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Dimethyl sulfoxide solvates of the aluminium(III), gallium(III) and indium(III) ions. A crystallographic, EXAFS and vibrational spectroscopic study†

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The isostructural hexakis(dimethyl sulfoxide)-aluminium(III), -gallium(III) and -indium(III) iodides crystallise in the trigonal space group $R\bar{3}$ (no. 148), $Z = 3$, at 295 ± 1 K. The metal ions are located in a $\bar{3}$ symmetry site with M–O bond distances of 1.894(4), 1.974(4) and 2.145(3) Å, and M–O–S bond angles of 127.1(3), 124.1(3) and 123.1(2)°, for M = Al, Ga and In, respectively. The unit cell parameters are $a = 10.762(2)$, $c = 24.599(3)$ Å, $V = 2467.2(5)$ Å^3 for $[Al(OS(CH_3)_2)_6]I_3$, $a = 10.927(2)$, $c = 23.868(4)$ Å, $V = 2468.1(6)$ Å^3 for $[Ga(OS(CH_3)_2)_6]I_3$, and $a = 11.358(2)$, $c = 21.512(4)$ Å, $V = 2403.5(7)$ Å^3 for $[In(OS(CH_3)_2)_6]I_3$. The increasing compression of the octahedral MO_6 coordination entities along one three-fold axis for M = Al, Ga and In, respectively, explains why the largest ion indium(III) has the smallest unit cell volume. EXAFS measurements on the dimethyl sulfoxide solvated gallium(III) and indium(III) ions in solution and in the solid perchlorate and trifluoromethanesulfonate salts, show similar bond distances as in the solid iodide solvates. Raman and infrared spectra have been recorded for the hexakis(dimethyl sulfoxide)metal(III) iodides and the nature of the metal–sulfoxide bond has been evaluated by normal coordinate methods. The symmetric and asymmetric M–O stretching modes correspond to the vibrational frequencies 465 and 540 cm^{-1} for $[Al(OS(CH_3)_2)_6]I_3$, 491 and 495 cm^{-1} for $[Ga(OS(CH_3)_2)_6]I_3$, and 444 and 440 cm^{-1} for $[In(OS(CH_3)_2)_6]I_3$, respectively.

Introduction

The oxygen coordination of the aluminium(III), gallium(III) and indium(III) ions is well characterised in crystal structures. The mean Al–O bond distance for hexaaquaaluminium(III) complexes in the solid state is *ca.* 1.88 Å.[1,2] Tetrahedral aluminium complexes with oxygen donor ligands, as *e.g.* sodium tectohexaoxoalumodisilicate hydrate, $Na(AlSi_2O_6)\cdot H_2O$,[3] display much shorter Al–O bond distances, about 1.65 Å. Oxygen-coordinated gallium(III) complexes are normally octahedral with mean Ga–O bond distances close to 1.97 Å.[1,2] A four-coordinated gallium(III) complex with tetrahedral oxygen environment, $LiGaO_2\cdot 6H_2O$, showed a significantly shorter Ga–O bond distance, 1.826(5) Å.[4] Octahedral indium(III) complexes display mean In–O bond distances close to 2.13 Å.[1,2]

The coordination number of the hydrated trivalent metal ions in group 13, aluminium(III),[5] gallium(III),[6] indium(III)[6] and thallium(III),[7] is six, while the hydration number in aqueous solution of the trivalent metal ions in group 3 increases with increasing atomic number. Scandium(III) probably coordinates seven water molecules in a monocapped trigonal prism,[8] yttrium(III) eight in a square antiprism,[9] and lanthanum(III) nine waters in a tricapped trigonal prism.[10] Thus, even though thallium(III) and indium(III) have larger ionic radii in six-coordination than Sc^{3+}, 0.885, 0.800 and 0.745 Å,[11] respectively, their hydration numbers are smaller. This indicates more covalent bond character for the group 13 metal ions with d^{10} electron configuration.[7,12]

The six-coordinated structure of the hydrated aluminium(III) ion is maintained in concentrated aqueous solutions, and large angle X-ray scattering (LAXS) shows mean Al–O bond distances in the range 1.87–1.90 Å.[5] Structural studies on non-aqueous aluminium(III) solvates do not seem to have been reported so far. The hydrated gallium(III) ion octahedrally coordinates six water molecules, with mean Ga–O bond distances reported as 1.944(3) and 1.969(5) Å in the solid state,[13,14] and 1.959(6) Å in aqueous solution.[6] In crystal structures the hydrated indium(III) ion octahedrally coordinates six water molecules with the In–O bond distances 2.112 and 2.134 Å,[13] and in aqueous solution 2.131(7) Å.[6]

Few structural investigations have been performed of the dimethyl sulfoxide solvated group 13 metal ions. Even though dimethyl sulfoxide is an ambidentate solvent, coordination *via* the sulfur atom takes place only for soft metal ions, *e.g.* palladium(II), platinum(II) and rhodium(III),[15] and the relatively hard group 13 metal ions are solvated *via* the oxygen atom. Previously, discrete hexakis(dimethyl sulfoxide)indium(III) and thallium(III) complexes have been crystallographically

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† Electronic supplementary information (ESI) available: normalized X-ray absorption edges, calculated separate contributions of the different scattering paths to the EXAFS oscillations for the dimethyl sulfoxide solvated gallium(III) and indium(III) ions in the solid state and solution; correlation between compression ratio (s/h) and bond lengths in $[M(dmso)_6]^{3+}$ complexes; correlation between metal–oxygen (M–O) force constants and bond lengths in $[M(dmso)_6]^{3+}$ complexes. See http://www.rsc.org/suppdata/dt/b2/b212140a/

