Inorganic Chemistry

Structure of the Solvated Thallium(I) Ion in Aqueous, Dimethyl Sulfoxide, *N,N'*-Dimethylpropyleneurea, and *N,N*-Dimethylthioformamide Solution

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The structure of the solvated thallium(I) ion in aqueous, dimethyl sulfoxide, *N,N'*-dimethylpropyleneurea, and *N,N*-dimethylthioformamide solution has been studied by means of large-angle X-ray scattering (LAXS) and complemented by EXAFS studies on two systems. The first solvation shell around the thallium(I) ion comprises significantly different bond distances to the solvent molecules in solution, indicating a stereochemically active lone electron pair. The first hydration shell around the thallium(I) ion in aqueous solution can be modeled by two Tl–O bond distances at 2.73(2) Å and about two more at 3.18(6) Å. Thallium(I) ions solvated by dimethyl sulfoxide, *N,N'*-dimethylpropyleneurea, and *N,N*-dimethylthioformamide seem to have two short and four long Tl–solvent bond distances. The mean Tl–O bond distances of the two groups were 2.66(4) and 3.18(6) Å for dimethyl sulfoxide and 2.73(4) and 3.27(8) Å for *N,N'*-dimethylpropyleneurea. For the sulfur donor solvent *N,N*-dimethylthioformamide the corresponding groups of Tl–S bond distances were refined to 2.96(2) and 3.33(3) Å.

Introduction

The large monovalent thallium(I) ion, with the ionic radius 1.50 and 1.59 Å in 6- and 8-coordination, respectively,[1] has weak electrostatic interactions with its ligands. Also the covalent contribution to the bonding is expected to be weak because of its $d^{10}s^2$ valence shell electron configuration with a lone electron pair. Accordingly, the thallium(I) ion is weakly solvated in most solvents[2,3] and crystallizes normally without coordinated solvent molecules. For constructing models to evaluate the weak and irregular coordination around the solvated thallium(I) ion in the current structural study, a literature search was performed. A large number of crystal structures are reported where thallium(I) is surrounded by oxygen atoms.[4,5] Due to the weak interactions no frequent well-defined coordination figure is found. The most common coordination number in these compounds is 8, but 6- and 7-coordination also occur. The Tl–O bond distances in the thallium(I) compounds and complexes are in most cases in

the range 2.7–3.2 Å,[4,5] but occasionally single Tl–O bond distances can be as short as 2.45 Å.[6,7] In some structures the lone electron pair seems to be stereochemically active, while in others the coordination figure is highly symmetric.

The aim of the present study is to investigate the structure of the solvated thallium(I) ion in aqueous, dimethyl sulfoxide (Me₂SO), *N,N'*-dimethylpropyleneurea (dmpu), and *N,N*-dimethylthioformamide (dmtf) solution, where no packing forces influence the bonding. However, the weak and irregular coordination between the thallium(I) ion and its surrounding solvent shell make structure studies difficult with available techniques. Consequently, no structural information seems to be available for the thallium(I) ion in any solvent. *N,N'*-Dimethylpropyleneurea is an oxygen donor solvent with a rather bulky molecular structure that occupies large space at coordination. Many metal ions attain, due to steric reasons,

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Table 1. Concentrations (mol·dm^{-3}), Density (ρ), and Linear Absorption Coefficient^a (μ) of the Aqueous, Dimethyl Sulfoxide (Me$_2$SO), *N,N'*-Dimethylpropyleneurea (DMPU), and *N,N*-Dimethylthioformamide (DMTF) Solutions Used in the Large-Angle X-ray Scattering (L) and EXAFS (E) Measurements

sample	[T1$^+$]	[X$^-$]	[solvent]	ρ/g·cm^{-3}	μ/g·cm$^{-1\ a}$	method
TlF in water	2.000	2.000	54.43	1.427	49.89	L
TlF in water	0.20	0.40, pH = 3 (HClO$_4$)				E
TlNO$_3$ in Me$_2$SO	1.034	1.034	12.31	1.318	29.82	L
Tl NO$_3$ in DMPU	0.900	0.900	8.06	1.273	22.73	L
TlCF$_3$SO$_3$ in DMTF	1.000	3.00	10.75	1.609	29.46	L
TlCF$_3$SO$_3$ in DMTF	0.50	1.50				E

^{a} Linear absorption coefficient for Mo Kα radiation.

a lower coordination number when solvated by *N,N'*-dimethyl-propyleneurea than in their hydrates or dimethyl sulfoxide solvates.[8] *N,N*-Dimethylthioformamide is a solvent with high permittivity and some hydrogen bonding ability,[9,10] allowing even highly charged species to be dissolved without ion-pair formation, an unusual property for a sulfur donor solvent.

