Solvation of the Bismuth(III) Ion by Water, Dimethyl Sulfoxide, *N,N′*-Dimethylpropyleneurea, and *N,N*-Dimethylthioformamide. An EXAFS, Large-Angle X-ray Scattering, and Crystallographic Structural Study

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The structure of the solvated bismuth(III) ion in aqueous, dimethyl sulfoxide, *N,N′*-dimethylpropyleneurea, and *N,N*-dimethylthioformamide solution has been studied by means of EXAFS and large-angle X-ray scattering (LAXS). The crystal structures of the solid compounds octakis(dimethyl sulfoxide)bismuth(III) perchlorate, $[Bi(OS(CH_3)_2)_8](ClO_4)_3$, hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) perchlorate, $[Bi(OCN_2(CH_2)_3(CH_3)_2)_6](ClO_4)_3$, and nonaaquabismuth(III) trifluoromethanesulfonate, $[Bi(H_2O)_9](CF_3SO_3)_3$ (redetermination), have been determined. The aqueous solutions must be strongly acidic, since the hydrated bismuth(III) ion starts to hydrolyze into $Bi_6O_4(OH)_4^{6+}$ complexes already at an excess of strong acid at 1.0 mol·dm^{-3}. For very acidic aqueous perchlorate solutions, the LAXS and EXAFS data gave a satisfactory fit for eight-coordination of the bismuth(III) ion, with a mean Bi−O bond distance of 2.41(1) Å. The crystal structure of octakis(dimethyl sulfoxide)bismuth(III) perchlorate shows that the bismuth(III) ion coordinates eight dimethyl sulfoxide molecules via the oxygen atoms in a distorted square antiprismatic configuration. The mean Bi−O bond distance is 2.43 Å and the mean Bi···S distance 3.56 Å. For the dimethyl sulfoxide solution, the corresponding mean distances were found to be 2.411(6) and 3.535(12) Å. The *N,N′*-dimethylpropyleneurea-solvated bismuth(III) ion is octahedrally coordinated in both solid state and solution with the Bi−O bond distances of 2.324(5) and 2.322(3) Å, respectively. The bismuth(III) ion is six-coordinated in the sulfur donor solvent *N,N*-dimethylthioformamide with a mean Bi−S bond distance of 2.794(8) Å. A comparison with the structure of the solvated lanthanum(III) ion shows that the bismuth(III) ion is smaller for all coordination numbers. New effective ionic radii for the bismuth(III) ion in different coordination numbers are proposed, based on results in this study and in the literature.

Introduction

The bismuth(III) ion hydrolyzes very easily in aqueous solution. In solutions with a total bismuth(III) concentration higher than about 0.1 mol·dm^{-3}, high acidity with a 2−3 mol·dm^{-3} excess of strong acid is required to avoid hydrolysis. The reported aqueous chemistry of bismuth(III) is therefore dominated by hydrolysis studies and structure determinations of hydrolysis products.[1]

The existence of polynuclear bismuth(III) hydrolysis complexes with an assumed general formula of $Bi_nO_{n-1}^{(n+2)+}$ was recognized early.[2] Later, the composition of $Bi_6(OH)_{12}^{6+}$ was proposed from a number of studies.[1] Olin showed conclusively in a series of carefully conducted potentiometric studies in the bismuth(III) concentration range of 0.1−50 mmol·dm^{-3} at an ionic strength of 3 mol·dm^{-3} (ionic medium $NaClO_4$) that the dominating species is a hexamer with the general composition $Bi_6O_n(OH)_{12-2n}^{6+}$, with a minor trace of the monomer $Bi(OH)^{2+}$.[3] An ambiguity still existed for the oxygen atom arrangement and water content of the hydrolyzed hexameric species. Even though an early large-angle X-ray scattering (LAXS) study showed an octahedral arrangement of the six bismuth(III) ions, it was not possible to localize the oxygen atoms.[4] Two crystal structures of the nitrate and perchlorate salts[5,6] were found to contain hexameric $Bi_6O_4(OH)_4^{6+}$ entities with the Bi···Bi distances in the ranges of 3.607−3.754 and 3.633−3.726 Å, respectively. The mean Bi−O bond distances are 2.16 and 2.40 Å, for the bridging oxide and hydroxide groups, respectively.[5,6] It was later confirmed by a LAXS study that the predominating hexameric species in aqueous solution is the $Bi_6O_4(OH)_4^{6+}$ complex, with structural parameters very similar to those in the solid state.[7]

The first reported structure of a monomeric hydrated bismuth(III) ion was the crystal structure of nonaaquabismuth(III) trifluoromethanesulfonate, $[Bi(H_2O)_9](CF_3SO_3)_3$, determined at −140 °C.[8] The compound, which is isostructural with the nonaaqualanthanide(III) trifluoromethanesulfonates,[9,10] consists of discrete $[Bi(H_2O)_9]^{3+}$ and $CF_3SO_3^-$ ions. The nine-coordinated

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water molecules form a tricapped trigonal prism around the bismuth(III) ion with the Bi−O bond distances of 2.448 Å for the six oxygen atoms in the prism and 2.577 Å for the three oxygen atoms capping the rectangular surfaces of the prism. In the current work, a redetermination was performed at room temperature to provide model parameters for comparisons with the EXAFS investigations on aqueous solutions. Our attempts to solve the crystal structure of hexaaquabismuth(III) perchlorate, $Bi(OH_2)_6(ClO_4)_3$, failed, since suitable crystals could not be obtained from the very acidic solutions without coprecipitation of perchloric acid hydrate.

It is noteworthy, however, that the hydrated bismuth(III)[8] and hydrated lanthanide(III) ions[9−11] do have different hydration numbers in their perchlorate and trifluoromethanesulfonate salts. To investigate the structure of the hydrated bismuth(III) ion in aqueous solution, we compared EXAFS measurements on acidic aqueous solutions of bismuth(III) perchlorate and bismuth(III) trifluoromethanesulfonate with those of the solid nonaaquabismuth(III) trifluoromethanesulfonate, and we carried out LAXS studies on four aqueous solutions with somewhat different compositions.

To investigate the coordination of the bismuth(III) ion in nonaqueous solvents, we determined by EXAFS and/or LAXS methods the structure of the solvated bismuth(III) ion in the oxygen donor solvents dimethyl sulfoxide and *N,N*′-dimethylpropylene urea and in the sulfur donor solvent *N,N*-dimethylthioformamide. The crystal structures of the solid solvates of bismuth(III) perchlorate with dimethyl sulfoxide and *N,N*′-dimethylpropylene urea have been determined to provide models for analyzing the solution data.

Dimethyl sulfoxide is an aprotic ambidentate solvent. However, coordination via the sulfur atom takes place only for soft metal ions, e.g., palladium(II), platinum(II), and rhodium(III),[12] and the relatively hard bismuth(III) ion is strongly solvated via the oxygen atom. A recent crystal structure study of octakis(dimethyl sulfoxide)bismuth(III) nonaiodobismuthate(III) shows that the bismuth(III) ion is surrounded by eight oxygen atoms arranged in a distorted dodecahedral configuration.[13] Several of the coordinated dimethyl sulfoxide molecules are disordered with alternative sulfur positions. The mean Bi−O bond distance is 2.43 Å (range of 2.35−2.49 Å, probably affected by the disorder to some extent), and the mean Bi−O−S angle is 144°, within a large range of 119−153°.

N,N′-Dimethylpropyleneurea is an oxygen donor solvent. The rather bulky structure of the molecule requires a large space during coordination. Due to steric reasons, most metal ions attain a lower coordination number when solvated by *N,N*′-dimethylpropyleneurea than by dimethyl sulfoxide or than when hydrated.[14] The hexakis(*N,N*′-dimethylpropyleneurea)bismuth(III) cation has been structurally characterized in the solid state in the dodecaiodotribismuthate(III) salt. The Bi−O bond distance was found to be 2.312 Å for an almost regular octahedral coordination of six *N,N*′-dimethylpropyleneurea molecules.[15]

N,N-Dimethylthioformamide is a solvent with high permittivity and some hydrogen bonding ability,[16a,b] allowing highly charged species to be dissolved without ion-pair formation, which is an unusual property for a sulfur donor solvent. The structure of the *N,N*-dimethylthioformamide-solvated bismuth(III) ion (with perchlorate as counterion) has only been studied in solution by means of EXAFS, since attempts to precipitate crystals gave orthorhombic sulfur. When anhydrous bismuth(III) trifluoromethanesulfonate is dissolved in *N,N*-dimethylthioformamide, the solution becomes intensively red; this most probably indicates a reduction of bismuth(III) to bismuth(I). Preliminary EXAFS results of this solution gave a Bi−S bond distance of about 2.88 Å with a low coordination number, about two.