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Table 1 Crystallographic data for **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{12}H_{36}S_6O_6I_3Al$	$C_{12}H_{36}S_6O_6I_3Ga$	$C_{12}H_{36}S_6O_6I_3In$
M	876.45	919.19	964.62
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$R\bar{3}$ (no. 148)	$R\bar{3}$ (no. 148)	$R\bar{3}$ (no. 148)
a/Å	10.7617(11)	10.9272(13)	11.3584(17)
c/Å	24.599(3)	23.868(4)	21.512(4)
α, β, γ/°	90, 90, 120	90, 90, 120	90, 90, 120
V/Å^3	2467.2(5)	2468.1(6)	2403.5(7)
T/K	295 ± 2	295 ± 2	295 ± 2
Z	3	3	3
D_m/g cm^{-3}	1.80	1.85	1.97
D_c/g cm^{-3}	1.770	1.855	1.999
μ(Mo-Kα)/mm^{-1}	3.279	4.052	4.040
Measured reflections	7819	6431	6285
Unique reflections (R_{int})	1342 (0.125)	1085 (0.046)	1059 (0.065)
Observed reflections	885	651	579
Final R_1, wR_2 [$I > 2\sigma(I)$][a]	0.067, 0.118	0.029, 0.081	0.024, 0.051
(all data)	0.100, 0.131	0.062, 0.126	0.065, 0.060

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

characterized in the perchlorate salts, with M–O bond distances of 2.140(3) and 2.224(3) Å, respectively.[16,17] In the current work iodide has been chosen as counter ion to the hexakis(dimethyl sulfoxide) solvates of the aluminium(III), gallium(III) and indium(III) ions in order to avoid the structure determination problems caused by disordered perchlorate ions.[16,17] Interpretation of the vibrational spectra is also facilitated because the non-coordinated iodide ions give no additional vibrational frequencies. The strength and nature of the metal–oxygen bond and its effect on the dimethyl sulfoxide ligand has been evaluated by normal coordinate analysis and compared with other dimethyl sulfoxide solvates.

Experimental

Chemicals

Hexakis(dimethyl sulfoxide)aluminium(III) iodide, 1, hexakis(dimethyl sulfoxide) gallium(III) iodide, 2, and hexakis(dimethyl sulfoxide)indium(III) iodide, 3. Anhydrous group 13 metal iodides (Aldrich) were suspended in dichloromethane, and dimethyl sulfoxide (Merck) was slowly added in six-fold excess. The aluminium and gallium iodides then formed white fine-crystalline precipitates of **1** and **2**, respectively. Crystals suitable for X-ray crystallography were obtained after recrystallisation from acetonitrile. Addition of dimethyl sulfoxide to the indium iodide suspension gave a colourless solution, which after evaporation at reduced pressure yielded colourless crystals of **3**.

Hexakis(dimethyl sulfoxide)gallium(III) and indium(III) perchlorate. Gallium(III) oxide and indium(III) hydroxide were slurried in water and concentrated perchloric acid (AnalR, 70%) was added dropwise. The reaction mixture was refluxed for 2 h until a clear solution formed. After boiling off some of the water the solution was evaporated in a desiccator until hydrated metal(III) perchlorates precipitated. The salts were dissolved in a minimum amount of acetone and then six equivalents of 2,2-dimethoxypropane (Merck), which reacts with water to form methanol and acetone,[18] were added.[19] The reaction mixture was stirred vigorously for 5–10 min. When adding a six-fold excess of dimethyl sulfoxide the dimethyl sulfoxide solvates precipitated immediately. The stirring was continued for another 5–10 min before filtering off the crystals. Recrystallisation was performed from dimethyl sulfoxide.

Anhydrous gallium(III) and indium(III) trifluoromethanesulfonate. Gallium(III) oxide and indium(III) hydroxide were slurried in water and trifluoromethanesulfonic acid (Alfa, 100%) was added dropwise in a fairly large excess. After refluxing for 2 h clear solutions had formed, which were filtered. Water and excess acid was boiled off at *ca.* 450 K, leaving anhydrous gallium(III) and indium(III) trifluoromethanesulfonate salts. Dimethyl sulfoxide solutions of gallium(III) and indium(III) trifluoromethanesulfonate were prepared by dissolving the hygroscopic anhydrous salts in dimethyl sulfoxide under nitrogen atmosphere. Crystals were obtained by evaporating the solutions under reduced pressure in a desiccator.

X-Ray crystallography

The data collections were made on small crystals of **1**, **2** and **3** enclosed in thin-walled glass capillaries at room temperature, by means of a STOE imaging-plate diffractometer.[20] Absorption corrections were performed with the programs X-RED and X-Shape.[21] Symmetry equivalent reflections were used to optimise crystal shape and size. The structures were solved by direct methods using SHELXS-97,[22] and refined using the full-matrix least-squares method on F^2, SHELXL-97.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at calculated positions and refined using a riding model. Systematic absences for **1**, **2** and **3** in the collected diffraction data were consistent with the space group $R\bar{3}$ (no. 148). Selected crystallographic and experimental details are summarised in Table 1.

CCDC reference numbers 199307–199309.

See http://www.rsc.org/suppdata/dt/b2/b212140a/ for crystallographic data in CIF or other electronic format.

EXAFS

Gallium and indium K edge X-ray absorption data were collected in transmission mode at the Stanford Synchrotron Radiation Laboratory (SSRL), USA, 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, detuned to 50% of maximum intensity at the end of the scans to reduce higher order harmonics.