Experimental Section

Preparation of Samples. Anhydrous thallium(I) fluoride (ICN) and thallium(I) nitrate (Merck) were used as purchased. Dimethyl sulfoxide (Merck) and *N,N'*-dimethylpropyleneurea (BASF) were distilled over calcium hydride (Fluka) and stored over 3 Å molecular sieves in dark bottles. *N,N*-Dimethylthioformamide was prepared by reacting phosphorus pentasulfide (Merck) and *N,N*-dimethyl-formamide (Merck) in benzene, according to a procedure devised by Gutmann et al.[11] After repeated distillations the ^{1}H NMR spectrum no longer showed traces of unreacted *N,N*-dimethylfor-mamide. Anhydrous thallium(III) trifluoromethanesulfonate was prepared as described elsewhere.[12]

The aqueous thallium(I) solution was prepared by dissolving a weighed amount of thallium(I) fluoride in deionized water, slightly acidified with some drops of perchloric acid to prevent hydrolysis. The fluoride salt was chosen as the fluoride ion forms weaker complexes than the anions in other available thallium(I) salts.[13] Weighed amounts of thallium(I) nitrate were dissolved in freshly distilled dimethyl sulfoxide and *N,N'*-dimethylpropyleneurea. An-hydrous thallium(III) trifluoromethanesulfonate was dissolved in *N,N*-dimethylthioformamide shortly before the structural studies. However, the experimental result showed that thallium(III) was completely reduced to thallium(I) by the solvent, because only one signal in [205]Tl NMR at 1414 ppm was observed. The oxidation product of *N,N*-dimethylthioformamide, probably a sulfone, could not be detected in the LAXS study. A similar reaction also takes place in *N,N'*-dimethylpropyleneurea independent of the anion (trifluoromethanesulfonate and perchlorate) giving a single signal at 781 ppm. The composition of the studied solutions is summarized in Table 1.

EXAFS. Tl L$_{III}$ edge X-ray absorption data were collected in transmission mode at beam line 4-1, Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA, 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 discard higher order harmonics. The solutions were kept in cells with 6.3 μm X-ray polypropylene foil windows and 1$-$5 mm Teflon spacers. Energy calibration of the X-ray absorption spectra was performed by simultaneously recording the spectrum of a thallium foil and assigning the first L$_{III}$-edge inflection point to 12660 keV.[14] Four scans of each sample were recorded, energy calibrated, and averaged. The EXAFS functions were extracted using standard procedures for preedge subtraction, spline removal, and data normalization,[15] using the EXAFSPAK program package.[16] To obtain quantitative information the k^3-weighted EXAFS oscillations were analyzed by nonlinear fitting of the model parameters by means of the WinXAS program package.[17] Model fitting including both single and multiple scattering pathways was performed with theoretical phase and amplitude functions calculated by means of the ab initio code FEFF7.[18]

Large-Angle X-ray Scattering. The scattering of Mo Kα X-ray radiation (λ = 0.7107 Å) from the free surface of an aqueous thallium(I) fluoride solution, of dimethyl sulfoxide, and *N,N'*-dimethylpropyleneurea solutions of thallium(I) nitrate, and of thallium(I) in *N,N*-dimethylthioformamide solution was measured by means of a large-angle $\theta-\theta$ diffractometer. The solutions were contained in a Teflon cup inside an airtight radiation shield with beryllium windows. The scattered radiation was monochromatized in a focusing LiF crystal monochromator, and the intensity was measured at discrete points in the range 1 < θ < 65°; the scattering angle is 2θ. A total of 100 000 counts was accumulated at each preset angle, 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. The experimental setup and the theory of the data treatment and modeling have been presented elsewhere.[19] All data treatment was carried out by means of the KURVLR program.[20] The experimental intensities were normalized to a stoichiometric unit of volume containing one thallium atom, using the scattering factors f for

