

Structure of the Dimethyl Sulfoxide Solvated Thallium(III) Ion in Solution and in the Solid State

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The structure and vibrational spectra of the dimethyl sulfoxide solvated thallium(III) ion have been studied in a dimethyl sulfoxide solution and in the solid state. X-ray crystallography shows a trigonal unit cell, space group $R\bar{3}$ (No. 148), for the $[\text{Tl}(\text{dmsO})_6](\text{ClO}_4)_3$ compound with $Z = 3$, $a = b = 11.9764(13)$ [11.8995(9)] Å, $c = 20.802(2)$ [20.467(2)] Å, and $V = 2584.0(5)$ [2509.9(4)] Å³ at 295 [150] K. The crystal structure comprises a highly symmetric hexakis(dimethyl sulfoxide)thallium(III) ion, with thallium in a $\bar{3}$ symmetry site and a Tl–O bond distance of 2.224(3) Å at 295 K. The octahedral TlO_6 kernel is compressed along the threefold axis with an O–Tl–O bond angle of 96.20(11)°. The Tl–O–S bond angle of 120.7(2)° corresponds to a Tl···S distance of 3.292(2) Å. One perchlorate ion centered on the $\bar{3}$ axis was described by a statistically disordered model. A low-temperature EXAFS study (10 K) resulted in the Tl–O and Tl···S distances of 2.221(4) and 3.282(6) Å, respectively, consistent with a Tl–O–S bond angle of 120(1)°. The low Debye–Waller factors confirm a regular coordination without the disorder of the dimethyl sulfoxide ligands, which would have resulted from the alternative choice of space group $R3$ for the crystal structure. Raman and infrared spectra have been recorded and assigned, with the bands at 435 and 447 cm^{-1} corresponding to the vibrational frequency of the symmetric and asymmetric Tl–O stretching modes, respectively. EXAFS data of a 0.5 mol dm^{-3} thallium(III) trifluoromethanesulfonate in a dimethyl sulfoxide solution were consistent with that of a hexasolvated ion with mean Tl–O and Tl···S distances of 2.22(1) and 3.33(2) Å, respectively, which correspond to a mean Tl–O–S bond angle of 124(2)°. The anomalously large disorder parameter for the Tl–O distances is consistent with a weak pseudo-Jahn–Teller effect. The ²⁰⁵Tl, ¹³C, and ¹H NMR spectra of the complex in solution show single signals at 1886, 39.5, and 2.3 ppm, respectively.

Introduction

Dimethyl sulfoxide is a polar aprotic solvent forming electrolyte solutions even with highly charged metal ions, thus allowing studies of their coordination and bonding properties. Stable solid dimethyl sulfoxide solvates can often be obtained and can be useful as sources of anhydrous metal ions in the syntheses of new compounds. Dimethyl sulfoxide is an ambidentate ligand, usually coordinating via the oxygen atom, but to a number of soft electron-pair acceptors, it is also coordinating via the sulfur atom.¹ An additional requirement for sulfur coordination seems to be a high availability of d electrons for metal-to-sulfur back-bonding, which is favored for the d⁶ and d⁸ transition-metal ions.¹

Thallium(III) can be classified as a medium-soft metal ion in contrast to the other trivalent ions of group 13, aluminum(III), gallium(III), and indium(III), which are regarded as hard from their coordination properties.² A characteristic property of thallium(III) is its high oxidizing power in the absence of strongly complex-forming ligands. The standard redox potential for the reduction to thallium(I) at 298 K in an acidic aqueous solution (with a unit activity of H⁺) is $e^\circ(\text{Tl}^{3+}/\text{Tl}^+) = 1.25 \text{ V}$.³ Even though thallium(III) is expected to strongly coordinate soft sulfur donor ligands, which is a stabilizing factor, it is spontaneously reduced to thallium(I) by the sulfur donor solvent *N,N*-dimethylthioformamide.⁴ Thus, thallium(III) is only stable in a few solvents with a relatively high redox potential. We found the dimethyl sulfoxide solvated thallium(III) ion to be stable both in solution (by NMR studies) and in the solid state. Because the isoelectronic d¹⁰ mercury(II) ion, which is softer

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than thallium(III), is solvated by six dimethyl sulfoxide molecules via the oxygen atoms in solution and in solid solvates,^{5–7} it seemed probable that thallium(III) would show similar coordination features. However, for mercury(II), theoretical considerations show that vibronic coupling in a weak pseudo-Jahn–Teller effect destabilizes a regular octahedral symmetry.⁸ The stronger the bonding, the less stable the octahedral coordination becomes, and no mercury(II) structure with near-regular six-coordination of sulfur ligands has been reported, while six-coordination of oxygen ligands was found to give anomalously large Debye–Waller factors in aqueous and dimethyl sulfoxide solutions.⁵