The solutions were kept in cells with 6.3 µm X-ray polypropylene foil windows and 1–5 mm Teflon spacers. The solids were finely ground and diluted with boron nitride (BN) to prevent self-absorption and pin-hole effects, and to achieve an absorption change over the edge of about one logarithmic unit. Energy calibration of the X-ray absorption spectra was performed by simultaneously recording the edge spectrum of a gallium or indium foil during the data collection, and assigning the first K-edge inflection point of the metal to 10368.2 and

27940.0 eV, respectively.[24] After energy calibration, 3–4 scans were averaged for each sample. The EXAFSPAK program package was used for the data treatment.[25] The EXAFS oscillations were extracted using standard procedures for pre-edge subtraction, spline removal and data normalisation.[26,27] Model fitting, including both single and multiple back-scattering pathways, was performed with theoretical phase and amplitude functions calculated *ab initio* using the FEFF7 computer code.[28] The k^3-weighted EXAFS oscillation was analysed by a non-linear least-squares fitting procedure of the model parameters.

Raman and infrared spectra

Raman spectra of the solids **1**, **2** and **3** were obtained using a Renishaw System 1000 spectrometer, equipped with a Leica DMLM microscope, a 25 mW diode laser (782 nm), and a Peltier-cooled CCD detector. The mid-infrared absorption spectra of the solid compounds were obtained by means of a Bio-RAD FTS 6000 FT-IR spectrometer (KBr pellet). The far-infrared spectrum was recorded with the sample enclosed in a polyethylene disk. Normal coordinate analyses of the spectra and force field calculations were performed by means of Wilson's **GF** matrix method. A PC-based program package developed by J. and L. Mink[29] was used to compute force constants and to fit calculated vibrational frequencies, using a symmetrised valence force field.

Results and discussion

Crystal structures of 1, 2 and 3

The crystal structures of **1**, **2** and **3** were satisfactorily described in the space group $R\bar{3}$. The trivalent metal ions were located in a site of $\bar{3}$ symmetry surrounded by six equidistant oxygen-bonded dimethyl sulfoxide ligands, Fig. 1. The M–O bond distances 1.894(4), 1.974(4) and 2.145(3) Å were obtained for the $[M(dmso)_6]^{3+}$ complexes with M = Al, Ga and In, respectively. The In–O bond distance in the $[In(OS(CH_3)_2)_6]I_3$ complex is in good agreement with that previously found for $[In(OS(CH_3)_2)_6](ClO_4)_3$, 2.140(3) Å.[16] However, for the mixed ligand $[InX_3(OS(CH_3)_2)_3]$ compounds with X = Cl and Br, the In–O bond distances became longer, 2.195 and 2.199 Å, respectively.[30] This shows that chloride and bromide as ligands bind more strongly to indium than dimethyl sulfoxide, while iodide is not able to compete with dimethyl sulfoxide for coordination to indium. The non-bonded iodide ions in **1**, **2** and **3**, located between the $[M(dmso)_6]^{3+}$ complexes, are each in contact with 12 methyl groups. The $I^- \cdots C$ distances are in the range between 3.97 to 4.34 Å for the indium compound, with somewhat smaller spread for the gallium (3.97–4.32 Å) and aluminium (4.00–4.30 Å) compounds.

All trivalent group 13 metal ions form solvates with six dimethyl sulfoxide ligands, including thallium(III) perchlorate with the Tl–O bond distances 2.224(3) Å,Table 2. Of the trivalent d^0 ions in group 3, the scandium(III) iodide forms a hexakis(dimethyl sulfoxide)scandium(III) solvate isostructural with **1**, **2** and **3**, with an Sc–O bond distance of 2.075(3) Å.[31] Yttrium(III) and lanthanum(III) coordinate eight dimethyl sulfoxide molecules in a square antiprismatic fashion, with the mean Y–O and La–O bond lengths 2.36(1) and 2.48 Å,[10,32,33] respectively. When comparing yttrium(III) and thallium(III), with similar ionic radii in six-coordination, 0.900 and 0.885 Å,[11] respectively, the stronger tendency to octahedral coordination for the trivalent ions of group 13 is again obvious, as for the hydrates.

For the $[M(dmso)_6]^{3+}$ complexes with M = Al, Ga, Sc, In and Tl, the M–O bond distances increase from 1.894 to 2.224 Å (Table 2). The increasing oxygen–oxygen distances within the MO_6 kernel allow substantial deviations from a regular octahedral symmetry for the relatively large indium(III) and thallium(III) ions by compression along the three-fold axis in $\bar{3}$ symmetry. This can be measured by the compression ratio *s*/*h* (*cf.* Fig. 1). The smallest ions, aluminium(III), gallium(III) and scandium(III), have similar compression ratios of about 1.287 in the iodide salts of the hexakis(dimethyl sulfoxide) solvates, while the compression ratio increases to 1.335 for hexakis(dimethyl sulfoxide)indium iodide (Table 2). This is reflected in the cell volume, which for the isostructural iodide solvates is smallest for the largest ion, In(III). A comparison between the isostructural solvated indium(III) and thallium(III) perchlorates shows similar effects, with compression ratios of 1.373 and 1.455, respectively.[34] Again the larger ion, thallium(III), has the smaller cell volume (Table 2).