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neutral atoms, including corrections for anomalous dispersion,[21] $\Delta f'$ and $\Delta f''$, and values for Compton scattering.[22] Least-squares refinements of the model parameters were carried out by means of the STEPLR program,[23] where the expression $U = \sum [si_{exp}(s) - si_c(s)]^2$ is minimized. The refinements of the model parameters were made for data in the high-s region where the intensity contribution from the long-range distances can be neglected.[24] To obtain a better alignment of the intensity function before the refinements, a Fourier back-transformation procedure was used to correct the $i_{exp}(s)$ functions by removing spurious nonphysical peaks below 1.2 Å in the experimental radial distribution function (RDF).[25]

Results and Discussion

Hydrated Thallium(I) Ion. The radial distribution function of an aqueous solution of 2.0 mol·dm^{-3} thallium(I) fluoride shows two peaks, at 2.9 and 4.3 Å, with shoulders at about 3.3 and 4.8 Å (Figure 1). The first peak corresponds to several interactions, a Tl–O bond distance in the hydrated thallium(I) ion, the F···(H)–O distance of the hydrated fluoride ion, reported to be 2.60–2.69 Å in aqueous solution,[26] and O–(H)···O distances within the aqueous bulk, about 2.89 Å in pure water.[27] The shoulder at 3.2 Å appears to be a second Tl–O bond distance in the hydrated thallium-(I) ion. The peak and the shoulder at 4.3 and 4.8 Å, respectively, are assumed to be caused by a second hydration sphere of thallium(I). The most plausible model was found to include two Tl–O bonds at about 2.7 Å and two at about 3.2 Å. Higher coordination numbers result in unrealistically large temperature factors.

The O···O distances within the first solvation shell of the thallium(I) ions were not included in the models, because the large temperature factors of the Tl–O bond distances indicate a large spread also of the O···O distances within the first coordination sphere. This is consistent with the lack of such features in the experimental RDF, and it is not possible from the present LAXS data to draw conclusions about the configuration of water ligands around the thallium-(I) ion aqueous solution. However, the presence of two different groups of Tl–O bond distances implicates that the lone electron pair on thallium(I) is stereochemically active. Therefore, the configuration around the hydrated thallium-(I) ion may be similar to that proposed for the hydrated tin(II) ion,[28,29] which comprises two short and two long M–O bond distances opposite the lone electron pair. Least-squares refinements of such a model resulted in Tl–O bond distances
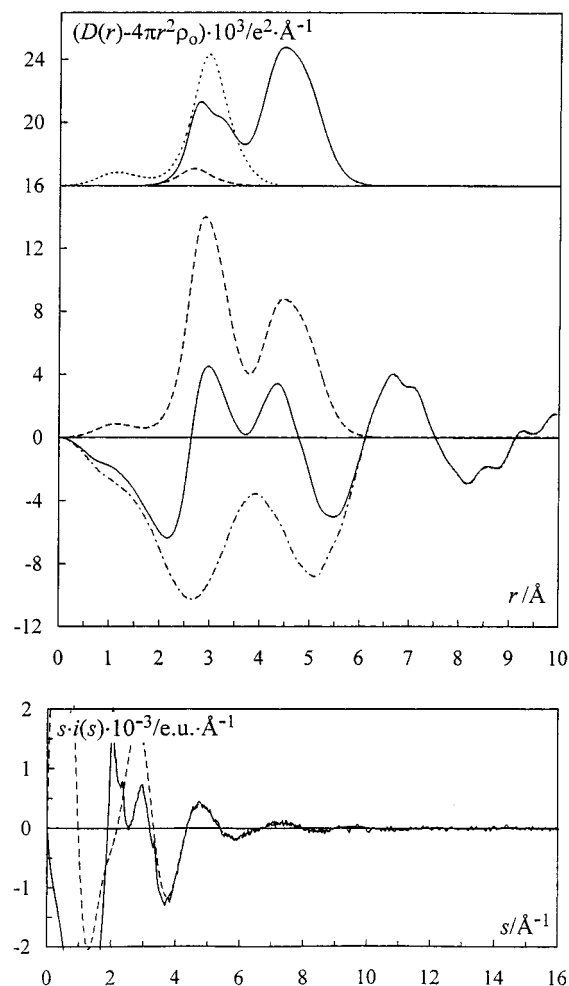
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Figure 1. LAXS: (top) separate model peak shapes for all contributing interactions, Tl–O in the first and second hydration shell (solid line), F···O for the hydrated fluoride ion (dashed line), and hydrogen-bonded O···O distances in the aqueous bulk (dotted line); (middle) experimental $D(r) - 4\pi r^2 \rho_0$ (solid line), model (dashed line), difference (dash–dotted line); (bottom) reduced LAXS intensity functions, $si(s)$ (solid line), model $si_{calc}(s)$ (dashes).