In acidic aqueous solution, the thallium(III) ion coordinates six water oxygen atoms with $d(\text{Tl–O})$ of 2.235(5) and 2.21(2) Å, as determined by means of LAXS and EXAFS, respectively.^{9,10} The compound $[\text{Tl}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ contains octahedrally hexahydrated thallium(III) ions.¹⁰ Disorder in the crystal structure prevented the precise determination of the Tl–O bond distance, but octahedral six-coordination, sometimes severely distorted, is also found in the compounds thallium(III) oxide (Tl_2O_3 ; mean Tl–O distance 2.27 Å),¹¹ $\text{RbTl}(\text{SO}_4)_2$ (2.23 Å),¹² $\text{CsTl}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (2.24 Å),¹³ $\text{Tl}(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_3$ (2.21 Å),¹⁴ and $\text{TlOHSO}_4 \cdot 2.5\text{H}_2\text{O}$ (2.24 Å).¹⁵ In a plot of the observed hydration number versus Shannon's effective radius for trivalent metal ions, thallium(III) is found to have metal–oxygen bond distances similar to those of the smaller octahydrated lanthanide(III) ions and the yttrium(III) ion.^{16,17} Also, thallium(III) has a larger radius than scandium(III), which has a mean Sc–O bond distance of 2.075(3) Å in the crystal structure of $[\text{Sc}(\text{dmsO})_6]\text{I}_3$,¹⁸ of 2.09 Å in octahedral six-coordinated $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ hydrates,¹⁸ and of 2.16 Å in pentagonal-bipyramidal seven-coordinated hydrates.¹⁹ Thus, the anomalously low oxygen coordination number six of the thallium(III) ion probably is, as for mercury(II), a result of considerable covalency in the metal–oxygen bonds.

In the present study, the structure of the dimethyl sulfoxide solvated thallium(III) ion is investigated in solution and in the solid state. One purpose is to compare the coordination and bonding of solvated thallium(III) ions with that of other solvated metal ions with a d^{10} electronic configuration (e.g., mercury(II)) to trace possible pseudo-Jahn–Teller effects.²⁰ Another is to study the effect on the structure and the vibrational spectra

Table 1. Crystallographic Data for $[\text{Tl}(\text{dmsO})_6](\text{ClO}_4)_3$ at (1) Ambient and (2) Low Temperature^a

	1	2
chemical formula	$\text{C}_{12}\text{H}_{36}\text{Cl}_3\text{O}_{18}\text{S}_6\text{Tl}$	
fw (g mol ⁻¹)	971.49	
space group	$R\bar{3}$ (No. 148)	
a (Å)	11.9764(13)	11.8995(9)
c (Å)	20.802(2)	20.467(2)
α, β, γ (deg)	90, 90, 120	
V (Å ³)	2584.0(5)	2509.9(4)
Z	3	
T (K)	295 ± 2	150 ± 2
λ (Å)	0.7107	
D_{obsd} (g cm ⁻³)	1.872(3)	
D_{calcd} (g cm ⁻³)	1.873	1.928
μ (mm ⁻¹)	5.349	5.507
R_1, wR_2 ($I > 2\sigma(I)$)	0.0323, 0.0789	0.0302, 0.0678

^a R values are defined as $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

of the dimethyl sulfoxide molecule, as part of a more general study of its properties as a ligand.

Experimental Section

Chemicals. (a) **Anhydrous Thallium(III) Trifluoromethanesulfonate.** From an aqueous solution of thallium(III) nitrate nonahydrate (Alfa), brown thallium(III) oxide/hydroxide precipitated when raising the pH to about 9 by adding a fairly concentrated sodium hydroxide solution. The solid phase was repeatedly centrifuged and washed until no nitrate was detectable in the supernatant. Trifluoromethanesulfonic acid (Riedel-deHaën) with 20 mass % of water was added to the fresh solid phase. The mixture was boiled for 5–10 min, whereby the thallium(III) oxide/hydroxide partly dissolved. The acidic aqueous phase was decanted, and the remaining solid phase was treated with another portion of acid. The obtained acidic aqueous phases were combined and heated in an oven at 450 K. After the water and excess acid were boiled off, a pale-yellow solid of anhydrous thallium(III) trifluoromethanesulfonate remained. This salt immediately reacts with moisture, forming brown thallium(III) oxide/hydroxide, and must therefore be stored at high temperature (>450 K) or in a carefully closed dry vessel. The anhydrous salt was dissolved in dimethyl sulfoxide (Merck) freshly distilled over calcium hydride (Fluka), to prepare a 0.5 M solution of thallium(III) trifluoromethanesulfonate for the EXAFS study.

(b) **Hexakis(dimethyl sulfoxide)thallium(III) Perchlorate.** A small volume (0.08 cm³) of a 1.2 mol dm⁻³ acidic aqueous solution of thallium(III) perchlorate^{9,10} was slowly added under stirring to 1 cm³ of freshly distilled dimethyl sulfoxide, momentarily giving a white precipitate that quickly dissolved. The resulting colorless solution was evaporated for 3 days in darkness at reduced pressure in a vacuum desiccator until white cube-shaped crystals of hexakis(dimethyl sulfoxide)thallium(III) perchlorate were formed. The density of the crystals was determined by the flotation method,²¹ by using a mixture of carbon tetrachloride and carbon tetrabromide; an Anton Paar DMA35 densitometer was used to measure the density of the solvent mixture. The agreement with the calculated density at ambient temperature (Table 1) confirmed that the molecular formula for the compound was correct.