A few coordination compounds in which bismuth(III) only coordinates sulfur atoms have been structurally characterized, e.g., tris(diethyldithiophosphinato)bismuth(III),[17]tris(diethylpropyldithiophosphinato)bismuth(III) benzene,[18] and tris(diisopropyldithiophosphinato)bismuth(III).[19] All these complexes have distorted octahedral coordination geometry with the mean Bi−S bond distances of 2.804, 2.788, and 2.788 Å, respectively. The structure determination of bismuthinite, Bi_2S_3, revealed two seven-coordinated bismuth sites with different coordination figures, for which the three shortest Bi−S distances (in the range of 2.54−2.76 Å) form a trigonal pyramid with bismuth in the apex position.[20]

Experimental Section

Preparation of Samples. Nonaaquabismuth(III) trifluoromethanesulfonate, $[Bi(H_2O)_9](CF_3SO_3)_3$, was prepared by refluxing an aqueous slurry of bismuth(III) oxide (Fluka) and trifluoromethanesulfonic acid (Riedel-de-Haën, purum) for 3 h. When a clear liquid phase was obtained, the excess of bismuth(III) oxide was filtered off. The concentration of excess trifluoromethanesulfonic acid was kept at 2−3 $mol\cdot dm^{-3}$ to minimize hydrolysis. Crystals were obtained from a highly concentrated solution at room temperature. The density of the crystals was determined by the floatation method.[21] Anhydrous bismuth(III) trifluoromethanesulfonate was prepared by drying one part of the solution in an oven at 190 °C for 1 week. This compound was dissolved in freshly distilled dimethyl sulfoxide (Merck), *N,N*′-dimethylpropylene urea (BASF), and *N,N*-dimethylthioformamide; the synthesis of *N,N*-dimethylthioformamide has been described elsewhere.[22] The aqueous bismuth(III) perchlorate solutions were prepared by refluxing an excess (2−3 $mol\cdot dm^{-3}$) of perchloric acid (AnalR, 70%) with a bismuth(III) oxide−water slurry until clearness, and then filtering off undissolved Bi_2O_3. Crystals of the hydrated bismuth(III) perchlorate, $Bi(OH_2)_6(ClO_4)_3$, precipitated when a highly concentrated solution was cooled, and the crystals were used to prepare solvates of dimethyl sulfoxide and *N,N*′-dimethylpropylene urea. After being dried in a vacuum desiccator, the salt was dissolved in acetone, and 2,2-dimethoxypropane (Merck) was added to the solution in a stoichiometric ratio to react with water, forming acetone and methanol.[23] Six equivalents of dimethyl sulfoxide or *N,N*′-dimethylpropyleneurea was added to this mixture, which was stirred for 5 min, and the volume was thereafter reduced to ca. 50% by evaporation. Hexakis(dimethyl sulfoxide)bismuth(III) perchlorate precipitated directly upon cooling, while the *N,N*′-dimethylpropylene urea solvate started to precipitate after several weeks of storage. The hexakis(*N,N*′-dimethylpropyleneurea)bismuth(III) perchlorate loses solvent molecules and/or decomposes when exposed to air. When the hexakis(dimethyl sulfoxide)bismuth(III) perchlorate was

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Table 1. Concentrations (mol·dm^{-3}), Densities (ρ), and Linear Absorption Coefficients (μ) of the Aqueous Dimethylsulfoxide (Me_2SO), *N,N′*-Dimethylpropylene Urea (DMPU), and *N,N*-Dimethylthioformamide (DMTF) Solutions Used in the EXAFS and/or LAXS Measurements

sample	label	[Bi^{3+}]	[X^-]	[H^+]	[solvent]	ρ (g·cm^{-3})	μ (cm^{-1})
$Bi(ClO_4)_3$ in water^{a,b}	Biaq1	0.662	3.856	1.870	46.84	1.366	19.51
$Bi(ClO_4)_3$ in water^{b}	Biaq2	0.800	5.100	2.700	38.50	1.371	23.39
$Bi(CF_3SO_3)_3$ in water^{b}	Biaq3	0.800	3.200	0.800	36.16	1.297	22.38
$Bi(CF_3SO_3)_3$ in water^{b}	Biaq4	1.134	3.902	0.500	35.82	1.464	31.09
$Bi(ClO_4)_3$ in $Me_2SO^{a,b}$		0.40	1.20		12.35	1.164	12.68
$Bi(CF_3SO_3)_3$ in DMPU^{a}		0.10	0.30		7.92	1.081	3.41

[a] EXAFS. [b] LAXS.

recrystallized in dimethyl sulfoxide, octakis(dimethyl sulfoxide)bismuth(III) perchlorate was obtained. No crystals were formed from solutions of bismuth(III) trifluoromethanesulfonate in *N,N′*-dimethylpropyleneurea. An attempt to crystallize an *N,N*-dimethylthioformamide solvate of bismuth(III) perchlorate resulted in the formation of elemental sulfur, as with the other three-valent metal ions studied previously in this laboratory. The bismuth(III) content of both solids and solutions was analyzed by EDTA titration using pyrocatecholviolet as the indicator.[24] The composition of the studied solutions is given in Table 1, and the bismuth(III) content in the solids is in close agreement with the given composition.

Warning! Organic solvates of perchlorate salts are powerful explosives and should be handled with great caution.[25,26]

EXAFS. Bi−L(III)-edge X-ray absorption data were collected in transmission mode using 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. A Si[220] double monochromator was detuned to 50% of the maximum intensity at the end of the scans to remove higher-order harmonics. The solutions were kept in cells with Mylar 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 was performed by simultaneously recording a bismuth foil and assigning its first L(III)-edge inflection point to 13 422 keV.[27] Typically, 3−4 scans of the solutions and 2−3 scans of the solids were recorded, energy calibrated, and averaged. The EXAFS functions were extracted using standard procedures for pre-edge subtraction, spline removal, and data normalization.[28] To obtain quantitative information, the k^3-weighted EXAFS oscillations were analyzed by a nonlinear least-squares fitting procedure of the model parameters. All data treatment was performed by means of the EXAFSPAK program package.[29] The *k*-range used in the analysis was typically 2−12 Å^{-1} for the solids and 2−10.5 Å^{-1} for the solutions. Model fitting was performed using theoretical phase and amplitude functions, including single back-scattering and multiple-scattering paths, calculated by the ab initio code FEFF (version 6.01).[30] The shifts of the threshold energy, $\Delta E°$, and the amplitude reduction parameter, S_o^2, were obtained by using the solid nonaaquabismuth(III) trifluoromethanesulfonate as the model compound for the EXAFS analyses. All calculations and refinements have been performed on deglitched EXAFS raw data.

When the spectrum of a solution was similar to that of the corresponding solvated solid compound, the crystal structure was used to derive a starting model for describing the structure in solution with a mean Bi−O bond distance (in nine-coordination two Bi−O bond distances) and an ideal configuration, as in the case of dimethylsulfoxide. However, if these spectra differ significantly as in the case of water, theoretical EXAFS functions were calculated with the FEFF program for a number of possible model configurations and compared with the experimental EXAFS spectrum. The model giving the best fit to the experimental data was used as the starting model. The coordination number was held fixed in these calculations mainly for three reasons: (a) the number of distances, the amplitude reduction factor, and the Debye−Waller factor are strongly correlated, (b) a solvated metal ion in solution always has a well-defined coordination number, and (c) the multiple scattering pattern within the first coordination sphere is often specific for a certain configuration. Such structural parameters should therefore not be refined together with coordination numbers (no example of a metal solvate in solution with large amounts of two configurations present at the same time has been presented so far). Furthermore, the coordination number is strongly correlated to the Bi−O bond distance: six-octahedral configuration, d(Bi−O) ≈ 2.31 Å;[15] eight-square antiprismatic or dodecahedral configuration, d(Bi−O) ≈ 2.43 Å;[13] nine-tricapped trigonal prismatic configuration, d(Bi−O) ≈ 6 × 2.45 + 3 × 2.58 Å (mean 2.49 Å).[8] The differences in ionic radius between five- and six-coordinated bismuth(III) ions and between six- and eight-coordinated bismuth(III) ions are reported by Shannon to be 0.06 and 0.14 Å, respectively.[31] Models with eight-coordinated bismuth(III) ions and six- and three-coordinated bismuth(III) ions were tested on the EXAFS data for a complex with a mean Bi−O bond distance longer than 2.4 Å, and for the Bi−O bond distances close to 2.3 Å, five- and six-coordinated models were used. The model with the best fit to the experimental data was selected as the final one.