at 2.732(10) and 3.18(3) Å. The F···(H)–O distance in the hydrated fluoride ion, assumed to be surrounded by six water molecules, was refined to 2.63(4) Å, which is in accordance with previous results.[26] The O–(H)···O distance within the aqueous bulk and between the hydrogen bonded water molecules in the first and second hydration sphere was obtained as 2.94(1) Å. This is longer than in pure water, 2.89 Å, indicating that the thallium(I) ion is a structure breaker in aqueous solution. The structural parameters are summarized in Table 2. The fits of the model to the experimental intensity data and to the radial distribution function (RDF) are displayed in Figure 1.

A Tl L$_{III}$ edge EXAFS study of an 1.0 mol·dm^{-3} aqueous solution of thallium(I) nitrate showed the backscattering to be weak, and the Fourier transform had a very broad feature around 3 Å (Figure 2). Curve-fitting using backscattering parameters ab initio calculated by the FEFF program gave

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Table 2. Model Fitting of LAXS and EXAFS Data: Mean Bond Distances, d/Å, Debye−Waller Factor, σ^2/Å^2, Number of Distances, N, Shift in the Threshold Energy in the EXAFS Studies, ΔE_0/eV, and Amplitude Reduction Factor, S_o^2, of the Solvated Thallium(I) Ion in Solid and Solution as Determined by EXAFS (E) and LAXS (L) at Room Temperature