Warning! Perchlorate salts in organic solvents are powerful explosives and should always be treated with great caution.^{22,23}

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EXAFS Data. Thallium L_{III} edge X-ray absorption data were collected in transmission mode at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated conditions. The SSRL storage ring operates at 3.0 GeV and a maximum current of 100 mA. A Si[220] double monochromator provided monochromatic radiation in the scan range and was detuned to 50% of the maximum intensity at the end of the scans to reduce higher-order harmonics. The measurements were performed at wiggler beam lines, with the solid sample at beam line 7-3 equipped with a continuous-flow helium cryostat keeping the sample temperature at 10 K and the other samples at beam line 4-1. The solutions were kept in a cell with a 1 mm Teflon spacer and Mylar foil windows. The solid was finely ground and diluted with boron nitride (BN) to prevent self-absorption and to achieve an absorption change over the edge of about one logarithmic unit. The mixture was pressed into a pellet and sealed between Kapton tape windows in a 1 mm aluminum frame. Energy calibration of the X-ray absorption spectra was performed at beam line 7-3 by simultaneously recording the absorption spectrum of selenium and assigning the first inflection point of the selenium K edge to 12 658 keV.²⁴ Four scans were recorded, energy-calibrated, and averaged. For beam line 4-1, the L_{III} edge at 12 658 eV of a thallium metal foil was used for an energy calibration, and an aqueous solution of thallium(III) perchlorate was used as a standard for the ΔE_0 parameter, corresponding to $k = 0$. The EXAFS oscillations were extracted using standard procedures for pre-edge subtraction, spline removal, and data normalization.^{25,26} Model fitting, including both single- and multiple-backscattering pathways, was performed with theoretical phase and amplitude functions calculated ab initio by means of the computer code FEFF (version 6.01).²⁷ The k^3 -weighted EXAFS oscillation was analyzed by a nonlinear least-squares fitting procedure of the model parameters. All of the data treatment was made using the EXAFSPAK program package.²⁸

Raman and Infrared Spectra. A Raman spectrum of the solid hexakis(dimethyl sulfoxide)thallium(III) perchlorate was obtained using a Renishaw System 1000 spectrometer, equipped with a Leica DMLM microscope, a 25 mW diode laser (780 nm), and a Peltier-cooled CCD detector. For the solutions, Raman spectra were measured by means of an FT-Raman accessory of a Bio-Rad FTS 6000 FTIR spectrometer. The 1024 nm line from a Spectra-Physics Nd:YAG laser was used to irradiate the sample with about 150 mW. The mid-infrared absorption spectrum of the solid compound was obtained by means of a Bio-Rad FTS 6000 FTIR spectrometer (Nujol mull and NaCl windows). The far-infrared spectrum was recorded with the sample enclosed between polyethylene disks.

X-ray Crystallography. The data collection at room temperature was made on a $[\text{Tl}(\text{dms})_6](\text{ClO}_4)_3$ crystal, with the approximate dimensions of $0.20 \times 0.30 \times 0.34 \text{ mm}^3$ enclosed in a thin-walled glass capillary, by means of a Siemens SMART CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda_{\text{max}} = 0.710 73 \text{ \AA}$). Low-temperature (150 K) measurements were made with a crystal mounted on a glass fiber with epoxy glue by means of a STOE imaging-plate diffractometer. No intensity variation due to decomposition of the crystal was observed. Data collection and refinement parameters are summarized in Table 1. The data were corrected for absorption effects using the SADABS program of the SAINTPLUS program package for the room-temperature data and the numerical method provided by the

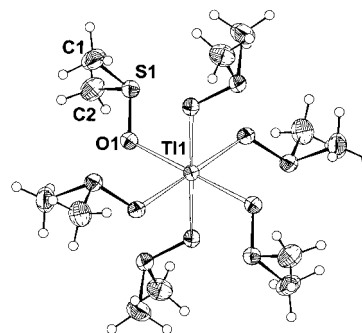


Figure 1. Hexakis(dimethyl sulfoxide)thallium(III) complex at 295 K viewed along the $\bar{3}$ axis in the crystal structure of $[\text{Tl}(\text{dms})_6](\text{ClO}_4)_3$ (50% probability ellipsoids).

X-SHAPE program package for the 150 K study.²⁹ Symmetry equivalent reflections were used to optimize the crystal shape and size. The structure was solved by direct methods using SHELXS-97³⁰ and refined using the full-matrix least-squares method on F^2 , SHELXL-97.³¹ The hydrogen atoms were introduced in calculated positions and refined isotropically.