Large-Angle X-Ray Scattering. A $\theta-\theta$ diffractometer was used to measure the scattering of Mo Kα radiation, $\lambda = 0.7107$ Å, from the free surface of aqueous and dimethyl sulfoxide solutions of bismuth(III) salts in an open Teflon cup. After inducing monochromatization via a focusing LiF crystal, we accumulated 100 000 counts at 450 fixed θ-values in the range of $1 < \theta < 65°$. The entire range of the scattering angle, 2θ, was scanned twice, which corresponds to a statistical error of about 0.3% in the measured intensity values. The divergence of the primary X-ray beam was limited by a 1°, 1/4°, or 1/12° slit for different θ ranges, with an overlap for scaling purposes. The experimental setup and the data treatment procedure, carried out by means of the KURVLR program,[32] have been described previously.[33] The experimental intensities were normalized to a stoichiometric unit of volume containing one bismuth atom using the scattering factors f for neutral atoms, with corrections for anomalous dispersion, $\Delta f'$ and $\Delta f''$,[21] and the calculated Compton scattering.[34] Least-squares refinements of the model parameters were carried out by the STEPLR program,[35] where the expression $U = \sum s^2[i_{\exp}(s) - i_{\mathrm{calc}}(s)]^2$ is minimized. Since the models describe distinct atomic pair interactions, only the data in the high s-region, $s > 4$ Å^{-1}, where the intensity contribution from the diffuse and long-

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Table 2. Crystallographic Data for Bismuth Solvates

chemical formula	$[Bi(H_2O)_9](CF_3SO_3)_3$	$[Bi((CH_3)_2SO)_8](ClO_4)_3$	$[Bi((CH_3)_2N_2(CH_2)_3CO)_6](ClO_4)_3$
formula wt (g·mol^{-1})	818.24	1132.40	1276.38
temp (°C)	20 ± 2	20 ± 2	20 ± 2
wavelength (Å)	0.7107 (Mo Kα)	0.7107 (Mo Kα)	0.7107 (Mo Kα)
space group	$P6_3/m$ (No. 176)	$P2_1/m$ (No. 11)	$P1$ (No.1)
a (Å)	13.837(2)	12.672(3)	14.4290(10)
b (Å)		19.438(4)	14.4264(10)
c (Å)	7.4070(10)	18.510(4)	14.4206(10)
α (deg)	90	90	103.9390(10)
β (deg)	90	100.86(3)	103.9280(10)
γ (deg)	120	90	103.9360(10)
vol (Å^3)	1228.3(4)	4477(15)	2681.7(3)
Z	2	4	2
ρ_{obsd} (g·cm^{-3})			1.717
ρ_{calcd} (g·cm^{-3})	2.213	1.680	1.581
μ (cm^{-1})	75.70	45.50	35.13
R_{int}	0.0483	0.0817	0.0462
R indices R1, wR2 [$I > 2*(I)$]^{a,b}	0.0288, 0.0331	0.0569, 0.1159	0.0656, 0.1772
R indices R1, wR2 [all data]	0.0486, 0.0417	0.1575, 0.1463	0.1794, 0.2197

^{a} SHELXTL: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|F_o|)^2]^{1/2}$; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o$. ^{b} $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$.

range distances can be neglected, are included.[33,36] Prior to the refinements, a Fourier back-transformation procedure, removing spurious nonphysical peaks below 1.2 Å in the experimental modified radial distribution function (RDF), was used to obtain a better alignment of the $i_{exp}(s)$ intensity function.[37] The initial model parameters for the structure of the hydrated perchlorate ion were taken from previous studies.[38] For the LAXS data of the hydrated and dimethyl sulfoxide-solvated bismuth(III) ions, at least two structural models with different configurations, the tricapped trigonal prism and the square antiprism, have been tested. Finally, the refined models obtained from the EXAFS and LAXS studies were compared. In this study, the results from both techniques were in agreement for all systems studied.

Crystallography. Single crystals of the bismuth(III) solvates were carefully selected and mounted in a capillary tube, which was sealed with melting glue. For nonaaquabismuth(III) trifluoromethanesulfonate, a Syntex $P2_1$ diffractometer was used to collect a unique data set within $0 < 2\theta < 60°$ in the ω-scan mode. A Bruker three-circle diffractometer with CCD detection[39] was used for the data collection of the octakis(dimethyl sulfoxide)bismuth(III) perchlorate and hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) perchlorate crystals. All reflections were collected around the hemisphere for $0 < 2\theta < 57°$. The crystallographic data are summarized in Table 2.

The data treatment of the nonaaquabismuth(III) trifluoromethanesulfonate was made by means of the SHELXTL PLUS program in its PC version.[40] After an empirical absorption correction,[41] the initial refinement gave an extinction coefficient equal to zero. The final residuals at convergence are R = 0.0288 and R′ = 0.0331, with the reflection weight being $[\sigma^2(F) + 0.0004F^2]$. The hydrogen atoms were located by means of Fourier difference maps.

The least-squares refinements of octakis(dimethyl sulfoxide)bismuth(III) perchlorate and hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) perchlorate were made by means of the SHELXTL-97 program in PC version,[41] and the SADABS program was used for absorption corrections.[42] For octakis(dimethyl sulfoxide)bismuth(III) perchlorate, the extinction coefficient was refined to 0.00186(12). After absorption corrections, the refinements converged, with the final residuals R1 = 0.0569 and wR2 = 0.1159. The reflection weight is $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, $a = 0.0689$, and $b = 0.10$. For hexakis(*N,N′*-dimethylpropylene urea)bismuth(III) perchlorate, all reflections were corrected for absorption, and no extinction coefficient was introduced. The final residuals at convergence were R1 = 0.0656 and wR2 = 0.1772, with the reflection weight being the same as for octakis(dimethyl sulfoxide)bismuth(III) perchlorate.

Results and Discussion

The XANES region of the XAS spectra is not sensitive to the different coordination geometries of the bismuth(III) solvates studied in this work (see Figure S1 in the Supporting Information; an "S" denotes Supporting Information). The methodology of the treatment of EXAFS data and the different models tested for each system are described in the Experimental Section.

Hydration and Hydrolysis of Bismuth(III). The redetermination of the crystal structure of $[Bi(OH_2)_9](CF_3SO_3)_3$ at room temperature gave a result consistent with the low-temperature study reported earlier.[8] Crystallographic data are given in Table 2, with fractional atomic coordinates, equivalent isotropic displacement coefficients, and the bond distances and angles given in Tables S1 and S2. The bismuth(III) ion coordinates nine water molecules, which form a tricapped trigonal prism (see Figure 1). The Bi−O(2) bond distance with the water oxygen atoms in the prism is 2.435(2) Å, and the O(2)−Bi−O(2) angle is 91.5°. The remaining three water molecules are capping the rectangular surfaces of the prism at a markedly longer Bi−O(1) bond distance, 2.595(6) Å, with the O(1)−Bi−O(1) angle of 120°. The bond distances and angles within the trifluoromethanesulfonate ion are in good agreement with earlier reported values.[43] There are three different O···(H)−O hydrogen bond distances in the structure, all between those of a water molecule coordinated to bismuth and an oxygen atom in an adjacent trifluoromethanesulfonate ion. The O(2) atom in the prism forms bifurcated hydrogen bonds to the O(a) and O(b) atoms in two different trifluoromethanesulfonate ions, with the O···O distances of 2.765(4) and 2.816(6) Å and the O−H−O angles of 158.8(7.7)° and 163.7(3.4)°, respectively. The third and longest hydrogen bond, O(1)···O(b) 2.942(5) Å, is formed between the capping water molecule and a trifluoromethanesulfonate oxygen atom, with an O−H···O angle of 166.0(4.1)°.