solvent	interactn	N	d	σ^2	ΔE_0	S_o^2	method
water	Tl−O$_{sh}$	2	2.732(10)	0.0040(6)			L
	Tl−O$_{lo}$	2	3.18(3)	0.014(2)			
	F···O	6	2.63(4)	0.0036(5)			
	O···O	3	2.935(10)	0.0049(8)			
	Tl−O$_{sh}$	2	2.75(4)	0.012(4)	0.5(4)	0.95(3)	E
	Tl−O$_{lo}$	2	3.00(4)	0.017(8)			
Me$_2$SO	Tl−O$_{sh}$	2	2.660(16)	0.0041(6)			L
	Tl−O$_{lo}$	4	3.178(30)	0.012(1)			
	Tl···S$_{sh}$	2	3.672(10)	0.0072(6)			
	Tl···S$_{lo}$	4	4.048(14)	0.018(1)			
DMPU	Tl−O$_{sh}$	2	2.72(2)	0.0062(11)			L
	Tl−O$_{lo}$	4	3.31(2)	0.013(2)			
DMTF	Tl−S$_{sh}$	2	2.964(5)	0.0045(5)			L
	Tl−S$_{lo}$	4	3.325(12)	0.0125(4)			
Tl(I)	Tl−S$_{sh}$	2	2.99(2)	0.013(2)	0.5(4)	0.95(3)	E
	Tl−S$_{lo}$	4	3.17(2)	0.025(4)			
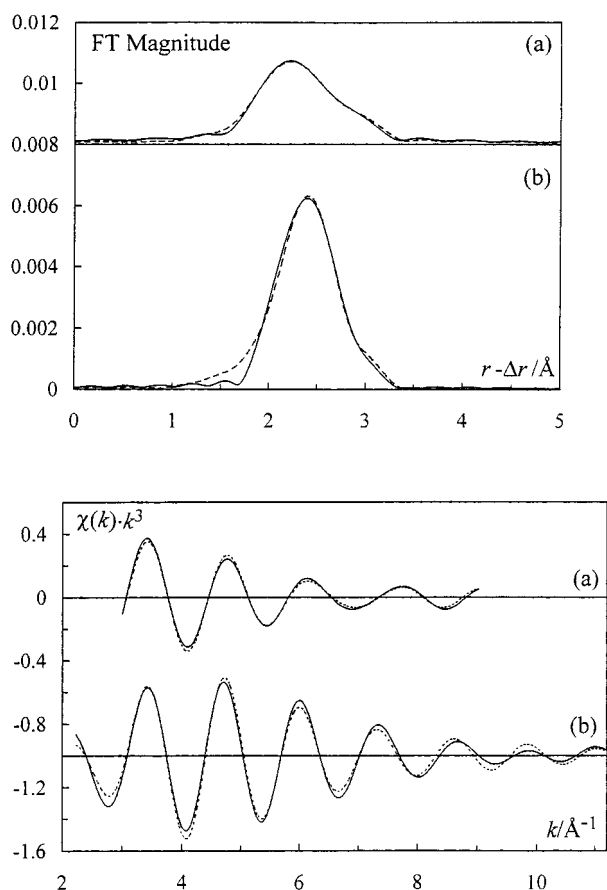
Figure 2. EXAFS: (top) Fourier transforms of EXAFS data (solid lines); (bottom) Fourier-filtered EXAFS data (solid lines) with a model formed by ab initio calculated scattering paths from the program FEFF (dotted lines), (a) acidic aqueous solution of thallium(I) fluoride and (b) *N,N*-dimethylthioformamide solution of thallium(I) trifluoromethanesulfonate.

two groups of Tl−O bond distances, 2.70(2) and 3.00(4) Å. Thus, the LAXS and EXAFS measurements show good agreement for the short Tl−O bond distance, while there is a substantial difference in the long Tl−O mean bond distance; a similar result is obtained for the thallium(I) ion in *N,N*-dimethylthioformamide; see below. We propose that the short Tl−O bond distance is well-defined enough to be fairly accurately determined by both methods, while the distribution of the long and poorly defined Tl−O bond distances is large. The relative contribition from long and

weak interactions is much less in EXAFS than in LAXS data.[30] Therefore, it is likely that the long Tl−O mean bond distance from the LAXS measurement gives a better average than the result from the EXAFS study, where the most well-defined (the shortest) Tl−O distances get higher weight. The fits of the EXAFS data and the Fourier transform are shown in Figure 2, the structural parameters are given in Table 2, and the individual contributions to the model are shown in Figure S1a.

Broad peaks often remain at ca. 4 Å in the LAXS difference function for aqueous solutions of large and weakly hydrated ions (cf. Figure 1, Figures 1−6 in ref 31, and Figure 2 in ref 32). This probably reflects a distribution of O−(H)···O distances shorter than normal in the water structure, caused by a partial breakdown of the hydrogen bonding due to the presence of the large structure-breaking ions poorly fitting into the bulk structure. Detailed theoretical modeling to explain these experimental observations is still lacking.

The reason the hydrated thallium(I) ion in aqueous solution has a somewhat different structure than the nonaqueous solvates (see below) is probably the hydrogen bonding. In pure water the hydrogen bonding is stronger (O−(H)···O, 2.89 Å) than between the water molecules in the first and second hydration sphere of thallium(I), ca. 2.94 Å; see Table 2. It seems therefore reasonable that the hydrogen bonding system in water strongly affects the structure of the hydrated thallium(I) ion in aqueus solution, while in the aprotic solvents the solvation of the thallium(I) ion is much less affected by the intermolecular interactions in the solvent.