Systematic absences in the collected diffraction data were consistent with the space groups $R\bar{3}$ (No. 146) and $R\bar{3}$ (No. 148). Normalized E value intensity statistics gave a low value of $|E^2 - 1| \approx 0.62$, which indicates the acentric space group or possible twinning, but the structure could be solved and described in both space groups. In the acentric ($R\bar{3}$) model of the $[\text{Tl}(\text{dms})_6]^{3+}$ complex, the absolute structure could not be determined, and the structure had to be refined as a racemic twin. Also, some peculiarities appeared in the Tl–O bond lengths. The description of the complex improved substantially with fewer parameters when the centrosymmetric ($R\bar{3}$) space group was used. However, for one of the perchlorate groups centered on the $\bar{3}$ axis, the description became worse, and this anion was modeled as disordered. A data set was then collected at low temperature (150 K), but the same problems persisted, and this issue could not be resolved. From our crystallographic data, we cannot distinguish between a twinning or a statistical disorder of this perchlorate ion in the centrosymmetric space group $R\bar{3}$, but the geometrical description of the $[\text{Tl}(\text{dms})_6]^{3+}$ complex is satisfactory with the disordered perchlorate model. The isostructural $[\text{In}(\text{dms})_6](\text{ClO}_4)_3$ compounds, which also were described in $R\bar{3}$,³² give further support for this choice. Disordered perchlorate groups are also present in that structure, although they have been modeled in a different way.

Results and Discussion

Crystal Structures. The structure of the hexakis(dimethyl sulfoxide)thallium(III) complex was satisfactorily described in the space group $R\bar{3}$, with the thallium(III) ion located in a site of $\bar{3}$ symmetry surrounded by six equidistant oxygen-bonded dimethyl sulfoxide ligands (Figure 1). The Tl–O bond distances in the $[\text{Tl}(\text{dms})_6]^{3+}$ complex (2.224(3) [2.240(4)] \AA) show a deviation larger than expected between the two different determinations at 295 and 150 K. Figure S1 in the Supporting Information reveals that, at 150 K, the thermal ellipsoids of the thallium, oxygen, and sulfur atoms all are elongated principally along the c axis, while, at 295 K, the appearance is normal. These anomalous features at low temperature indicate some disorder of the $[\text{Tl}(\text{dms})_6]^{3+}$ complex, which may be due to partial twinning or cooperative packing effects involving the

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Table 2. Bond Lengths (Å) and Angles (deg) for $[M(\text{dms})_6]^{n+}$ Complexes in $\bar{3}$ Symmetry Compared with Mean Values for Uncoordinated Dimethyl Sulfoxide Molecules in Crystalline Solvates

metal atom anion	Tl(III) perchlorate ^a	Tl(III) perchlorate ^b	In(III) perchlorate ^c	In(III) iodide ^d	Ga(III) iodide ^d	Sc(III) iodide ^e	Hg(II) triflate ^f	uncoordinated DMSO ^g
M–O	2.224(3)	2.240(4)	2.140(3)	2.145(3)	1.974(4)	2.075(3)	2.347(5)	
compression ratio s/h^h	1.455(3)	1.465(3)	1.373(4)	1.335(4)	1.285(6)	1.287(4)	1.390(6)	
closest O...O distance	2.948(5)	2.973(5)	2.915(5)	2.945(4)	2.746(6)	2.887(5)	3.182(7)	
O–S	1.544(4)	1.537(3)	1.542(3)	1.541(3)	1.538(5)	1.530(3)	1.543(5)	1.495(4)
S–C(1)	1.758(8)	1.781(7)	1.763(8)	1.787(5)	1.774(8)	1.761(5)	1.766(8)	1.773(4)
S–C(2)	1.770(7)	1.795(7)	1.771(6)	1.765(5)	1.773(8)	1.769(5)	1.764(9)	
O–M–O'	96.20(13)	96.40(14)	94.2(1)	93.3(1)	91.8(2)	91.9(2)	94.6(2)	
M–O–S	120.7(2)	119.6(2)	124.0(2)	123.1(2)	124.1(3)	132.5(2)	116.4(3)	
O–S–C(1)	103.2(3)	102.2(3)	102.9(2)	104.1(2)	102.9(3)	103.7(2)	104.1(3)	105.7(2)
O–S–C(2)	104.2(3)	104.3(3)	103.6(3)	103.3(2)	104.6(4)	103.8(2)	106.5(4)	
C(1)–S–C(2)	99.8(4)	100.0(4)	99.6(3)	98.5(3)	98.3(4)	98.9(3)	98.6(5)	98.0(3)

^a This work. ^b 150 K (note that some disorder affects the distances). ^c Reference 32. ^d Reference 37. ^e Reference 18. ^f Reference 7. ^g Reference 1. ^h Definitions as those in Figure 4 and ref 38; $s/h = 1.225$ for a perfect octahedron.

disordered perchlorate ions. Thus, it seems likely that the rather long Tl–O distance obtained and also the unexpectedly long S–C and rather short S–O bond distances in the dimethyl sulfoxide ligands at 150 K (Table 2) probably are affected by systematic errors from this disorder.