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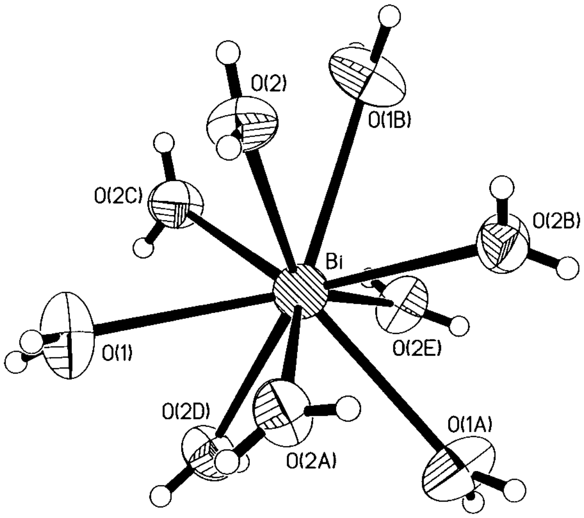

Figure 1. Tricapped trigonal prismatic structure of the $[Bi(OH_2)_9]^{3+}$ ion in the solid $[Bi(OH_2)_9](CF_3SO_3)_3$.

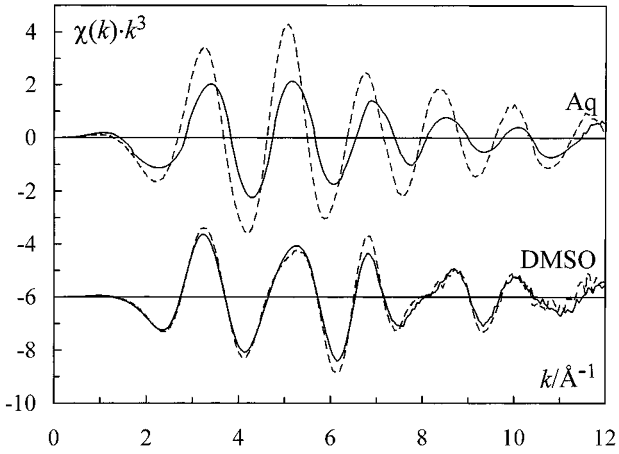

Figure 2. EXAFS spectra of the solvated bismuth(III) ion in aqueous and dimethyl sulfoxide solution (dashed lines) compared with EXAFS spectra of the solid solvates (solid lines) $[Bi(OH_2)_9](CF_3SO_3)_3$ and $[Bi(Me_2SO)_8](ClO_4)_3$.

In the present study, we have used a large excess of strong acid, perchloric or trifluoromethanesulfonic acid, of 1.0−2.0 mol·dm^{-3} to suppress the hydrolysis more or less completely. This gives a high perchlorate concentration, 4−5 mol·dm^{-3} (Table 1), and the LAXS data indicate that one or two perchlorate ions enter the inner coordination sphere (see below). Comparisons of the EXAFS spectra of the solid nonaaquabismuth(III) trifluoromethanesulfonate and an acidic aqueous solution of bismuth(III) perchlorate show significant differences, indicating different structures of the hydrated bismuth(III) ion in the acidic aqueous solution and in the solid state (see Figure 2). The mean Bi−O bond distance of the aqueous bismuth(III) perchlorate solution was found to be almost 0.1 Å shorter than the mean Bi−O bond distance in solid nonaaquabismuth(III) trifluoromethanesulfonate, 2.49 Å, and no peak was found in the Fourier transformation corresponding to the Bi···Bi distances in the dominating hydrolysis product, $Bi_6O_4(OH)_4^{6+}$ (see Figure S2).[4−7] The obtained Bi−O bond distance indicates eight-coordination, since the mean Bi−O bond distance in the dodecahedral configuration is close to 2.43 Å[13] while six-coordinated octahedral bismuth(III) complexes have a Bi−O bond distance close to 2.32 Å.[15] Theoretical EXAFS parameters calculated by the FEFF program, assuming square antiprismatic configuration around the bismuth(III) ion, were used in the curve-fitting procedure. The Bi−O bond distance was refined to 2.408(5) Å (see Table 3). The amplitude of the EXAFS function of solid nonaaquabismuth(III) trifluoromethanesulfonate is almost twice that for the aqueous solution of bismuth(III) perchlorate (see Figure 2). This is because the Debye−Waller parameter for the six Bi−O distances in the prism of the tricapped trigonal prismatic configuration, $\sigma^2 = 0.0072$ Å^2, is much smaller than for Bi−O in the aqueous solution, 0.013 Å^2. This shows that the distribution of the Bi−O bond distances is much wider in the eight-coordinated configuration than in the prism, despite the similar Bi−O bond distances. The fit of the model function is shown in Figure 3, and the contributions from the individual scattering paths are given in Figure S3.

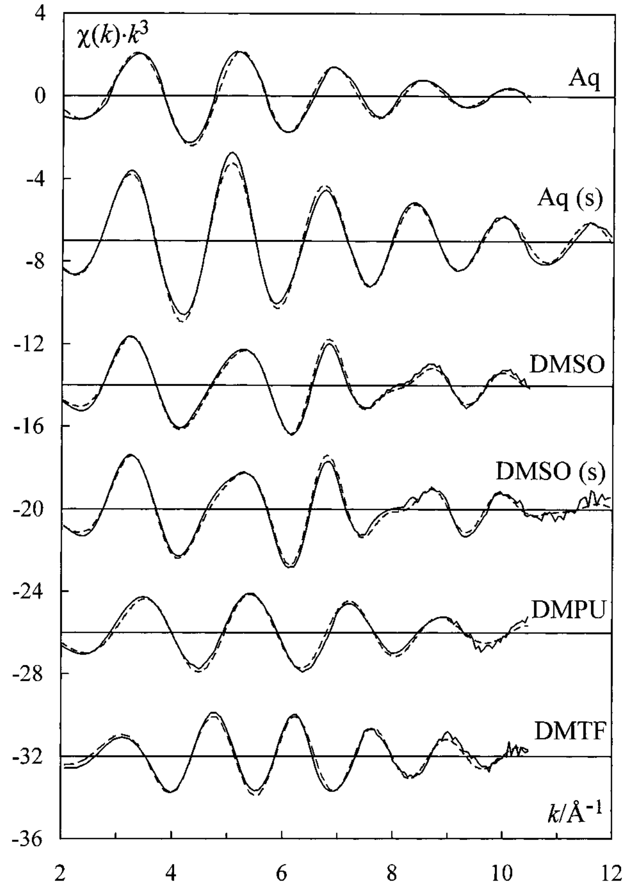

Figure 3. Experimental EXAFS data (solid lines) fitted with a model (Table 3) formed by ab initio-calculated scattering paths from the FEFF program (dashed lines).

Four aqueous solutions of bismuth(III) perchlorate or trifluoromethanesulfonate with varying excesses of corresponding strong acid have been studied by means of LAXS (see Table 1). Two of the solutions, Biaq1 (Figure 4) and Biaq2, with different excess amounts of perchloric acid, were found not to contain any measurable amount of hydrolysis products. The other two aqueous solutions, Biaq3 (Figure 5) and Biaq4, show features at about 3.7 Å in their radial distribution functions corresponding to Bi···Bi distances in the hexameric hydrolysis product $Bi_6O_4(OH)_4^{6+}$.[7] Thus, they are partly hydrolyzed despite the excess of about 1 mol·dm^{-3} strong acid (see Table 1).