Dimethyl Sulfoxide Solvated Thallium(I) Ion. The RDF from the LAXS data of a dimethyl sulfoxide solution of thallium(I) nitrate shows three peaks below 5 Å. The first peak at 1.5 Å corresponds to intramolecular distances within the dimethyl sulfoxide molecule and the nitrate ion, and two

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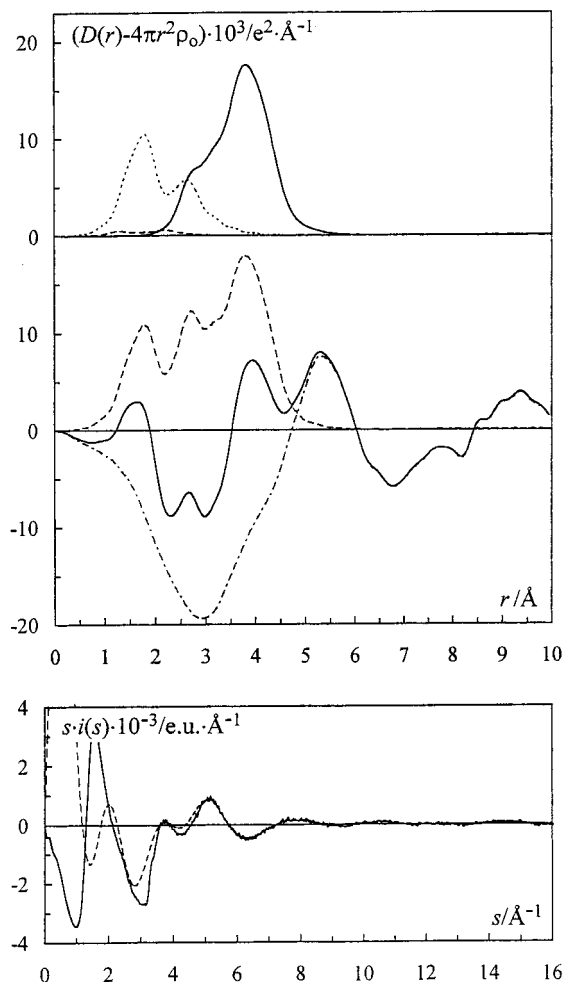
Figure 3. LAXS: (top) separate model peak shapes for the Tl—O and Tl···S distances of the dimethyl sulfoxide solvated thallium(I) ion (solid line), the nitrate ion (dashed line), and the dimethyl sulfoxide solvent molecules (dotted line); (middle) experimental $D(r) - 4\pi r^2\rho_0$ (solid line), model (dashed line), difference (dash−dotted line); (bottom) reduced LAXS intensity functions, $si(s)$ (solid line), model $si_{calc}(s)$ (dashes).
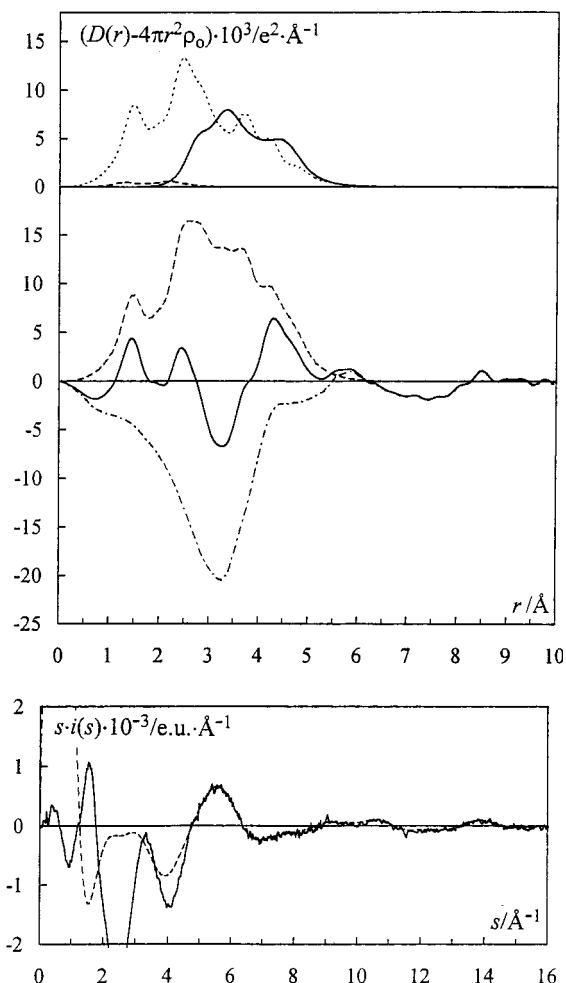