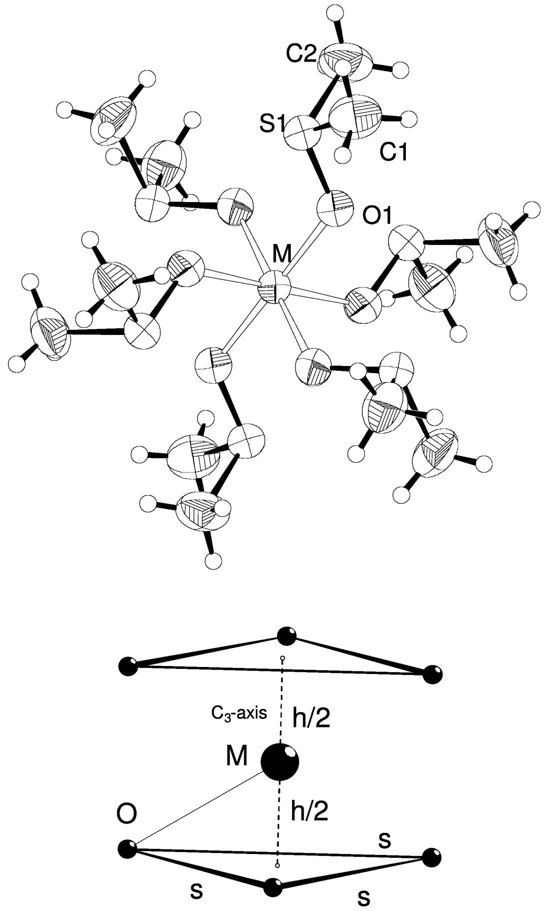

Fig. 1 (Top) The hexakis(dimethyl sulfoxide)-aluminium(III), -gallium(III) or -indium(III) complexes in the isomorphous $[M(dmso)_6]I_3$ crystal structures. The figure shows the gallium complex with 50% probability ellipsoids; (bottom) the octahedral MO_6 centre in the $[M(dmso)_6]^{3+}$ structure is compressed along the three-fold axis. For a perfect octahedron $s/h = \sqrt{3}/2 = 1.225$, where *s* is the side of and *h* is the distance between the equilateral triangular surfaces.

Despite the difference in M–O bond distance the aluminium and gallium iodide structures have quite similar compression ratios and cell volumes, which shows that there are other factors than ionic size to consider. The conformation of the $(CH_3)_2SO$ ligand in the $[M(dmso)_6]^{3+}$ complexes, reflected by the 3.0° larger M–O–S angle for the aluminium solvate (*cf.* Table 2), also affects the cell volume.

The M–O–S angle is affected to some degree by the covalency of the M–O bond. Small angles, below 120°, are found for covalent M–O bonds, as *e.g.* in hexakis(dimethyl sulfoxide)mercury(II) triflate, 116.4(3)° (*cf.* Table 2),[35] while for complexes with low covalency much larger angles are observed, as for hexakis(dimethyl sulfoxide)scandium(III) iodide, 132.5(3)°. The smallest angle M–O–S angle for the hexakis(dimethyl sulfoxide) complexes of the trivalent group 13 metal ions is found for thallium(III), 120.7(2)°, and the largest for aluminium, 127.1(3)°

Table 2 Bond lengths (Å) and angles (°) for $[M(dmso)_6]^{n+}$ complexes in symmetry

Metal atom Anion	Tl(III) Perchlorate[a]	In(III) Perchlorate[b]	In(III) Iodide[c]	Ga(III) Iodide[c]	Al(III) Iodide[c]	Sc(III) Iodide[d]	Hg(II) Triflate[e]	Uncoordinated dimethyl sulfoxide[f]
M–O	2.224(3)	2.140(3)	2.145(3)	1.974(4)	1.894(4)	2.075(3)	2.347(5)	
Compression ratio *s*/*h*[g]	1.455(3)	1.373(4)	1.335(4)	1.285(6)	1.287(3)	1.287(4)	1.390(6)	
Cell volume	2584.0(5)	2622.0(12)[h]	2403.5(7)	2468.1(6)	2467.2(5)	2507.6(6)	2593.8(6)[h]	
Closest O ··· O distance	2.948(5)	2.915(5)	2.945(4)	2.746(6)	2.636(5)	2.887(5)	3.182(7)	
O–S	1.544(4)	1.542(3)	1.541(3)	1.539(5)	1.540(5)	1.530(3)	1.543(5)	1.495(4)
S–C(1)	1.758(8)	1.763(8)	1.787(5)	1.773(8)	1.776(7)	1.761(5)	1.766(8)	1.773(4)
S–C(2)	1.770(7)	1.771(6)	1.765(5)	1.774(8)	1.776(8)	1.769(5)	1.764(9)	
O-M-O′	96.20(13)	94.2(1)	93.3(1)	91.8(2)	91.9(2)	91.9(2)	94.6(2)	
M–O–S	120.7(2)	124.0(2)	123.1(2)	124.1(3)	127.1(3)	132.5(2)	116.4(3)	
O–S–C(1)	103.2(3)	102.9(2)	104.1(2)	104.6(4)	104.0(3)	103.7(2)	104.1(3)	105.7(2)
O–S–C(2)	104.2(3)	103.6(3)	103.3(2)	102.9(3)	102.6(3)	103.8(2)	106.5(4)	
C(1)–S–C(2)	99.8(4)	99.6(3)	98.5(3)	98.3(4)	98.4(4)	98.9(3)	98.6(5)	98.0(3)

[a] Ref. 17. [b] Ref. 16. [c] This work. [d] Ref. 31. [e] Ref. 35. [f] Mean values for uncoordinated dimethyl sulfoxide molecules in crystals, ref. 15. [g] Ref. 34; *s*/*h* = 1.225 for a regular octahedron. [h] With hexagonal unit cell ($Z = 3$).