Much longer Tl–O(dms) bond distances are found for the six-coordinated compound $[\text{TlCl}_5(\text{dms})](\text{Hpyr})_2$ (2.42(2) Å)³³ because of the stronger coordination of the relatively soft chloride ions. Long Tl–O bond distances are also found for the dimetallic compound $[(\text{dms})_4\text{Tl}–\text{Pt}(\text{CN})_5] \cdot (\text{dms})$ (2.287–2.311 Å)³⁴ despite the five-coordination, and an even longer Tl–O bond distance (2.46 Å) occurs in the six-coordinated molecular compound $[(\text{CN})_5\text{Pt}–\text{Tl}(\text{bipy})(\text{dms})_3]$.³⁵ For both of these dimetallic compounds, the long Tl–O distances are caused by the metal–metal bond, which leads to an effective oxidation state lower than three for thallium.³⁶

The M–O–S bond angles (120.7(2)° [119.6(2)°]) are smaller for $[\text{Tl}(\text{dms})_6]^{3+}$ than for the isostructural $[\text{In}(\text{dms})_6]^{3+}$ and $[\text{Ga}(\text{dms})_6]^{3+}$ complexes (Table 2)^{32,37} and are also smaller than the average M–O–S value for oxygen-bonded dimethyl sulfoxide ligands 124.7(5)°. However, the M–O–S angle is much smaller (116.4(3)°) for the softer electron acceptor mercury(II) in a $[\text{Hg}(\text{dms})_6]^{2+}$ complex of $\bar{3}$ symmetry and much larger (132.5(2)°) for the hard d⁰ ion scandium(III) in the $[\text{Sc}(\text{dms})_6]\text{I}_3$ complex (Table 2).

Average values from a survey of oxygen-coordinated sulfoxides show that the M–O bonding generally causes the S–O distance to become longer and the average C–S–C angle to increase slightly, while the O–S–C angle decreases.¹ Table 2 shows a similar comparison between the strongly bound dimethyl sulfoxide ligands in regular $[\text{M}(\text{dms})_6]^{n+}$ complexes with $\bar{3}$ site symmetry for M = Tl(III), In(III), Ga(III), Sc(III), and Hg(II) and the mean values for uncoordinated dimethyl sulfoxide molecules in crystalline solvates. The most significant effect on the dimethyl sulfoxide geometry in this comparison is that the S–O bond length becomes 0.04–0.05 Å longer when coordinated.

EXAFS. The thallium L_{III} edge EXAFS data for the solid hexakis(dimethyl sulfoxide)thallium(III) perchlorate and the dimethyl sulfoxide solution of thallium(III) trifluoromethane-

Table 3. EXAFS Results for the $[\text{Tl}(\text{dms})_6]^{3+}$ Ion in Crystal^a at 10 K and in Dimethyl Sulfoxide Solution^b at 295 ± 2 K

interaction	d (Å) ^c		σ (Å) ^d	
	crystal	solution	crystal	solution
6Tl–O	2.221(4)	2.22(1)	0.047(3)	0.081(4)
6Tl...S	3.282(6)	3.33(2)	0.053(3)	0.12(1)
12Tl–O–S ^e	3.45(3)	3.53(5)	0.055(4)	0.13(2)
24Tl–O–O ^e		3.77(4)		0.08(3)
(3 × 6)Tl–O–Tl–O ^e	4.44(4)		0.06 ^f	

^a For the crystal, the threshold energy shift $\Delta E_0 = -4.5(2)$ eV and the amplitude reduction factor $S_0^2 = 0.86(2)$. ^b For the solution, $\Delta E_0 = -6.6(4)$ eV and $S_0^2 = 0.66(2)$; the low value could be due to sample fluorescence, adding to the signal in the detector and thereby decreasing the EXAFS amplitude. ^c Mean bond distance. ^d Debye–Waller displacement parameter. ^e Multiple-scattering pathways. ^f Not refined.

sulfonate were modeled with the main contributions from the Tl–O and Tl...S single backscattering, which are expected at about 2.2 and 3.3 Å, respectively, and the three-legged Tl–O–S backscattering pathway at about 3.5 Å. For the solution, the triangular Tl–O–O pathway (multiplicity 24) at about 3.8 Å gave a minor contribution, while, for the solid, the linear Tl–O–O and Tl–O–Tl–O multiple-scattering pathways within the TlO₆ entity with twice the Tl–O bond distance (4.4 Å) were necessary for a good fit of the model (see the section on pseudo-Jahn–Teller effects). Figures 2 and 3 show the fit of the EXAFS model functions with the refined parameter values listed in Table 3. Least-squares refinement gave the mean Tl–O and Tl...S distances of 2.221(4) and 3.282(6) Å, respectively, for the solid compound and 2.22(1) and 3.33(2) Å for the solution, respectively. Assuming the S–O distance to be 1.54 Å (compare to Table 2), this corresponds to the mean Tl–O–S bond angles of 120(1)° and 124(2)°, respectively, and indicates a slightly wider angle with a larger spread in the solution.