Figure 4. LAXS: (top) separate model peak shapes for the N,N'-dimethyl-propyleneurea-solvated thallium(I) ion (solid line), the trifluoromethane-sulfonate ion (dashed line), and the N,N'-dimethylpropyleneurea solvent molecules (dotted line); (middle) experimental $D(r) - 4\pi r^2\rho_0$ (solid line), model (dashed line), difference (dash−dotted line); (bottom) reduced LAXS intensity functions, $si(s)$ (solid line), model $si_{calc}(s)$ (dashes).

other peaks at 2.7 and 3.9 Å correspond to Tl—O and Tl···S distances within the dimethyl sulfoxide solvated thallium(I) ion. Besides these peaks there is a weak shoulder at about 3.2 Å (Figure 3). The contribution from the nitrate ion is very small, and the structure of the nitrate ion in the solid state has been applied for the modeling.[33] When the same basic coordination model as in aqueous solution is applied for the thallium ion, a 2 + 2 configuration, the contributions from the longer Tl—O and Tl···S distances become too small. The most plausible model with a satisfactory fit to the experimental data comprises two short and four long Tl—O bonds to the solvent molecules. Refinement gave Tl—O bond distances in two groups at 2.66(2) and 3.18(3) Å, respectively, and the corresponding Tl···S distances were refined to 3.67(2) and 4.05(2) Å, respectively. Assuming an S—O bond length of 1.52(1) Å for the weakly coordinated dimethyl sulfoxide ligands, this corresponds to mean Tl—O—S angles of 120(3) and 114(3)°,[12] respectively. The structural parameters are summarized in Table 2, and the fits of the model

functions to the experimental intensity and the radial distribution functions are shown in Figure 3.

N,N′-Dimethylpropyleneurea-Solvated Thallium(I) Ion. The RDF from the LAXS study of a 0.90 mol·dm^{-3} N,N'-dimethylpropyleneurea solution of thallium(I) nitrate displays three peaks below 5 Å at 1.5, 2.5, and 4.3 Å, all of which correspond to intramolecular distances within the N,N'-dimethylpropyleneurea molecule and the nitrate ion; see Figure 4. The Tl—O distances in the N,N'-dimethylpropy-leneurea solvated thallium(I) ion give rise to a broad feature around 3 Å. An acceptable fit to the experimental data is achieved when using a model with two groups of Tl—O bond distances in a coordination geometry similar to that for the dimethyl sulfoxide solvated ion. The refinements correspond to two short Tl—O distances at a mean value of 2.73(2) Å and four long at 3.27(4) Å. The structure of the nitrate ion in the solid state[33] has been applied. The structural parameters of the model are summarized in Table 2, and the fit to the experimental intensity data and the radial distribution function (RDF) is shown in Figure 4.

N,N-Dimethylthioformamide-Solvated Thallium(I) Ion. The RDF obtained from a LAXS study of an N,N-dimeth-