Table 3 Bond distances, *d*/Å, Debye–Waller factors, σ^2/Å^2, and number of distances, *n*, of the dimethyl sulfoxide solvated gallium(III) and indium(III) ions as determined by EXAFS at room temperature; E_o/eV is the refined threshold energy and S_o^2 the refined amplitude reduction factor

State		*d*	σ^2	*n*	E_o	S_o^2
0.25 M $Ga(ClO_4)_3$ in Me_2SO solution	Ga–O	1.955(2)	0.0065(2)	6	10378.0(3)	1.27(3)
	Ga ··· S	3.108(4)	0.0112(6)	6		
	Ga–O–S	3.194(18)	0.019(4)	12		
	MS	3.964(14)	0.0054(20)	3 × 6		
Solid $[Ga(dmso)_6](CF_3SO_3)_3$	Ga–O	1.954(2)	0.0050(2)	6	10379.3	1.19(4)
	Ga ··· S	3.117(3)	0.0079(4)	6		
	Ga–O–S	3.280(23)	0.015(4)	12		
	MS	3.982(25)	0.0080(40)	3 × 6		
1.00 M $In(CF_3SO_3)_3$ solution	In–O	2.135(2)	0.0054(2)	6	27949.0(4)	1.03(3)
	In ··· S	3.320(6)	0.0094(5)	6		
	In–O–S	3.481(9)	0.0036(9)	12		
	MS	4.19(3)	0.011(5)	3 × 6		
Solid $[In(dmso)_6](ClO_4)_3$	In–O	2.143(2)	0.0043(2)	6	27951.9	0.96(3)
	In ··· S	3.282(3)	0.0071(3)	6		
	In–O–S	3.519(11)	0.012(2)	12		
	MS	4.35(7)	0.034(20)	3 × 6		

(Table 2). The S–O distance of the O-coordinated dimethyl sulfoxide ligands is, however, almost constant at about 1.54 Å, which is almost 0.05 Å longer than in the free dimethyl sulfoxide molecule, *cf.* Table 2.

EXAFS Studies

Dimethyl sulfoxide solvates of gallium(III) and indium(III). EXAFS data for the dimethyl sulfoxide solvated gallium(III) and indium(III) ions in the solid state and solution were collected with different anions, perchlorate and trifluoromethanesulfonate. The results (Table 3) show that the structures of the hexakis(dimethyl sulfoxide)gallium(III) and indium(III) complexes are insensitive to the counter-ions. The bond distances were modelled with the main contributions from M–O and M ··· S single backscattering, and the three-legged M–O–S backscattering pathways (*cf.* Fig. S2, ESI †). The fit of the model improved for both solutions and solids by introducing the linear M–O–O and M–O–M–O multiple scattering pathways (multiplicity 3 × 6) within the octahedral MO_6 core at twice the M–O bond distance. Figs. 2 and 3 show the fit of the EXAFS model functions, and Figs. 4 and 5 the corresponding Fourier transforms with the refined parameter values listed in Table 3 for the dimethyl sulfoxide solvated gallium(III) and indium(III) ions, respectively. Least-squares refinement gave the

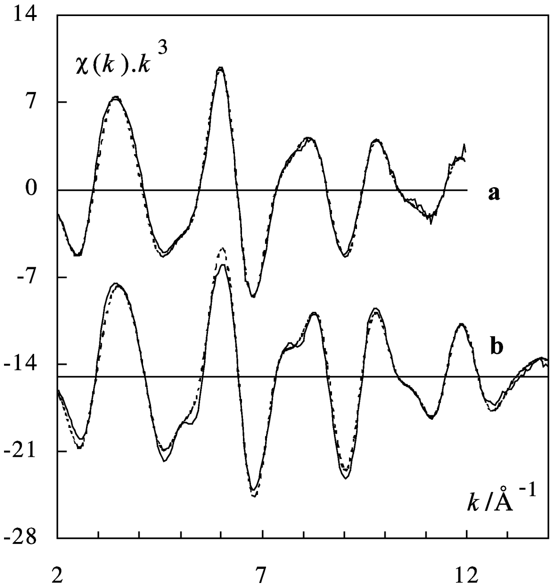

Fig. 2 The EXAFS data and model fit of the (a) dimethyl sulfoxide solution of gallium(III) perchlorate, (b) solid hexakis(dimethyl sulfoxide)-gallium(III) trifluoromethanesulfonate, solid line – experimental data, dashed line – calculated model function with the parameters in Table 3.

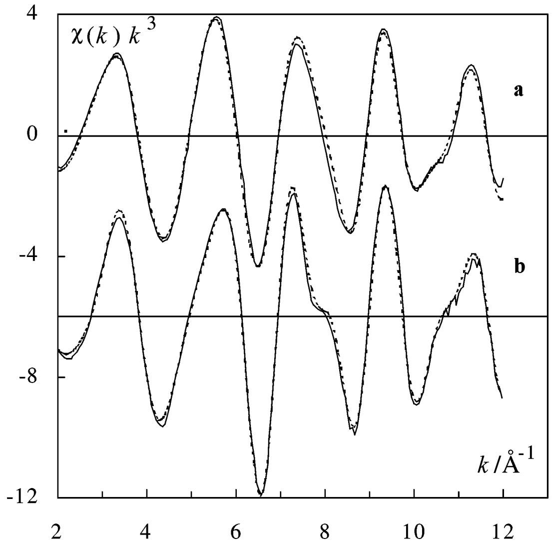

Fig. 3 The EXAFS data and model fit of the (a) dimethyl sulfoxide solution of indium(III) trifluoromethanesulfonate, (b) solid hexakis(dimethyl sulfoxide)indium(III) perchlorate, solid line – experimental data, dashed line – calculated model function with the parameters in Table 3.