Pseudo-Jahn–Teller Effects. The relatively small Tl–O and Tl...S disorder parameters (σ) in the EXAFS Debye–Waller factor ($\exp(-2\sigma^2k^2)$) for the solid compound at low temperature (compare to Table 3) are consistent with the expected thermal movements of the atoms and indicate that there is no disorder of the ligands in the complex. This further supports the choice of the space group $R\bar{3}$ with a single Tl–O bond distance for the crystal structure. For thallium(III) in dimethyl sulfoxide solution, the disorder parameter $\sigma = 0.081(4)$ Å is about twice as large as that for the solid (Table 3). Because the disorder parameter in EXAFS and LAXS is a measure of the root-mean-square distribution of the interatomic distances, this shows a larger spread in the metal–oxygen bond distances around the thallium(III) ion in solution than in the solid state. Similar effects were previously observed for the mercury(II) ion.^{5,8} LAXS

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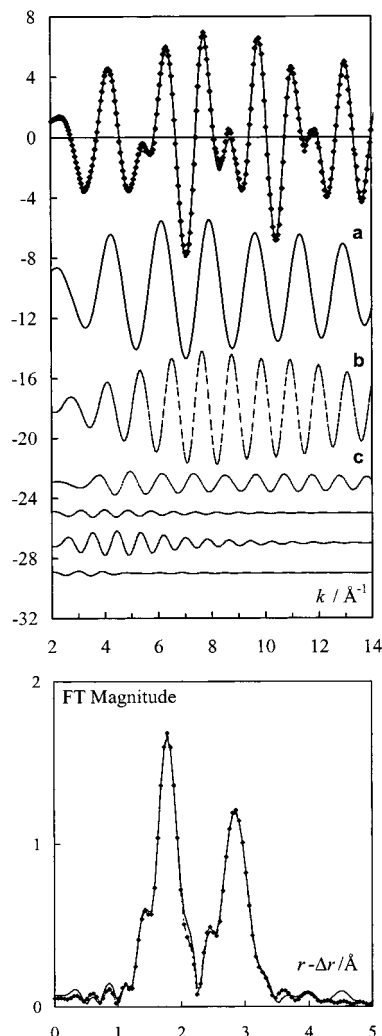


Figure 2. (Top) Ti L_{III} edge EXAFS data (top, dots) with model fit (solid line) of [Ti(dmsO)₆](ClO₄)₃ at 10 K. Below, separate contributions of different backscattering pathways (see Table 3): (a) Ti–O, (b) Ti···S, and (c) Ti–O–S three-legged pathway and three linear Ti–O–Ti–O scattering pathways of twice the Ti–O bond distance (bottom). (Bottom) Fourier transformed EXAFS data for solid [Ti(dmsO)₆](ClO₄)₃ at 10 K (solid line), without the phase shift, and the fitted model function (dots).

studies of the six-coordinated mercury(II) and cadmium(II) solvated ions in a dimethyl sulfoxide solution resulted in the σ value of 0.074(3) Å for the Hg–O interaction and a significantly smaller corresponding σ value for Cd–O (0.042(3) Å).⁵ The corresponding σ values for the M···S distances show the same tendency (0.12(1), 0.095(4), and 0.087(4) Å for M = Ti, Hg, and Cd, respectively). There may be some different systematic errors in the σ values from the EXAFS and LAXS methods, but the large σ values for the somewhat smaller thallium(III) ion clearly show an anomalously large spread in the Ti–O distances in solution. This can be interpreted as an increase in the vibrational amplitude because of vibronic mixing of electronic states with close energy levels, a weak pseudo-Jahn–Teller effect.²⁰ In such a case, the direction of distortion may have any symmetry possible in the point group of the system, giving a dynamic contribution to the disorder.²⁰

For an octahedral ML₆ complex, threefold orbital degenerate terms are possible, and the vibronic coupling may then give rise to a cooperative static pseudo-Jahn–Teller effect, with energy minima for static distortions of the octahedra along one of the trigonal axes.²⁰ This is consistent with the observed

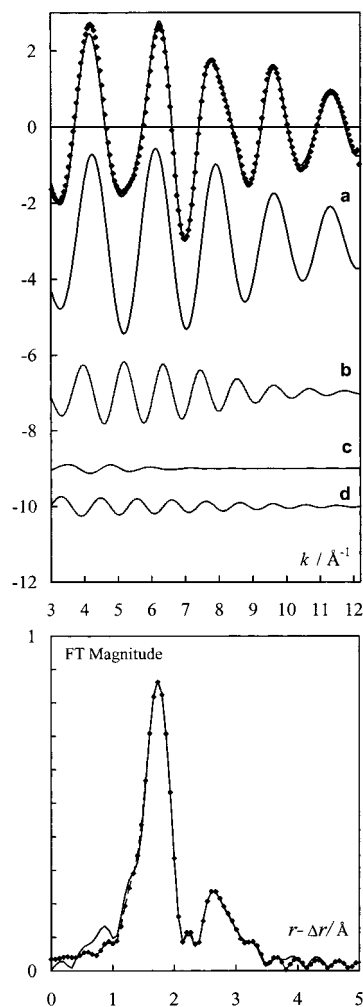


Figure 3. (Top) Ti L_{III} EXAFS data of thallium(III) trifluoromethanesulfonate in a dimethyl sulfoxide solution (top, dots) with a model fit (solid line). Below, separate contributions from the different backscattering pathways: (a) Ti–O, (b) Ti···S, (c) Ti–O–S, and (d) Ti–O–O. (Bottom) Fourier transformed EXAFS data of thallium(III) trifluoromethanesulfonate in a dimethyl sulfoxide solution (solid line), without phase shift, and the fitted model function (dots).