Three well-defined peaks at 1.4, 2.4, and 4.5 Å were found in the RDFs of the aqueous bismuth solutions Biaq1 and Biaq2 (cf. Figures 4 and S3). The peak at 1.4 Å corresponds to the Cl−O bond distance in the perchlorate ion. The main peak at 2.4 Å consists of at least two contributions, the mean Bi−O$_I$ bond distance to the first hydration shell and the O···O distance

Table 3. Mean Bond Distances (d), Displacement Parameters ($l = 2\sigma$ for EXAFS or σ for LAXS), Number of Distances (N), and the Shifts in the Threshold Energy in the EXAFS Studies (ΔE_0/eV) of the Solvated Bismuth(III) and Lanthanum(III) Ions in Solid and Solution, As Determined Crystallographically (C) and by EXAFS (E) and LAXS (L) at Room Temperature

solvent	state	interaction	N	d(Bi−X) (Å)	l (Å)	ΔE_0	d(La-X) (Å)	l (Å)	Δd (Å)	method	ref
water	solid[a]	M−O	6	2.435(2)			2.519		0.084	C	this work, 11
		M−O	3	2.595(6)			2.619		0.024		
	solid[a]	M−O	6	2.435	0.17(1)	−14.6(2)	2.519	0.13(1)	0.064[a]	E	this work, 44
		M−O	3	2.595	0.20(2)	−14.6	2.619		0.19(2)		
	solution	M−O	8	2.408(5)	0.23(1)	−14.6	6 × 2.515(8)	0.11(2)		E	this work, 44
	Biaq1						3 × 2.64(2)	0.005(2)			
	solution	M−O	8	2.412(5)	0.17(1)		6 × 2.515(15)	0.090(5)		L	this work, 44
	Biaq1						3 × 2.66(2)	0.11(1)			
		M···$\mathrm{O_{II}}$	14	4.466(8)	0.25(2)		18 × 4.63(2)	0.24(3)			
		Bi···Cl	1	3.76(4)	0.29(2)						
	solution	Bi−O	8	2.411(5)	0.14(1)						this work
	Biaq2	Bi···$\mathrm{O_{II}}$	12	4.480(8)	0.27(2)						
		Bi···Cl	2	3.76(4)	0.29(2)						
	solution	Bi−O	8	2.412	0.15						this work
	Biaq3[b]	Bi···$\mathrm{O_{II}}$	16	4.466	0.25						
		Bi- - -Bi	6	3.690(2)	0.16(1)						
		Bi−O	12	2.16	0.08						
		Bi−O	12	2.41	0.12						
	solution	Bi−O	8	2.412	0.15						this work
	Biaq4[c]	Bi···$\mathrm{O_{II}}$	16	4.466	0.25						
		Bi- - -Bi	6	3.690(2)	0.16(1)						
		Bi−O	12	2.16	0.08						
		Bi−O	12	2.41	0.12						
$\mathrm{Me_2SO}$	solid[d]	M−O	8	2.428[6]	2.46−2.51					C	this work, 45
		M···S	8	3.56							
	solid[d]	M−O	8	2.409(2)	0.21(1)	−14.6	2.486(3)	0.19(2)	0.077	E	this work, 44
		M···S	8	3.530(4)	0.21(1)	−14.6	3.675(6)	0.19(2)	0.145		
		M−O−S	16	3.671(15)	0.22(2)	−14.6	3.85(2)	0.19(4)	0.18		
	solid[d]	Bi−O	6	2.340(3)	0.21(1)	−14.6				E	this work
		Bi···S	6	3.449(5)	0.22(2)	−14.6					
		Bi−O−S	12	3.61(2)	0.28(4)	−14.6					
	solution	M−O	8	2.411(3)	0.22(2)	−14.6	2.504(3)	0.13(1)	0.093	E	this work, 44
		M···S	8	3.524(7)	0.25(2)	−14.6	3.675(6)	0.17(2)	0.15		
		M−O−S	16	3.673(16)	0.28(4)	−14.6	3.828(12)	0.16(2)	0.16		
	solution	M−O	8	2.411(5)	0.17(1)		2.50(2)	0.18(1)	0.09	L	this work, 44
		M···S	8	3.545(6)	0.18(1)		3.725(6)	0.18(1)	0.18		
dmpu	solid[e]	Bi−O	6	2.324[e]						C	this work
		Bi−C	6	3.47							
	solid[f]	Bi−O	4.8(1.0)	2.275(3)	0.24(2)	−14.6				E	this work
		Bi···C	4.8(1.0)	3.53(5)	0.37(6)	−14.6					
	solution	M−O	6	2.322(3)	0.21(2)	−14.6	2.447(5)	0.17(2)	0.125	E	this work, 44
		M···C	6	3.48	0.42(5)	−14.6	3.586(12)	0.18(3)	0.10		
dmtf	solution	Bi−S	6	2.794(8)	0.23(3)	−19.5				E	this work

[a] Mean M−O difference in distance for nine-coordination in $\mathrm{[M(H_2O)_9](CF_3SO_3)_3}$. [b] 48 ± 1% of the total bismuth(III) content is present as hexameric $\mathrm{Bi_6O_4(OH)_4^{6+}}$ species. [c] 52 ± 2% of the total bismuth(III) content is present as hexameric $\mathrm{Bi_6O_4(OH)_4^{6+}}$ species. [d] $\mathrm{[Bi(Me_2SO)_8](ClO_4)_3}$ Bi−O bond distances: 2.390(8), 2.418(9), 2.400(9), 2.395(8), 2.456(8), 2.445(7), 2.469(6), 2.454(6) Å. Bond distances after riding-motion correction, assuming O to ride on Bi: 2.420(8), 2.445(9), 2.450(9), 2.450(8), 2.465(8), 2.470(7), 2.484(6), 2.484(6) Å. [e] $\mathrm{[Bi(dmpu)_6](ClO_4)_3}$ Bi−O bond distances: 2.316(8), 2.318(8), 2.319(8), 2.322(8), 2.331(9), 2.339(8) Å. Bond distances after riding-motion correction, assuming O to ride on Bi: 2.337(8), 2.337(8), 2.340(8), 2.341(8), 2.354(9), 2.356(8) Å. [f] Solid hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) perchlorate seems to lose solvent molecules and/or decompose when not in contact with the mother liquid. The solid-phase studied by EXAFS is not identical with the one studied crystallographically.

within the perchlorate ion. The peak at 4.5 Å corresponds to the second hydration shell, Bi···$\mathrm{O_{II}}$. The shoulder around 3 Å corresponds to the hydrogen-bonded O···O distances within the aqueous bulk, between the water molecules in the first and second hydration sphere, $\mathrm{O_{I}}$···$\mathrm{O_{II}}$, and from water molecules hydrogen bonded to the perchlorate ion. The mean Bi−O bond distance has been refined to 2.412(5) Å and the Bi···$\mathrm{O_{II}}$ distance to 4.47(1) Å. After these model contributions were subtracted from the experimental RDFs for the Biaq1 and Biaq2 solutions, a minor peak at about 3.8 Å remained in the difference. This peak is broader and almost 0.1 Å longer than the Bi···Bi distances in the hydrolysis products of the partly hydrolyzed Biaq3 and Biaq4 solutions. Furthermore, the amount of $\mathrm{Bi_6O_4(OH)_4^{6+}}$ was estimated to be negligible for the Biaq1 and Biaq2 solutions (see below). The peak was interpreted as a Bi−(O)−Cl interaction from a coordinated perchlorate ion in the inner coordination sphere. The Bi···Cl distance was refined to 3.76(4) Å, which gave a smooth difference function. The fit of the model functions showed a coordination of about one perchlorate ion to the bismuth(III) ion in the Biaq1 solution, and for the Biaq2 solution with a higher perchlorate concentration, about two perchlorate ions were found to be coordinated. The water-to-perchlorate molar ratios are 12.1 and 7.5 for the Biaq1 and Biaq2 solutions, respectively (see Table 1). This shows that the bismuth(III) ion has a slightly higher affinity for the perchlorate ions than for the water molecules at this very high ionic strength. It has been reported that typically hard metal ions, such as the alkali metal and iron(III) ions, and also the softer thallium(I) ion which is isoelectronic with bismuth(III), form very weak but measurable interactions with perchlorate ions even in dilute