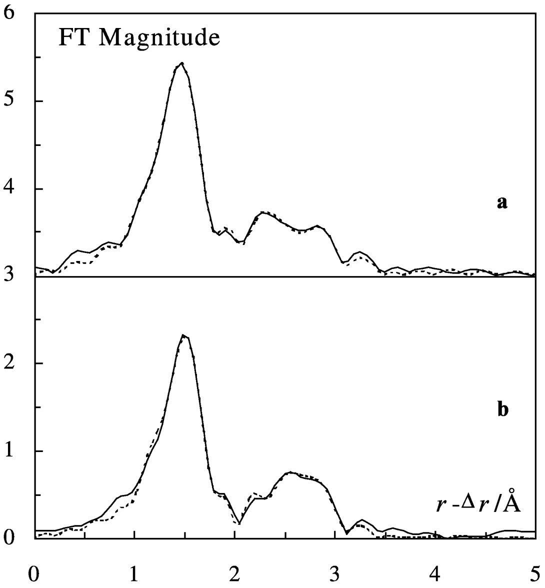

Fig. 4 Fourier transforms (FTs) for the EXAFS data of (a) dimethyl sulfoxide solution of gallium(III) perchlorate, (b) solid hexakis(dimethyl sulfoxide)gallium(III) trifluoromethanesulfonate, solid line – experimental data, dashed line – model function (*cf.* Fig. 2).

mean Ga–O and Ga ··· S distances 1.955(2) and 3.108(4) Å of the dimethyl sulfoxide solvated gallium(III) in solution, and 1.954(2) and 3.117(3) Å in solid hexakis(dimethyl sulfoxide)gallium(III) trifluoromethanesulfonate. This corresponds to similar Ga–O–S bond angles, 125.2(5) and 125.9(4)°, respectively. The above Ga–O bond distances are significantly shorter than in **2**, 1.974(4) Å, but in close agreement with Ga–O bond distances obtained for hexaaqua solvates in aqueous solution and the solid state.[6] The mean In–O and In ··· S distances of 2.135(2) and 3.320(6) Å, and 2.143(2) and 3.282(3) Å in the dimethyl sulfoxide solvated indium(III) ion in solution and in the solid hexakis(dimethyl sulfoxide)indium(III) perchlorate (Table 3), give In–O–S bond angles of 128.5(6) and 125.2(4)°, respectively. The In ··· S distances are significantly longer than the crystallographic value for the iodide **3**, 3.252(1) Å, while the Ga ··· S distances in **2**, 3.110(2) Å, are similar.

The EXAFS values for the In–O bond distances are similar to those in **3**, 2.145(3) Å, and in hexakis(dimethyl sulfoxide)indium(III) perchlorate (Tables 2 and 3),[16] and are also in agreement with the In–O bond distances observed in hexaaqua solvates in both aqueous solution and the solid state.[6] The relatively small and similar Debye–Waller factors (σ^2/Å^2) indicate small deviations from the mean M–O bond distances in the hexaaqua- and hexakis(dimethyl sulfoxide)-gallium(III) and -indium(III) ions both in the solid state and solution (*cf.* ref. 6 and Table 3).

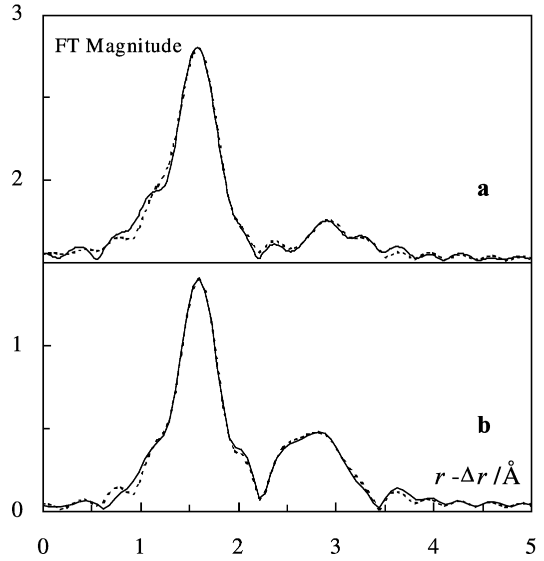

Fig. 5 Fourier transforms (FTs) for the EXAFS data of (a) dimethyl sulfoxide solution of indium(III) trifluoromethanesulfonate, (b) solid hexakis(dimethyl sulfoxide)indium(III) perchlorate, solid line – experimental data, dashed line – model function (*cf.* Fig. 3).

Vibrational spectra and force constant calculations

Raman and infrared spectra were recorded for compounds **1**, **2** and **3**, and the Raman spectra are displayed between 100 and 600 cm^{-1} in Fig. 6. A force field study was undertaken of the vibrational spectra to allow comparisons of the metal–oxygen bond character and how the coordination affects the dimethyl sulfoxide ligands. The centrosymmetric M(dmso)$_6^{3+}$ complexes can be described in the S_6 point group, with the normal vibrations belonging to the symmetry species 11 A$_g$ + 11 E$_g$ + 12 A$_u$ + 12 E$_u$, considering the methyl groups as point masses. All symmetric modes are Raman-active whereas the asymmetric ones are IR-active.