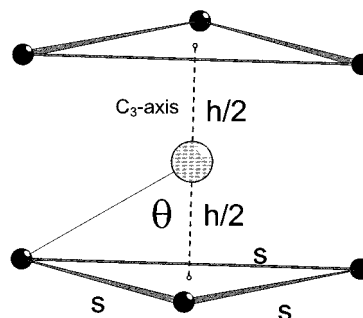


Figure 4. Octahedral TiO₆ center in the [Ti(dmsO)₆](ClO₄)₃ structure compressed along the threefold axis with the compression ratio $s/h = 1.455(3)$ [1.465(3)] at 298 [150] K. For a perfect octahedron, $s/h = (3/2)^{1/2} = 1.225$, where s is the side of the equilateral triangles and h is the distance between the triangles. The polar angle θ is defined as the angle between the C₃ axis and the Ti–O bond direction.³⁸

compression along the $\bar{3}$ axis of the octahedral TiO₆ unit in the crystal structure of [Ti(dmsO)₆](ClO₄)₃. The compression ratios are $s/h = 1.455(3)$ [1.465(3)] and the polar angles are $\theta = 59.24^\circ$ [59.41°] at 298 [150] K (compare to Figure 4). The corresponding values for a perfect octahedron are $s/h = 1.22$ and $\theta = 54.73^\circ$. The MO₆ octahedra (M = In, Ga, and Sc) of

the $[\text{M}(\text{dmsO})_6]^{3+}$ complexes in the isostructural perchlorates and iodides are less distorted,^{32,37} as could be expected for the smaller ions (Table 2). Even for these compressed octahedra, the closest distance between the oxygen atoms is larger than twice the van der Waals radius (2.80 Å)³⁹ except for the smallest and less distorted GaO_6 octahedron (Table 2). However, even though a pseudo-Jahn–Teller effect is expected for mercury(II) which is larger than thallium(III), the HgO_6 octahedron in $[\text{Hg}(\text{dmsO})_6](\text{CF}_3\text{SO}_3)_2$ is less compressed with $s/h = 1.39$ (Table 2), showing that size is not the only factor to consider. For the scandium(III) ion without d electrons, there should be no vibronic coupling between close electronic levels in the valence shell and, thus, no contribution to the distortion induced from electronic (pseudo-Jahn–Teller) effects. Indeed, the distortion is equal to that for the smallest gallium(III) ion with closer oxygen–oxygen contacts.

In solution, the distortions of the octahedral TlO_6 unit may be of any symmetry-allowed type (e.g., trigonal or tetragonal) without a preferred direction.²⁰ In combination with the anomalously low coordination number as discussed in the Introduction, the resulting dynamic disorder would also explain why the linear Tl–O–O and Tl–O–Tl–O multiple-scattering pathways do not contribute significantly for the complex in solution (compare to Figures 2a and 3a). The more ordered arrangement in the solid structure is also evident from the Fourier transforms (Figure 3), with a much larger $\text{Tl}\cdots\text{S}$ peak. The minor contribution from the triangular Tl–O–O pathway introduced for the solution is probably in the solid compound obscured by this large $\text{Tl}\cdots\text{S}$ contribution.

The standard deviations for the refined parameters given in Table 3 are estimated from the variation in the results, including the shift in the E_0 value (defining $k = 0$) for different models and data ranges. They are more than 3 times larger than the least-squares standard deviations based on the noise level of the EXAFS function and should better reflect the true level of accuracy. The different minor contributions in the models, as discussed previously, have also been considered and do not noticeably affect the results from the main contributions.

Vibrational Spectroscopy. The observed Raman and IR absorption frequencies of the crystalline $[\text{Tl}(\text{dmsO})_6](\text{ClO}_4)_3$ solvate are given in Table S2 in the Supporting Information. The assignment of the bands was based on their Raman/IR activity, relative intensities, shifts upon deuteration, and comparison with spectra of dimethyl sulfoxide and $[\text{Sc}(\text{dmsO})_6]\text{I}_3$.^{18,37} The Tl–O symmetric and asymmetric stretching vibration frequencies are found to occur at 435 and 447 cm^{-1} , respectively. Preliminary results from normal coordinate analyses show that there are major contributions from S–O stretching in the Raman band at 912 cm^{-1} and the IR bands at 927 and 897 cm^{-1} .³⁷ It is generally assumed that oxygen coordination decreases and that sulfur coordination increases the S–O stretching vibration frequency of the dimethyl sulfoxide ligands.⁴⁰ This is consistent with the much higher frequency for the bands dominated by S–O stretching in liquid dimethyl sulfoxide (at 1057 and 954 cm^{-1} in the Raman and IR spectra, respectively).³⁷ However, the mixed character of these normal modes (in particular with the CH_3 rocking) makes detailed conclusions of the changes in the chemical bonding merely on the basis of the shifts of certain bands questionable. Our force field studies give

a S–O stretching force constant of 472 N m^{-1} for liquid dimethyl sulfoxide and 426 N m^{-1} for the $[\text{Tl}(\text{dmsO})_6]^{3+}$ complex, indicating a substantial decrease in the S–O bond strength for dimethyl sulfoxide as a ligand.³⁷