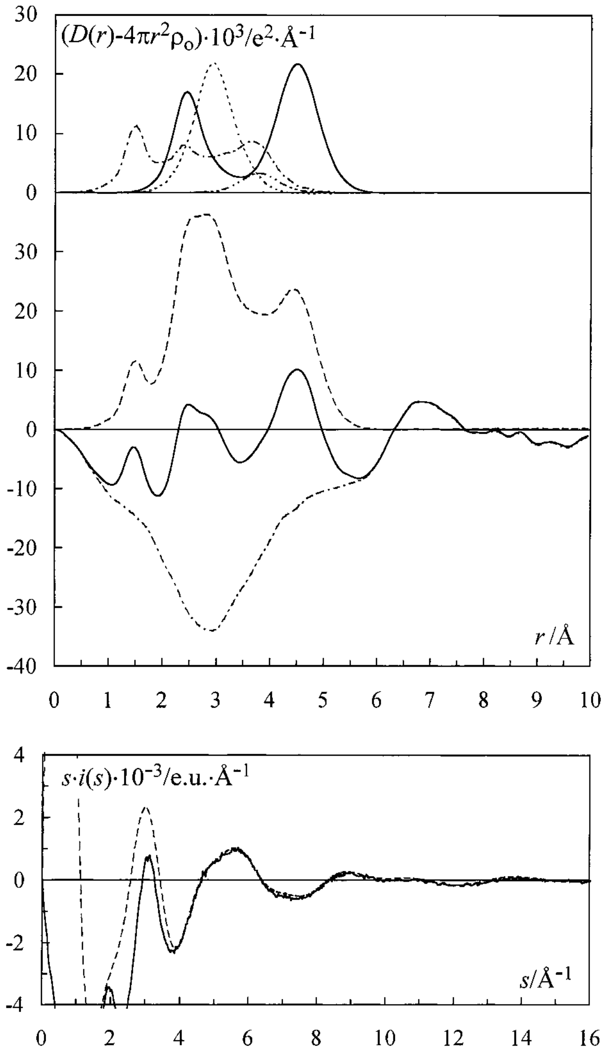

Figure 4. (Top) LAXS radial distribution curves for the Biaq1 solution. Upper part: Separate model contributions of the eight-hydrated bismuth(III) ion (Table 3) with the first and second sphere (solid line), of the Bi−(O)−Cl interaction of the perchlorate coordinated in the inner coordination sphere (dash-dot-dotted line), of the hydrated perchlorate ion (dash-dotted line), and of the $O_w\cdots O_w$ interaction in the aqueous bulk (dotted line). Lower part: Experimental RDFs of $D(r) - 4\pi r^2 r_o$ (solid line) and of the sum (dashed line) and the difference (dash-dotted line) of model contributions. (Bottom) Reduced LAXS intensity functions $si(s)$ (solid line) and model functions $si_{calc}(s)$ (dashed line).

solution.[46] It is therefore not surprising that bismuth(III) also forms weak complexes with perchlorate ions at the very high perchlorate concentrations and the high ionic strengths in the Biaq1 and Biaq2 solutions.

For the partly hydrolyzed Biaq3 and Biaq4 solutions, model functions, using the previously obtained structural parameters for the hydrated bismuth(III) ion (Table 3) and the $Bi_6O_4(OH)_4^{6+}$ complex,[7] gave satisfactory fits to the experimental intensity data. Refinements resulted in structural parameters of the $Bi_6O_4(OH)_4^{6+}$ complex in excellent agreement with those previously reported (see Table 3 and ref 7). The strong contribution from the Bi$\cdots$Bi interactions allows accurate determination of the

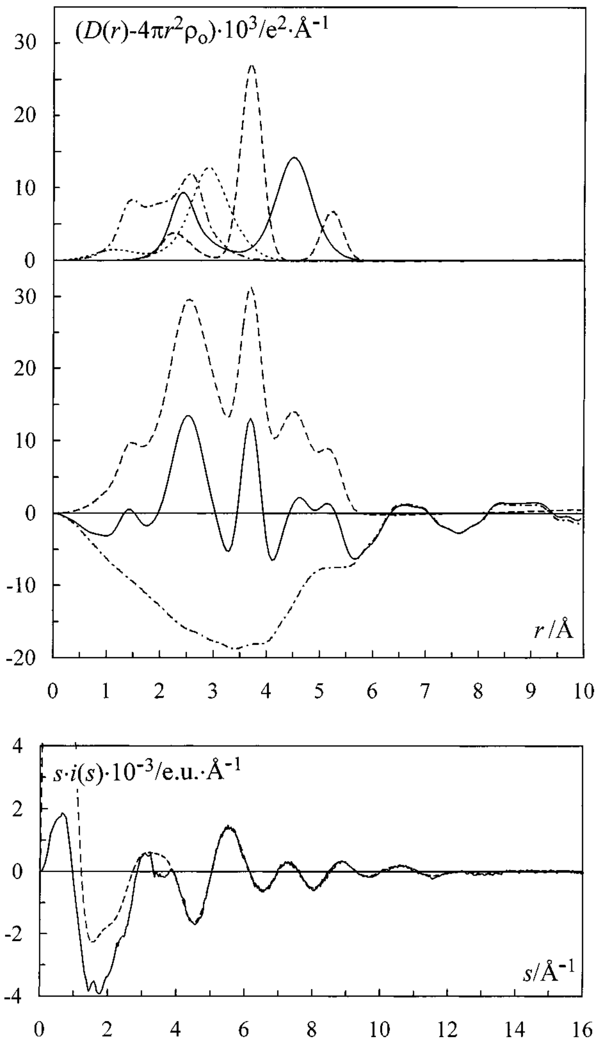

Figure 5. (Top) LAXS radial distribution curves for the Biaq3 solution. Upper part: Individual model contributions of the eight-hydrated bismuth(III) ion (Table 3) with the first and second sphere (solid line), of the $Bi_6O_4(OH)_4^{6+}$ complex (dashed line), of the hydrated perchlorate ion (dash-dotted line), and of the $O_w\cdots O_w$ interaction in the aqueous bulk (dotted line). Lower part: Experimental RDFs of $D(r) - 4\pi r^2 r_o$ (solid line) and of the sum (dashed line) and the difference (dash-dotted line) of model contributions. (Bottom) Reduced LAXS intensity functions $si(s)$ (solid line) and model functions $si_{calc}(s)$ (dashed line).

amount of hydrolyzed bismuth(III), which was found to be 48 ± 1 and 53 ± 2% of the total bismuth(III) content in the Biaq3 and Biaq4 solutions, respectively (see Figures 5 and S5). This corresponds to a stability constant of the hexameric species, evaluated as $K = [Bi_6O_4(OH)_4^{6+}][H_3O^+]^{12}[Bi^{3+}]^{-6}$, of 0.85 ± 0.10 (mol dm^{-3})$^{-7}$ from the result for the Biaq3 solution. The degree of hydrolysis found for the Biaq4 solution agrees with the value of this constant, and the estimated amount of $Bi_6O_4(OH)_4^{6+}$ in the Biaq1 and Biaq2 solutions becomes negligible, lower than $4\cdot 10^{-5}$ mol$\cdot$dm^{-3}.

Dimethyl Sulfoxide Solvation. The crystallographic data of the octakis(dimethyl sulfoxide)bismuth(III) perchlorate, $[Bi(OSMe_2)_8](ClO_4)_3$, are given in Table 2. The fractional atomic coordinates, the equivalent isotropic displacement coefficients, and the bond distances and angles are given in Tables S3 and S4. The structure is built up of discrete octakis(dimethyl sulfoxide)bismuth(III) complexes and perchlorate ions. The bismuth(III) ion is surrounded by eight oxygen atoms from the dimethyl sulfoxide molecules in a fairly regular square antiprism (see Figure 6). The Bi−O bond distances are in the range of

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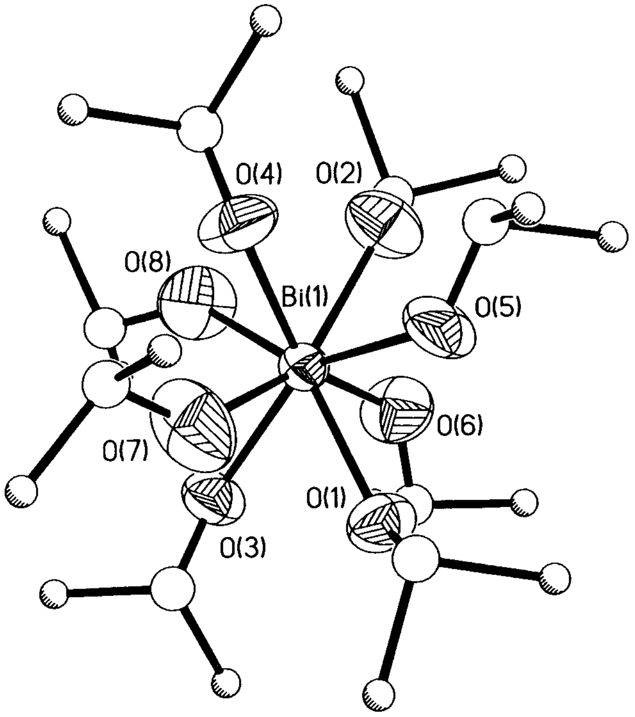

Figure 6. Structure of the $Bi(OS(CH_3)_2)_8^{3+}$ ion in the solid $[Bi(OS(CH_3)_2)_8](ClO_4)_3$.

