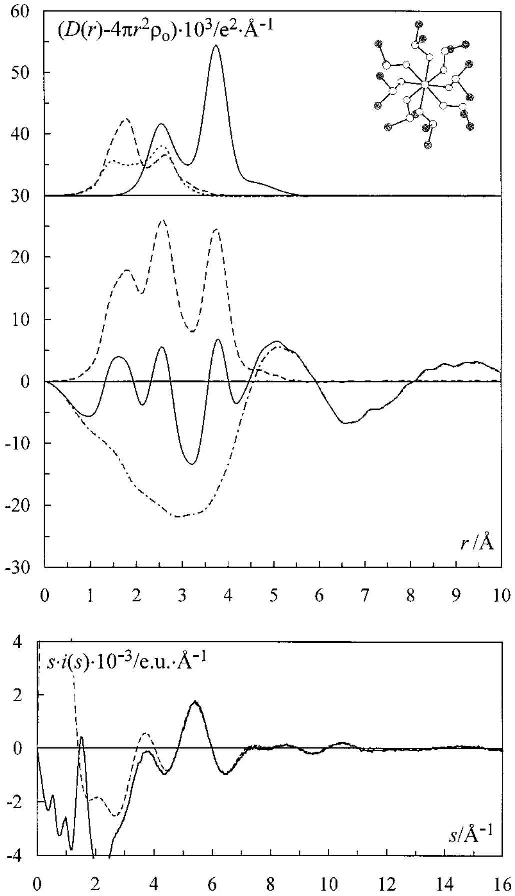

Figure 4. LAXS for 0.75 mol·dm^{-3} lanthanum(III) trifluoromethanesulfonate in dimethyl sulfoxide solution: (upper) separate model contributions with parameters from Table 2 (solid line, first (La−O$_I$) and second (La···O$_{II}$) hydration spheres; dashes, hydrated perchlorate ion; dots, bulk dimethyl sulfoxide); (middle) radial distribution functions, $D(r) - 4\pi r^2\rho_o$, and the sum of the calculated peak shapes (solid line, experimental; dashes, model; dots, difference experimental − model function); (lower) structure-dependent LAXS intensity functions multiplied by the scattering variable, $si(s)$ versus s (solid line, experimental data; dashes, model function).

The RDF of the dimethyl sulfoxide solution of lanthanum(III) trifluoromethanesulfonate has three well-defined peaks at 1.4, 2.5, and 3.7 Å. The first distance corresponds to the Cl−O bond distance within the tetrahedral perchlorate ion for which the O···O distances give a contribution at 2.4 Å. The major contributions to the peaks at 2.5 and 3.7 Å are the La−O bond and La···S distances within the dimethyl sulfoxide-solvated lanthanum(III) ion, respectively. No significant preference could be found for the two models tested, tricapped trigonal prism and square antiprism. Assuming eight-coordination, the La−O bond and La···S distances were refined to 2.50(2) and 3.725(6) Å, respectively, giving an La−O−S angle of 134(2)°, see Table 3 and Figure 4, which is in acceptable agreement with the results obtained by EXAFS. The fit with a tricapped trigonal prismatic model resulted in La−O bond distances ca. 0.03 Å shorter than in the hydrate, indicating that nine-coordination seems unlikely.

***N,N′*-Dimethylpropyleneurea-Solvated Lanthanum(III) Ion.** The *N,N′*-dimethylpropyleneurea-solvated lanthanum(III) ion has only been studied by EXAFS in solution because the solubility is too low for LAXS studies. Furthermore, it has not been possible to crystallize any solid salt of lanthanum(III) ions solvated by *N,N′*-dimethylpropyleneurea with the anions tested, trifluoromethanesulfonate, perchlorate, and iodide. The curve-fitting of the EXAFS data resulted in La−O and La···C distances of 2.438(4) and 3.410(12) Å, respectively (cf. Figure 2; separate contributions from the different scattering paths are given in Figure S2). The size of the oxygen atom in the coordinated water molecule has been estimated to be 1.34 Å.[38] By applying this size to the oxygen atoms of coordinated water, dimethyl sulfoxide, *N,N*-dimethylformamide, and *N,N′*-(dimethylpropylene)urea, together with the ionic radii of the scandium, yttrium, and lanthanum(III) ions given by Shannon for different coordination numbers, an excellent agreement with the experimentally observed M−O bond distances is observed;

Table 4. M−O Bond Distances, d/Å, and Proposed Solvation Numbers of the Lanthanum(III), Scandium, and Yttrium Ions in Different Solvents, Determined by EXAFS and/or LAXS Methods[a]

solvent	D_{N}	$d(\mathrm{La-O})_{\mathrm{obsd}}$	$d(\mathrm{La-O})_{\mathrm{calcd}}$	n	$d(\mathrm{Sc-O})_{\mathrm{obsd}}$	$d(\mathrm{Sc-O})_{\mathrm{calcd}}$[b]	n	$d(\mathrm{Y-O})_{\mathrm{obsd}}$	$d(\mathrm{Y-O})_{\mathrm{calcd}}$[c]	n	ref
water	18.0	2.52(2), 2.65(3)	2.55	6 + 3	2.19(1)	2.21	∼8	2.366(5)	2.36	8	*d*, 37, 40
water	18.0	2.545(2)	2.55	9	2.18(1)	not given	7	2.353(3)	2.36	8	11, 41, 42
DMSO	29.8	2.504(3)	2.50	8	2.085(4)	2.085	6	2.360(3)	2.36	8	*d*, 37, 43
DMF	26.6	2.4855(7)	2.50	8				2.347(3)	2.36	8	11, 43
DMA	27.8	2.4745(8)	2.50	8							11
DMPU		2.438(4)	2.44	7	2.084(4)	2.085	6	2.242(3)	2.24	6	*d*, 37, 43