NMR Characteristics. The ²⁰⁵Tl NMR spectrum of hexakis(dimethyl sulfoxide)thallium(III) perchlorate in a dimethyl sulfoxide solution displays, as expected, only a single signal, which occurs at 1886 ppm with the line width of 126 Hz. The solution was remeasured after 1 month, revealing no thallium(I). In an acidic aqueous solution, $\delta_{\text{Tl}} = 2093$ ppm of the hydrated Tl^{3+} ion.⁴¹ The difference of about 200 ppm to the hexasolvated thallium(III) ion in dimethyl sulfoxide is not surprising, considering that the ²⁰⁵Tl NMR chemical shift in an aqueous solution is sensitive both to the acid concentration and to the ionic medium.^{41,42}

A dimethyl sulfoxide solution of TlClO_4 displayed $\delta_{\text{Tl}} = 361$ ppm for the solvated thallium(I) ion. Thus, ²⁰⁵Tl NMR provides an efficient way to determine the oxidation state in solution. Usually, the ²⁰⁵Tl chemical shift occurs in the range between about +1800 and +3000 ppm for thallium(III) complexes and between –200 and +400 ppm for thallium(I). Clearly, the chemical shift $\delta_{\text{Tl}} = 1886$ ppm of $[\text{Tl}(\text{dmsO})_6]^{3+}$ is typical for thallium(III).

In an acetonitrile-*d*₃ solution of hexakis(dimethyl sulfoxide)thallium(III) perchlorate, a ¹³C NMR signal was detected at 39.5 ppm, while the corresponding chemical shift is 41.31 ppm in neat dimethyl sulfoxide. It is clear that the two CH_3 groups of the dimethyl sulfoxide ligands in the thallium(III) complex are equivalent on the actual NMR time scale. The ¹H NMR spectrum of the thallium(III) dimethyl sulfoxide complex in acetonitrile-*d*₃ solution exhibits one intense signal at 2.3 ppm, and a very small peak at 2.5 ppm of free dimethyl sulfoxide.

Conclusions

The crystal structure of the dimethyl sulfoxide solvate of thallium(III) perchlorate shows discrete octahedrally coordinated hexakis(dimethyl sulfoxide)thallium(III) complexes. Low-temperature EXAFS and crystallographic results are consistent with a regular structure of the complex in the solid state with the thallium(III) ion in a site with crystallographic $\bar{3}$ symmetry. The octahedral TlO_6 kernel, with the Tl–O bond distance of 2.224(3) Å at ambient temperature, is compressed along the threefold axis, which can be explained as a cooperative pseudo-Jahn–Teller effect.

For the solvated thallium(III) ion in dimethyl sulfoxide solution, EXAFS spectra are consistent with octahedral coordination, with the mean Tl–O bond distance of 2.22(1) Å. The anomalously large disorder parameter corresponds to a wider than normal distribution of the Tl–O distances, probably the result of a dynamic distortion caused by a weak pseudo-Jahn–Teller effect. Only one signal appears in each type of NMR spectra (²⁰⁵Tl, ¹³C, and ¹H NMR) of the complex in solution, showing that the two CH_3 groups of the dimethyl sulfoxide ligands are equivalent on the current NMR time scale.

The vibrational spectra of the solvated thallium(III) ion in $[\text{Tl}(\text{dmsO})_6](\text{ClO}_4)_3$ have been tentatively assigned. The Raman and IR spectra show symmetric and asymmetric Tl–O stretching vibration frequencies at 435 and 447 cm^{-1} , respectively. The increase in the S–O bond length in the dimethyl sulfoxide ligands can be correlated with the decrease in the vibrational frequency of the bands dominated by S–O stretching, corre-

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sponding to a much smaller SO stretching force constant (426 N m⁻¹) than that for liquid dimethyl sulfoxide (472 N m⁻¹).

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Supporting Information Available: Listings of atomic fractional coordinates for the crystal structure of [Tl(dmsO)₆](ClO₄)₃ at 295 K [150 K] (Table S1) and the crystallographic information file for the crystal structures (CIF). Figure S1 compares thermal ellipsoids (50% probability) in the crystal structure of the hexakis(dimethyl sulfoxide)-thallium(III) complex at 295 and 150 K. Table S2 lists observed frequencies and assignments of the vibrational spectra of solid [Tl(dmsO)₆](ClO₄)₃, and Figures S2 and S3 display the Raman and mid- and far-IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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