2.390−2.469 Å (2.420−2.484 Å after riding-motion correction),[47] and the mean bond distance is 2.428 Å (2.459 Å corrected, see footnotes to Tables 3 and S4). The O−Bi−O angles are in the range of 69.5−78.2° except O7−Bi−O8, which is larger (see Figure 6 and Table S4); the O−M−O angle in a regular square antiprism is 70.53°. The slightly larger O−Bi−O angles in the BiO_8 entity show that the square-planar faces are somewhat further apart than in a regular square antiprism. Five of the coordinated dimethyl sulfoxide molecules are disordered with inverted orientations. This is shown by the alternative positions found for sulfur atoms S3, S4, S6, S7, and S8, with occupancy factors of 0.105(13), 0.145(12), 0.174(18), 0.287(13), and 0.190(30), respectively.

The overlaid inverted orientations give, in some cases, poorly defined atomic positions of the dimethyl sulfoxide molecules, although the bond distances are in reasonable agreement with those in other coordination compounds where dimethyl sulfoxide acts as a ligand.[12] The Bi−O−S bond angles (with S in the main position) are in the range of 123−137°, with a mean value of 128.5°. The perchlorate ions are located between the octakis(dimethyl sulfoxide)bismuth(III) ions in the lattice, with the Cl−O bond distances appearing much shorter than normal due to positional disorder (see Table S4).

The absorption edges and the EXAFS spectra of the solid octakis(dimethyl sulfoxide)bismuth(III) perchlorate and the dimethyl sulfoxide solution of bismuth(III) perchlorate are quite similar (see Figures 2 and S1), while the hexasolvate, which precipitated first, differs significantly (see Figures S2d,e and S6). For the solution, the mean Bi−O bond distance was refined to 2.411(6) Å and the Bi···S distance to 3.53(2) Å (Table 3). The three-leg scattering path Bi−O−S at 3.67(1) Å gives a relatively large contribution to the EXAFS function. These distances correspond to a mean Bi−O−S angle of 127°, typical for a medium hard acceptor.[12] The refined model parameters for the dimethyl sulfoxide-solvated bismuth(III) ion are summarized in Table 3, and the fit is shown in Figure 3, with the contributions from the individual scattering paths given in Figure S3c.

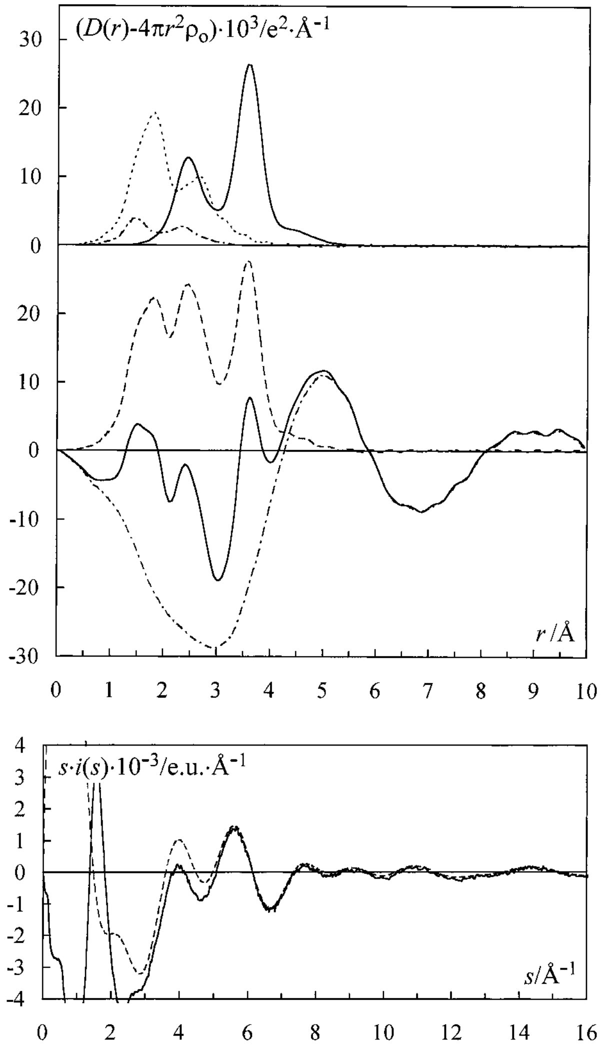

Figure 7. (Top) LAXS radial distribution curves for a 0.4 mol·dm^{-3} dimethyl sulfoxide solution of bismuth(III) perchlorate solution. Upper part: Separate model contributions of the BiO_8 core and the Bi···S distances within the octakis(dimethyl sulfoxide) bismuth(III) ion (solid line), of the perchlorate ion (dash-dotted line), and of the dimethyl sulfoxide molecules (dotted line). Lower part: Experimental RDFs of $D(r) - 4\pi r^2 r_o$ (solid line) and of the sum (dashed line) and the difference (dash-dotted line) of model contributions. (Bottom) Reduced LAXS intensity functions $si(s)$ (solid line) and model functions $si_{calc}(s)$ (dashed line).

For the solid hexakis(dimethyl sulfoxide)bismuth(III) perchlorate model, curve fitting gave a Bi−O bond distance of 2.336(4) Å, a typical value for a six-coordinated bismuth(III) ion with oxygen donor ligands.[15] The Bi···S distance and the three-leg Bi−O−S multiple-scattering pathway distance, 3.447(5) and 3.62(2) Å, respectively (Figure S7), correspond to a mean Bi−O−S angle of 126°.

The RDF from the LAXS experiment on the dimethyl sulfoxide solution of bismuth(III) perchlorate has three well-defined peaks, at 1.5 Å, including a shoulder at 1.8 Å, and at 2.5 and 4.5 Å (see Figure 7). The latter two sharp peaks correspond to the Bi−O and Bi···S distances within the dimethyl sulfoxide-solvated bismuth(III) ion, respectively. The first composite peaks are due to the Cl−O bond distances within the perchlorate ion and the interatomic distances within the

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[47] Johnson, C. K. *Crystallographic Computing*; Munksgaard: Copenhagen, 1970.

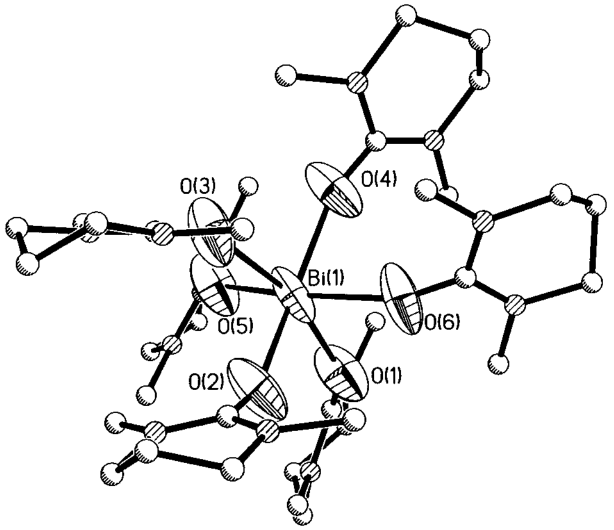

Figure 8. Structure of $[Bi(OCN_2(CH_3)_2(CH_2)_3)_6](ClO_4)_3$.

dimethyl sulfoxide molecule. The structural parameters for the perchlorate ion and the dimethyl sulfoxide molecule were taken from previously reported LAXS studies on dimethyl sulfoxide solutions.[36] Refinements of the Bi−O bond and Bi···S distances gave 2.411(5) and 3.545(6) Å, respectively, corresponding to a mean Bi−O−S angle of 129.6°. The displacement factors are fairly large, $l = 0.16$ and 0.22 Å, respectively, but not unreasonable for eight-coordination.[48,49] The fit of the model to the experimental data and the contributions of the individual interactions are shown in Figure 7.