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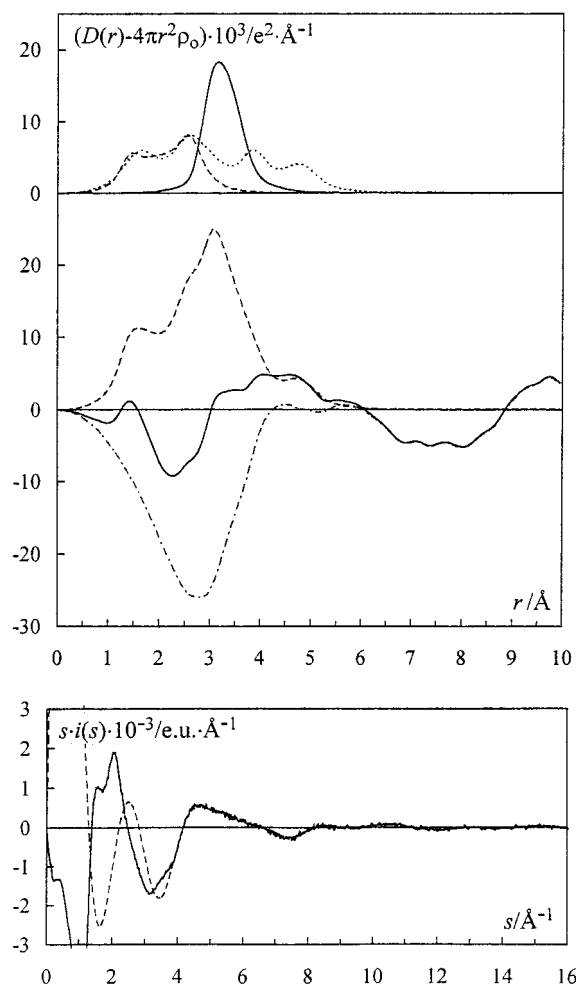
Figure 5. LAXS: (top) separate model peak shapes for the *N,N*-dimethylthioformamide-solvated thallium(I) ion (solid line), the trifluoromethanesulfonate ion (dashed line), and the *N,N*-dimethylthioformamide solvent molecules (dotted line); (middle) experimental $D(r) - 4\pi r^2 \rho_o$ (solid line), model (dashed line), difference (dash−dotted line); (bottom) reduced LAXS intensity functions, $si(s)$ (solid line), model $si_{calc}(s)$ (dashes).

ylthioformamide solution of thallium(III) trifluoromethanesulfonate shows four broad peaks below 5 Å, at 1.5, 3.0, 3.8 and 4.7 Å, and a distinct shoulder at 2.5 Å (Figure 5). The absence of a strong peak at about 2.47 or 2.67 Å, the expected Tl^{III}−S bond distances in tetrahedral and octahedral configuration, respectively,[34−38] shows that thallium(III) has been reduced to thallium(I). This was also confirmed by [205]Tl NMR measurements; see Experimental Section. The contributions at 1.5, 2.5, 3.8, and 4.7 Å correspond to intramolecular distances within the *N,N*-dimethylthioformamide molecule and the trifluoromethanesulfonate ion.[10,39] The solid-state structure of the trifluoromethanesulfonate ion, which has been found in previous LAXS studies in organic solvents to give a good description,[8] has been applied in the

modeling.[39] There seems to be two groups of Tl−S bond distances in the *N,N*-dimethylthioformamide-solvated thallium(I) ion, two close to 3.0 Å and another four at about 3.3 Å; refinements gave 2.96(1) and 3.33(2) Å (Table 2). The model fit is displayed in Figure 5.

An EXAFS study of the same solution gave Tl−S bond distances of 2.99(2) and 3.17(4) Å (Table 2). The mean value of the longer Tl−S bond distances is again found to be much shorter by EXAFS than by LAXS, probably for the same reason as discussed above (cf. Hydrated Thallium(I) Ion section). The model fit to the EXAFS data and the Fourier transform is shown in Figure 2, with the individual contributions from the model displayed in Figure S1b.

Conclusions

The thallium(I) ion is weakly solvated in all the studied solvents, and the thallium(I) solvates seem to have two groups of different Tl−solvent bond distances. This indicates that the lone electron pair has a significant stereochemical role for the solvated thallium(I) ion in a similar way as the lone electron pair has for the hydrated tin(II) ion.[28,29] The isoelectronic divalent lead(II) ion occasionally shows a stereochemical effect of the lone electron pair, especially in complexes with soft donor ligands, e.g. the lead(II) alkylxanthate and dithiocarbamate complexes,[40−42] while no such effect has been observed for the likewise isoelectronic but trivalent bismuth(III) ion.[8]

It is not possible from this study to give a detailed account of the coordination and ligand configuration around the solvated thallium(I) ion in solution. The large displacement factors of the mean bond distances in the models show that the bonds indeed are weak and with a wide distribution of the bond distances.

Supporting Information Available: Figures S1 and S2, showing the EXAFS contributions from separate backscattering pathways for the aqueous solution of thallium(I) fluoride and the *N,N*-dimethylthioformamide solution of thallium(I) trifluoromethanesulfonate. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010587Y

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