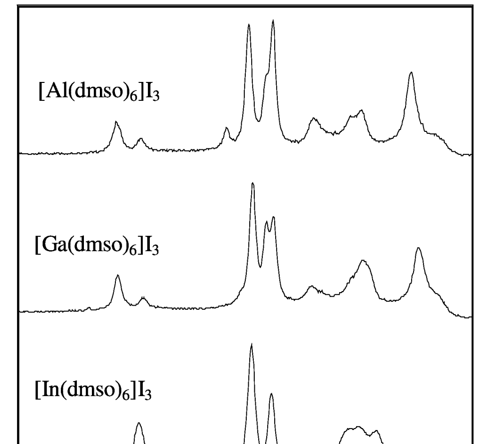

Fig. 6 Raman spectra for solid hexakis(dimethyl sulfoxide)aluminium(III), -gallium(III) and -indium(III) iodide (Renishaw System 1000 spectrometer with Leica DMLM microscope and diode laser, 782 nm).

Table 4 Observed and calculated frequencies (cm^{-1}) and potential energy distribution (PED) for M(dmso)$_6^{3+}$ complexes (M = Al, Ga, In and Tl)

Al(dmso)$_6^{3+}$		Ga(dmso)$_6^{3+}$		In(dmso)$_6^{3+}$		Tl(dmso)$_6^{3+}$			
Obs.[a]	Calc.	Obs.[a]	Calc.	Obs.[a]	Calc.	Obs.[a]	Calc.	Potential energy distribution	Assignment
A_g									
923	923	912	912	916	915	895	897	86 ν_s(SO), 10 ν_s(MO)	SO str.
724	724	726	726	723	723	721	722	98 ν_a(CS)	SC_2 asym. str.
691	691	690	690	685	685	683	681	94 ν_s(CS)	SC_2 sym. str.
465	467	491	490	444	442	435	428	47 ν_s(MO), 37 δ_s(CSO)	MO sym. str.
346	346	341	341	345	346	342	342	94 δ_s(CSC)	SC_2 scissor
319	323	318	315	321	315	316	309	61 δ_a(CSO), 17 X_s, 13 δ_s(CSO)	SC_2 twist
220	213	217	214	215	207	218	209	48 δ_s(CSO), 22 ν_s(MO), 13 δ_a(CSO), 6 δ_s(MOS)	SC_2 wag
154	145	129	122	120	115	136	122	73 δ_s(MOS), 17 ν_s(MO)	MOS sym. def.
	122		106		101	117	100		
	42		38		36		35		
	22		23		23		23		
E_g									
948	948	923	923	916	916	913	916	86 ν_s(SO), 10 ν_s(MO)	SO str.
724	724	726	726	723	723	721	722	98 ν_a(CS)	SC_2 asym. str.
691	691	690	690	685	686	683	681	96 ν_s(CS)	SC_2 sym. str.
491	491	491	491	444	450	435	435	46 ν_s(MO), 37 δ_s(CSO), 13 δ_s(MOS)	MO sym. str.
346	346	341	342	345	346	342	342	92 δ_s(CSC)	SC_2 scissor
327	325	318	327	321	327	316	320	57 δ_a(CSO), 28 X_s, 7 δ_s(CSO)	SC_2 twist
233	227	217	220	215	214	218	211	52 δ_s(CSO), 18 ν_s(MO), 6 δ_a(CSO)	SC_2 wag
167	159	158	143	145	135	136	131	25 δ_s(MOS), 18 X_s, 16 ν_s(MO), 11 δ_a(CSO)	MOS sym. def.
	111		105		102	117	100		
	37		27		26		26		
	23		24		23		23		
A_u									
898	894	898	898	903	904	897	910	85 ν_a(SO), 10 ν_a(MO)	SO str.
725	725	725	725	714	714	718	719	98 ν_a(CS)	SC_2 asym. str.
689	689	689	689	680	681	686	687	92 ν_s(CS)	SC_2 sym. str.
540	524	495	487	440	441	447	443	43 ν_a(MO), 30 δ_a(CSO), 22 δ_s(CSO)	MO asym. str.
346	346	357	356	350	348	344	346	83 δ_s(CSC)	SC_2 scissor
322	320	340	345	333	336	319	322	53 δ_a(CSO), 31 X_a	SC_2 twist
234	228	243	247	241	225	216	218	44 δ_s(CSO), 29 ν_a(MO), 18 δ_a(CSO)	SC_2 wag
171	166	211	210	175	175	157	138	42 δ_a(MOS), 31 δ_a(CSO)	MOS asym. def.
	102		130		124	115	116		
	38		41		38		34		
	21		20		19		19		
	20		18		18		18		
E_u									
898	900	898	898	903	903	927	918	90 ν_a(SO), 6 ν_a(MO)	SO str.
725	725	725	725	714	714	718	719	98 ν_a(CS)	SC_2 asym. str.
689	689	689	689	680	681	686	687	91 ν_s(CS)	SC_2 sym. str.
520	519	495	502	440	450	447	454	42 ν_a(MO), 33 δ_a(CSO), 12 δ_s(CSO)	MO asym. str.
346	346	357	356	350	348	344	346	89 δ_s(CSC)	SC_2 scissor
322	320	327	323	323	317	319	314	50 δ_a(CSO), 21 X_a, 10 δ_s(CSO)	SC_2 twist
234	241	262	269	241	239	216	222	53 δ_s(CSO), 21 ν_a(MO), 10 ν_a(SO)	SC_2 wag
171	166	211	195	175	168	157	148	37 δ_a(MOS),25 ν_a(MO), 22 δ_s(CSO)	MOS asym. def.
	111		108		104	115	101		
	29		36		33		27		
	22		26		25		23		
	20		18		18		18		

[a] Raman value.