No solvolysis or oligomerization similar to the hydrolysis reactions in aqueous solution can take place in aprotic solvents such as dimethyl sulfoxide and *N,N′*-dimethylpropylene urea, which simplifies the structure determination. The solvated bismuth(III) ion is eight-coordinated in dimethyl sulfoxide solution, probably in a square antiprismatic fashion, as found for the octakis(dimethyl sulfoxide)bismuth(III) perchlorate salt. The M−O−S angle in metal ion solvates is an indicator of the bonding character of the metal ion. M−O−S angles around 120° are found for soft electron-pair acceptors, e.g., mercury(II) and silver, while this angle increases to about 135° for typical hard acceptors, such as strontium and barium.[10,47] The Bi−O−S angles around 127° show that bismuth(III) ion is, as expected, a relatively hard electron-pair acceptor.

***N,N′*-Dimethylpropyleneurea Solvation.** Crystallographic data of hexakis(*N,N′*-dimethylpropyleneurea) perchlorate, $Bi(OCN_2(CH_3)_2(CH_2)_3)_6(ClO_4)_3$, are given in Table 2. The fractional atomic coordinates and equivalent isotropic displacement coefficients and the bond distances and angles are given in Tables S5 and S6, respectively. The crystal structure is built up of discrete hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) complexes and perchlorate ions. The bismuth(III) ion is surrounded by six oxygen atoms from the *N,N′*-dimethylpropyleneurea molecules in an almost regular octahedron (see Figure 8). The Bi−O bond distances are in the range of 2.316−2.339 Å (2.337−2.356 Å after riding-motion correction), and the trans O−Bi−O angles are all 162°. The C−O bond distances of the coordinated *N,N′*-dimethylpropyleneurea molecules are in the range of 1.216−1.223 Å, and the Bi−O−C angles are between 146.9° and 150.1°. The $H_3C−N$ and $H_2C−CH_2$ bond distances within the *N,N′*-dimethylpropyleneurea molecules are within the expected range. The structure of the hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) ion is thus very similar in the dodecaiodobismuthate(III) and perchlorate salts. The perchlorate ions, which are located between the hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) ions, again show signs of positional disorder (see Table S6).

The EXAFS study shows the solvated bismuth(III) ion to have a similar structure in solution and in the solid state, with six-coordinated *N,N′*-dimethylpropyleneurea molecules. Least-squares refinements gave a Bi−O bond distance of 2.322(3) Å for the solution. The structural parameters are summarized in Table 3, and the fit of the model is shown in Figure 3, with the contributions from the individual scattering paths given in Figure S3. The reason for the lower coordination number in the *N,N′*-dimethylpropyleneurea solvate than in the hydrate and the dimethyl sulfoxide solvate is certainly the steric effects of the more space-requiring *N,N′*-dimethylpropyleneurea ligand.

Several attempts were made to study the bismuth(III) coordination in the solid hexakis(*N,N′*-dimethylpropyleneurea)bismuth(III) perchlorate compound by EXAFS. However, this compound seems to lose *N,N′*-dimethylpropyleneurea molecules and/or to decompose when it is in contact with air during the sample preparation. The resulting desolvated compound gives an EXAFS spectrum significantly different from that of the corresponding solution (see Figure S6). Curve fitting gave a Bi−O bond distance of 2.275(5) Å and a Debye−Waller factor much larger than that for the solution (see Table 3). This indicates a coordination number lower than six and a large spread in Bi−O bond distances, possibly originating from a mixture of bismuth(III) ions with different solvate structures.

***N,N*-Dimethylthioformamide Solvation.** The EXAFS function obtained from the *N,N*-dimethylthioformamide solution of bismuth(III) perchlorate has a regular sinusiodical shape and shows in the corresponding Fourier transformation only very weak contributions besides the main Bi−S peak. Least-squares refinements resulted in a Bi−S bond distance of 2.794(8) Å, and no second shell could be detected. The obtained Bi−S bond distance is in close agreement with that in solids where bismuth(III) octahedrally binds six sulfur atoms.[17−19] This indicates that the bismuth(III) ion coordinates six *N,N*-dimethylthioformamide molecules in solution, probably in octahedral fashion. The structural model parameters are summarized in Table 3, and the fit of the model to the experimental data is given in Figure 3.

Concluding Remarks

The hydrated bismuth(III) ion is eight-coordinated in acidic aqueous solution, with a mean Bi−O bond distance of 2.41(1) Å. A weak ion-pair formation between bismuth(III) and perchlorate ions was found in aqueous solutions with very high perchlorate concentrations. The hydrated bismuth(III) ion hydrolyzes very easily, and an excess of strong acid of 1.5−2.0 $mol \cdot dm^{-3}$ was required to suppress hydrolysis reactions for a total bismuth(III) concentration higher than 0.5 $mol \cdot dm^{-3}$. With an excess of strong acid lower than 1 $mol \cdot dm^{-3}$, about 50% of the total bismuth(III) content was found to be hydrolyzed to hexameric $Bi_6O_4(OH)_4^{6+}$ complexes.

The bismuth(III) ion coordinates eight dimethyl sulfoxide molecules via the oxygen atom in solution, probably in square antiprismatic fashion in a similar way as in the solid state. With *N,N′*-dimethylpropylene urea, the bismuth(III) ion coordinates six oxygen atoms octahedrally, both in the solid state and in solution. The reason for this lower coordination number in

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comparison with that of dimethyl sulfoxide is the steric requirements of the bulky *N*,*N*′-dimethylpropylene urea ligand. In the sulfur donor solvent *N*,*N*-dimethylthioformamide, the bismuth(III) ion coordinates six solvent molecules.

From a survey of crystallographic studies of cell volumes, Shannon concluded that bismuth(III) and lanthanum(III) have essentially equal radii but that the size of the bismuth(III) ion depends on how stereochemically active its $6s^2$ lone pair is: "When Bi^{3+} is forced into high symmetry, a Bi^{3+} compound has a smaller volume than that of La^{3+}, but when the lone-pair character is dominant the Bi^{3+} compound is distorted and Bi^{3+} and La^{3+} compounds have approximately equal volumes".[31] On this basis, the ionic radii of bismuth(III) were given as equal to those of lanthanum(III) for different coordination numbers.[31] However, Table 3 shows that for the oxygen donor ligands in this study, the differences in mean bond lengths are 0.13, 0.09, and 0.06 Å for the coordination numbers 6, 8, and 9, respectively. The first two values are from solution studies, for which there are no symmetry constraints from a lattice. Nor do the crystal structures of the bismuth(III) solvates in this study show stereochemical activity of the lone pair. Moreover, we find without exception that the effective ionic radius of bismuth(III) is smaller than that of lanthanum(III). The difference increases with decreasing coordination number; thus, the increasing strength of the bond to the ligands emphasizes the difference. The radius of the oxygen atom in water is reported to be 1.34 Å,[50] which, together with the ionic radii for the metal ions given by Shannon,[31] has been shown to be in very good agreement with the experimentally observed M−O bond distances for almost all metal ions.[51,52] The observed mean Bi−O bond distances are 2.33, 2.41, and 2.49 Å for the six-, eight-, and nine-coordinations (see Table 3), and the effective ionic radii of the bismuth(III) ion are 0.99, 1.07, and 1.15 Å for these coordination numbers.

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Supporting Information Available: Fractional atomic coordinates and interatomic bond distances and angles of nonaaquabismuth(III) trifluoromethanesulfonate, octakis(dimethyl sulfoxide)bismuth(III) perchlorate, and hexakis(*N*,*N*′-dimethylpropylene urea)bismuth(III) perchlorate; normalized absorption edges, EXAFS Fourier transformations, and the different scattering paths of the studied bismuth(III) samples; radial distribution functions, including the individual model contributions, and the reduced intensity functions of the aqueous solutions Biaq2 and Biaq4; and comparisons of the EXAFS spectra of solid hexa- and octakis(dimethyl sulfoxide)bismuth(III) perchlorate and of *N*,*N*′-dimethylpropylene urea-solvated bismuth(III) ions in solution and solid state (partly decomposed) and their corresponding Fourier transformations. This material is available free of charge via the Internet at http://pubs.acs.org.

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