[a] The donor numbers D_{N} are taken from ref 39. The calculated M−O bond distances are obtained by adding the ionic radius of an ion with a certain coordination number given by Shannon, ref 15, and the radius of the oxygen atom in a coordinated water molecule, 1.34 Å, ref 38; this oxygen radius has also been applied for the other oxygen donor solvents given here. [b] The calculated Sc−O bond distance in eight-coordination is 2.21 Å; ionic radii for the scandium ion in seven- and nine-coordination are not given. [c] The calculated Y−O bond distance in seven-coordination is 2.30 Å. [d] This work.

see Table 4. From this comparison the La−O bond distance in the *N*,*N*′-dimethylpropyleneurea-solvated lanthanum, 2.44 Å, strongly indicates seven-coordination. It is not possible from these studies to determine whether the seven-coordination has a well-defined configuration or not; possible geometric figures in seven-coordination are pentagonal bipyramid (D_{5h} symmetry), monocapped octahedron (C_{3v}), and monocapped trigonal prism (C_{2v}). To our knowledge, no reliable report of a seven-coordinated solvate with only solvent molecules in the inner coordination sphere has been given so far in the solid state. The decrease in the coordination number as compared to other oxygen donor solvents is certainly due to the bulkiness of the *N*,*N*′-dimethylpropyleneurea molecule. The La···C distance of 3.410(12) Å gives an La−O−C angle of 131(2)°, which is in good agreement with the mean value of the three-leg La−O−C and the four-leg La−O−C−O scattering paths, 3.66(3) Å (Table 2), assuming the O−C bond distance to be 1.27 Å in coordinated *N*,*N*′-dimethylpropyleneurea molecules.[36] The solid-state structures of the *N*,*N*′-dimethylpropyleneurea-solvated bismuth(III), calcium, yttrium, and scandium ions shows that the M−O−C bond angle increases with decreasing metal ion radius; all these complexes are six-coordinated with M−O bond distances and M−O−C bond angles of 2.32 Å and 150°,[36] 2.32 Å and 163°, 2.22 Å and 169°, and 2.07 Å and 172°,[37] respectively. The La−O−C bond angle observed in this study, 131°, should therefore be representative of a system without significant steric hindrance between the *N*,*N*′-dimethylpropyleneurea ligands.

Conclusions

The solvated lanthanum(III) ion has different coordination numbers and figures in the three oxygen donor solvents water, dimethyl sulfoxide, and *N*,*N*′-(dimethylpropylene)urea, i.e., nine-coordination in a tricapped trigonal prism, eight-coordination in an assumed square antiprism, and a seven-coordinated solvate for which the configuration has not been established, respectively. Table 4 shows correlations between coordination numbers and the La−O distances including the previously studied oxygen donor solvents *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide,[10,11] for which solvation numbers of eight were proposed. However, of the three solvents dimethyl sulfoxide, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide, the shortest La−O mean bond distance is found for *N*,*N*-dimethylacetamide, although their donor numbers are similar (cf. Table 4). Since the steric ligand−ligand repulsion should be stronger for *N*,*N*-dimethylacetamide than for *N*,*N*-dimethylformamide,[10,11] this indicates a possible mean solvation number of less than eight for *N*,*N*-dimethylacetamide. The donor number introduced by Gutmann[44] empirically accounts for the Lewis basicity of the solvents toward Lewis acids of medium to hard character.[45] The lanthanide(III) ions are classified as hard Lewis acids.[11] The steric effects displayed by the ligands around the lanthanum(III) ion in bulky organic solvents have important consequences not only for the structure but also for the thermodynamic formation energies and ligand exchange mechanisms.

Acknowledgment. We gratefully acknowledge the Swedish Natural Science Research Council for financial support and the SSRL for allocation of beam time and laboratory facilities. SSRL is operated by the Department of Energy, Office of Basic Energy Sciences. The SSRL Biotechnology Program is supported by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and by the Department of Energy, Office of Biological and Environmental Research. We thank BASF, Ludwigshafen, Germany, for a gift of *N*,*N*′-dimethylpropyleneurea.

Supporting Information Available: Figure S1 showing the normalized absorption edges of the samples studied by EXAFS, Figure S2 displaying the fits of the experimental EXAFS data with models formed by ab initio calculated scattering paths from the program FEFF of all studied samples, and Figure S3 showing the experimental and calculated Fourier transforms (FTs) of samples studied by EXAFS experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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