The experimental and calculated frequencies of the fundamental modes for compounds **1**, **2** and **3** are given in Table 4, together with values from a corresponding analysis made for [Tl(dmso)$_6$](ClO$_4$)$_3$. We performed a normal coordinate analysis for pure dimethyl sulfoxide that enabled us to assign new bands in the region 400–600 cm^{-1} to M–O stretching modes;[36] for Al(dmso)$_6^{3+}$ 465 (A_g), 491 (E_g), 540 (A_u) and 520 (E_u) cm^{-1}; for Ga(dmso)$_6^{3+}$ 491 (A_g, E_g) and 495 (A_u, E_u) cm^{-1} and for In(dmso)$_6^{3+}$ 444 (A_g, E_g) and 440 (A_u, E_u) cm^{-1}. The observable splitting between the M–O stretching modes for Al(dmso)$_6^{3+}$ results from a significant vibrational coupling with CSO skeletal deformational modes of the ligand, which is clearly demonstrated by the potential energy distribution of the Al–O stretching modes. The AlO and SO stretch–stretch interaction terms (Table 5), which are out of sequence especially for the *trans*-direction, provide another explanation of the specific vibrational behaviour of the aluminium solvate.

The M–O force constants for the M(dmso)$_6^{3+}$ complexes, M = Al, Ga, In and Tl, decrease with increasing MO distance (*cf.* Tables 2 and 5, Fig. S7). The S–O stretching frequency of the dimethyl sulfoxide ligand is strongly affected by the coordination. The vibrational mode at about 954 cm^{-1} for free dimethyl sulfoxide, shown by the potential energy distribution to be dominated by the SO stretching, shifts to lower frequencies when coordinated *via* the oxygen atom, *cf.* Table 4.[37] Even though no significant difference is observed between the S–O bond distances in the M(dmso)$_6^{3+}$ complexes, M = Al, Ga, In and Tl (Table 2), the S–O stretching force constants increase in the Ga, In and Tl series as a consequence of the decreasing metal–oxygen bond strength. The Al(dmso)$_6^{3+}$ complex

Table 5 Calculated force constants for $M(dmso)_6^{3+}$ complexes (M = Al, Ga, In and Tl)

Coordinates	dmso	$Al(dmso)_6^{3+}$	$Ga(dmso)_6^{3+}$	$In(dmso)_6^{3+}$	$Tl(dmso)_6^{3+}$	Units
Stretching						
K(MO)		1.761 (1.779)	1.617 (1.670)	1.318 (1.552)	1.300 (1.469)	a[a]
K(OS)	5.061	4.599 (4.805)	4.168 (4.652)	4.274 (4.758)	4.279 (4.809)	a[a]
K(CS)	2.063	2.500	2.519	2.495	2.471	a
Stretch–stretch						
F(MO,MO) *trans*		−0.171	0.448	0.184	0.071	a
F(MO,MO) *cis*		−0.048	0.007	0.003	0.012	a
F(OS,OS) *trans*		−0.124	0.012	0.024	−0.034	a
F(OS,OS) *cis*		−0.031	−0.018	−0.001	−0.032	a
F(CS,CS)	0.228	−0.037	−0.019	−0.016	−0.012	a
Bending						
$H(SC_2)$	1.522	0.968	1.057	0.953	0.874	b
H(OSC)	1.070	0.664	0.367	0.396	0.134	b
τ(MOSC)		0.134	0.145	0.148	0.134	b
Bend–bend						
h(OSC,OSC)		0.201	0.227	0.026	0.022	b
Stretch–bend						
f(MO,OSC)		0.070	0.070	0.071	0.070	c

Units: a: N cm^{-1}; b: 10^{-16} N m rad^{-2}; c: 10^{-6} N rad^{-1}. [a] The MO and OS stretching force constants within parentheses have been obtained using a $M–OS(CH_3)_2$ simplified monoligand model.

deviates from this trend and also has a larger M–O–S angle (Table 2).

The S–C bond lengths of the free and coordinated dimethyl sulfoxide molecules are similar (Table 2). However, the S–C stretching force constants show a clear increase for the complexes, about 20–22% higher than for liquid dimethyl sulfoxide. For the Ga, In and Tl complexes a slightly decreasing S–C force constant can be correlated to the increasing SO bond strength (Table 5).

Conclusions

All the trivalent group 13 ions, aluminium(III), gallium(III), indium(III) and thallium(III), coordinate six dimethyl sulfoxide molecules, both in solution and in the solid solvates. Crystallographic results show the metal ions to be surrounded by six oxygen-bonded dimethyl sulfoxide ligands, forming an octahedral MO_6 entity compressed along a three-fold axis, with the highest compression ratios for the largest metal ions (Table 2).

Vibrational spectra of the solvated aluminium(III), gallium(III) and indium(III) ions in the $[M(dmso)_6]I_3$ compounds have been recorded and analysed. Symmetric and asymmetric M–O stretching modes were found to dominate the vibrational frequencies at 465 and 540 cm^{-1} for the aluminium, 491 and 495 cm^{-1} for the gallium, and at 444 and 440 cm^{-1} for the indium complexes, respectively. Previously, the corresponding normal modes for $Tl(dmso)_6^{3+}$ were found at 435 and 447 cm^{-1}. The S–O stretching force constant of the dimethyl sulfoxide ligand increases for the d^{10} ions M = Ga, In and Tl in the $M(dmso)_6^{3+}$ complexes, as expected from the decreasing M–O bond strength (Table 5). However, the S–O force constant for the $Al(dmso)_6^{3+}$ complex is higher and differs significantly from this trend even though the S–O bond distance is similar. This is probably connected to a more ionic M–O bond character of the d^0 ions Al(III) and Sc(III), which is also reflected in larger M–O–S angles (Table 2).

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